Original Article

Phase characterisation and mechanical behaviour of Fe–B modified Cu–Zn–Al shape memory alloys

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ABSTRACT

The microstructures, phase characteristics and mechanical behaviour of Cu–Zn–Al alloys modified with Fe, B, and Fe–B mixed micro-alloying additions have been investigated. Cu–Zn–Al alloys were produced by casting with and without the addition of the microelements (Fe, B and Fe–B). The alloys were subjected to a homogenisation – cold rolling – annealing treatment schedule, before the alloys were machined to specifications for tensile test, fracture toughness, and hardness measurement. Optical, scanning electron microscopy and X-ray diffraction analysis were utilised for microstructural and phase characterisation of the alloys. A distinct difference in grain morphology was observed in the alloys produced – the unmodified alloy had predominantly needle-like lath martensite structure with sharp grain edges while significantly larger transverse grain size and curve edged/near elliptical grain shape was observed for the modified Cu–Zn–Al alloys. Cu–Zn with fcc structure was the predominant phase identified in the alloys while Cu–Al with bcc structure was the secondary phase observed. The hardness of the unmodified Cu–Zn–Al alloy was higher than that of the modified alloys with reductions in hardness ranging between 32.4 and 51.5%. However, the tensile strength was significantly lower than that of the modified alloy grades (28.37–52.74% increase in tensile strength was achieved with the addition of micro-alloying elements). Similarly, the percent elongation and fracture toughness (10–23% increase) of the modified alloy was higher than that of the unmodified alloy grade. The modified alloy compositions mostly exhibited fracture features indicative of a fibrous micro-mechanism to crack initiation and propagation, characterised by the prevalence of dimpled rupture.

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1. Introduction

The attractive properties of shape memory alloys (SMAs) have been explored for a wide range of applications such as in sensing, medical, commercial and other industrial applications [1–3]. The current limitation to the use of SMAs is that commercially available SMAs are principally made out of Ni-Ti alloys which are expensive and also have a huge processing cost and facility burden [4]. This has made the search for more
cost-effective SMAs an ongoing pursuit by researchers. Cu-based and Fe-based SMAs have been identified as the most promising low cost alternatives to Ni-Ti alloys. The lower strain recoveries of Cu (~5%) and Fe (<5%) compared to that of NiTi alloy (8%) is compensated for by lower processing cost and amenability to fabrication routes and facilities utilised for conventional metal processing [5–7]. Cu-based SMAs are of special interest because of its modest recoverable strain (~5%) which is closest to that of NiTi alloy, cheaper production cost, and ease of fabrication, and high thermal and electrical conductivity [8–10]. Regrettably, these Cu-based alloys are associated with brittleness induced by coarse grain structure, high elastic anisotropy and high degree of order which reduces the cold workability of the alloys [10]. Furthermore, Cu-based alloys are susceptible to ageing which could lead to phase (martensite) stabilisation and change in transformation temperatures which affects its shape memory capacity [3,11,12].

Cu–Zn–Al alloys are the most studied Cu-based alloys and have been explored for use in applications such as fasteners, springs, couplings and thermal actuators where the use of other alloys would be technically and economically ineffective [13,14]. Cu–Zn–Al alloys have relatively higher strain recovery compared to other Cu-based alloys. However, similar to other Cu-based alloy grades, Cu–Zn–Al alloys are prone to brittle failure, and have low fracture and fatigue strength, and low workability [15]. Grain refinement has been proffered as a technique for the improvement of mechanical and shape memory properties of Cu-based SMAs [3,15]. In this regard, the use of micro-alloying elements [16], mechanical and thermo-mechanical processing [17–19]; have been explored to achieve grain refinement in Cu-based SMAs. The use of micro-alloying elements such as B, Ti, V, Ce, Fe, Co, Be, Zr have been the most reported of these approaches; and many of the investigations show that their presence has influence on the microstructure, transformation and shape memory properties of Cu-based SMAs [5,16,20]. B and Fe are the least expensive of these microalloying elements and have been reported to be very efficient grain modifiers [5,21]. However there have been divergent opinions on the optimum concentrations of these microalloying elements and the mechanisms for effecting grain modification in Cu-based SMAs in general and Cu–Zn–Al SMAs in particular. For instance, Wang et al. [22] reported that 0.01% B was the optimum concentration required to achieve grain refinement in Cu–Zn–Al alloy but Ferreira et al. [23] stated that B concentration within the range of 0.05–0.08% was sufficient for effective grain refinement. Fe concentration for effective grain modification and enhanced mechanical properties has also been subject of research discuss recently [24]. The present work, investigates the phase characteristics and microstructure of Fe, B, and Fe–B modified Cu–Zn–Al SMAs in details and its effect on the mechanical behaviour.

2. Materials and method

2.1. Alloy and sample preparation

The Cu–18Zn–6Al based alloys were produced in accordance with Alaneme [25]. Charge calculation was used to determine the amount of Cu, Zn and Al required to produce Cu–18Zn–6Al base composition containing two different weight percent each (0.05 wt.% and 0.1 wt.%) of Fe and B. Two other compositions containing mixtures of Fe and B (0.05 wt.% B and 0.05 wt.% Fe) (0.025 wt.% Fe and 0.075 wt.% B) were equally produced. The Fe and B weight percent selected are within the range reported in literature [22–24]. The charge for Cu–18Zn–6Al alloy without the addition of micro-alloying elements was also prepared as the control composition. The alloys were prepared via liquid metallurgy route, melted in a crucible furnace and cast into sand moulds inserted with metallic chill. The chemical composition of the Cu–Zn–Al shape memory alloys determined by EDS analysis is presented in Table 1. After casting, the alloys were subjected to homogenisation treatment at 800 °C for 4 h and cooled in air in accordance with Alaneme [25]. The alloys were then subjected to 10% cold rolling using a miniature cold rolling machine; after which the samples were annealed at 450 °C for 1 h and cooled in air to remove internal stresses developed in the samples during the cold deformation process. The samples for mechanical test, microstructural and phase characterisation were machined to prescribed test specifications. The samples were finally annealed at 400 °C for 2 h then water quenched at room temperature to eliminate stresses generated during the machining process.

2.2. Microstructural characterisation

2.2.1. Optical microscopy

A Zeiss optical microscope was used for microstructural investigation of the alloys produced to assess the grain structure and phase distribution. The specimens for microstructural examination were metallographically prepared following a series of grinding and polishing process. Subsequently the specimens were etched in a solution of 5 g ferric chloride, 10 ml HCl, and 95 ml ethanol, swabbing for 10–20 s; after which microstructural analysis was performed.

2.2.2. Scanning electron microscopy (SEM)

Detailed microstructural characterisation and compositional analysis was carried out using a Zeiss high resolution field emission gun scanning electron microscope (Zeiss FESEM) to complement the optical microscopy analysis. Back scattered electron (BSE) mode, secondary electron imaging and energy dispersive spectroscopy (EDS) were used for microstructural and fractographic analysis of the Cu–Zn–Al alloys produced.

| Table 1 – Chemical composition of the Cu–Zn–Al alloys. |
| Sample designation | Cu | Zn | Al | B | Fe |
| A | 76 | 17.90 | 6.10 | – | – |
| B | 75.95 | 18.02 | 5.98 | 0.05 | – |
| C | 75.90 | 17.50 | 6.50 | 0.1 | – |
| D | 75.95 | 18.40 | 5.60 | – | 0.05 |
| E | 75.90 | 17.33 | 6.67 | – | 0.1 |
| F | 75.90 | 18.05 | 5.95 | 0.05 | 0.05 |
| G | 75.90 | 18.09 | 5.91 | 0.075 | 0.025 |
2.3. X-ray diffraction analysis

The analysis of the crystalline phases present and their intensity was carried out on the Cu–Zn–Al alloys using X-ray diffractometry (XRD). The samples were prepared for XRD analysis following standard procedures. A PANalytical Empyrean diffractometer with PIXcel detector and Fe filtered Co-Kα as source of radiation, was used for the analysis. The analysis was performed from angle 2θ spectral range of 0° to 120°. The phases were identified using X’Pert Highscore plus software.

2.4. Mechanical properties

2.4.1. Hardness measurement

The hardness values of the alloys were evaluated on a hardness testing machine using a Digital Rockwell hardness tester adopting a HRA (60 kgf) scale. The sample preparation and testing procedure was performed in accordance with ASTM E18-16 standard [26]. Five hardness indents were made on each specimen and readings within the margin of ±2% were taken for the computation of the average hardness values of the specimens.

2.4.2. Tensile testing

The tensile properties of the produced alloys were evaluated by tensile testing using a universal testing machine. Specimens for the test were machined to tensile test specifications of 5 mm diameter and 30 mm gauge length. The specimens were mounted on the testing platform and pulled monotonically at a strain rate of 10−3/s until fracture. The specimen preparation and testing procedure were in accordance with ASTM EB/EBM-15a standard [27]. For each alloy composition, three repeat tensile tests were performed to guarantee the reliability of the data generated. The tensile properties evaluated from the test are the ultimate tensile strength and % elongation.

2.4.3. Fracture toughness

The fracture toughness of the alloys was determined using circumferential notch tensile (CNT) testing in accordance with Alaneme [28] The specimens for the test were machined to gauge length of 27 mm, gauge diameter of 6 mm (D), notch diameter of 4.2 mm (d), and notch angle of 60°. The specimens were then subjected to tensile loading to fracture at room temperature using an Instron universal testing machine operated at a quasi-static strain rate of 10−3/s. The fracture load (Pf) obtained from the CNT specimens’ load–extension plots was used to evaluate the fracture toughness using the empirical relation [29]:

\[ K_{IC} = \frac{P_f}{D^{1/2}} \left[ 1.72 \left( \frac{D}{d} \right) - 1.27 \right] \]

(2.1)

where D and d are the specimen diameter and the diameter of the notched section respectively. 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 [30]:

\[ D \geq \left( \frac{K_{IC}}{\sigma_y} \right)^2 \]

(2.2)

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

3. Results and discussion

3.1. Microstructures of the Cu–Zn–Al alloys

3.1.1. Optical microscopy

Optical micrographs of the unmodified and modified alloys are presented in Figs. 1-4. Fig. 1 shows the optical micrograph of the unmodified alloy, characterised by needle-like lath structure which was acknowledged to be lath martensite structure. The lath structure observed in Fig. 1 is similar to the lath martensite structures in Cu–Zn–Al alloys reported in the works by Xu [31] and Dasgupta [32]. The alloys with B additions (Fig. 2) were observed to have undergone a change in the martensite morphology from sharp edged needle-like lath structure to curve edged rod like structure with the grains relatively larger than the unmodified Cu–Zn–Al alloy (Fig. 1). There also is a slight increase in grain size with increase in B composition (from 0.05 to 0.1 wt.%) if Fig. 2(b) is compared with Fig. 2(a). This implies that nucleation and growth condition in the alloy is influenced by the B concentration. The addition of Fe to the Cu–Zn–Al alloys (Fig. 3) show a structure with near elliptical phase morphology and significantly reduced needle-like martensite appearance. The grain size did not appear to be sensitive to Fe concentration (Fig. 3a and b) as with the case of B addition (Fig. 2). The mixed (Fe–B) composition (Fig. 4) was observed to have a combination of near elliptical grain shape with curve edged needle like lath martensite structure. The observations made are clear indicators that the micro-alloying elements (Fe, B, and Fe–B) actually modify the grain size and morphology of Cu–Zn–Al alloys.
3.1.2. SEM observations

The scanning electron microscopy images of the unmodified and modified Cu–Zn–Al alloys (Figs. 5–8) show structural features which are completely in conformity with the observations made from those of the optical micrographs of the alloys (Figs. 1–4). It is observed from Fig. 5(a) that the unmodified alloy microstructure consists of predominantly lath martensite structure. Fig. 6 which presents the BSE images of the boron modified Cu–Zn–Al alloy, is generally characterised by large grain size and a change in grain edge morphology from sharp to round/rod-like (that is compared with Fig. 5). Table 2 presents the change in transverse lath/grain thickness for the unmodified and modified Cu–Zn–Al alloys produced. Table 2 shows that the grain size increases with B addition from 13 μm for the unmodified composition to about 28–38 μm for the B modified composition. Also grain size is confirmed to be sensitive to the concentration of B, as the average transverse grain size increased from 28 μm for the 0.05 wt.% B modified Cu–Zn–Al alloy composition to 38 μm for the 0.1 wt.% B modified Cu–Zn–Al alloy grade. This suggests that nucleation and grain growth is influenced by the presence and concentration of B in the Cu–Zn–Al alloy. Similar grain morphologies are observed for the Fe modified (Fig. 7) and the Fe–B modified Cu–Zn–Al alloys (Fig. 8). The change in the grain morphology observed on the Fe modified Cu–Zn–Al alloy (Fig. 7) was quite significant, evolving towards an elliptical grain shape. The near-elliptical grain morphology observed is in agreement with results from previous studies [23,24] on Fe modified Cu–Zn–Al alloys. Also, it can be seen from Table 2 that although grain size increase occurs with the addition of Fe as micro-alloying element in Cu–Zn–Al alloy, the grain size increase was invariant to the Fe concentrations used as grain modifiers (that is 0.05 wt.% Fe and 0.1 wt.% Fe had similar grain size). Fig. 7(c) shows a representative EDS profile for the Fe modified Cu–Zn–Al alloy showing peaks of CuZn and the presence of Fe in the alloy.

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Average martensite lath thickness (μm)</th>
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<tbody>
<tr>
<td>A (Cu–Zn–Al)</td>
<td>13 ± 0.17</td>
</tr>
<tr>
<td>B (Cu–Zn–Al–0.05B)</td>
<td>28 ± 0.01</td>
</tr>
<tr>
<td>C (Cu–Zn–Al–0.1B)</td>
<td>38 ± 0.06</td>
</tr>
<tr>
<td>D (Cu–Zn–Al–0.05Fe)</td>
<td>29 ± 0.22</td>
</tr>
<tr>
<td>E (Cu–Zn–Al–0.1Fe)</td>
<td>28 ± 0.10</td>
</tr>
<tr>
<td>F (Cu–Zn–Al–0.05B–0.05Fe)</td>
<td>27 ± 1.23</td>
</tr>
<tr>
<td>G (Cu–Zn–Al–0.025B–0.075Fe)</td>
<td>26 ± 0.04</td>
</tr>
</tbody>
</table>

Fig. 2 – Optical micrographs of (a) 0.05B modified Cu–Zn–Al alloy and (b) 0.1B modified Cu–Zn–Al alloy.

Fig. 3 – Optical micrographs of (a) 0.05Fe modified Cu–Zn–Al alloy and (b) 0.1Fe modified Cu–Zn–Al alloy.
It was also observed that grain size increase and substantially modified grain edges (to near elliptical grain shape) occurred with the addition of Fe–B as micro-alloying additions in Cu–Zn–Al alloy. However, similar to the Fe micro-alloying additions, the grain size increase was invariant to the Fe–B concentrations used.

The micrographs suggest that although same cooling rate was adopted for all alloy compositions produced, the nucleation and grain growth rates were altered by the presence of the micro-alloying elements. The increase in grain size characteristic of the Fe, B, and Fe–B modified Cu–Zn–Al alloys investigated differs from the observations made in similar studies [5,23,24] wherein additions of Fe and B were observed to cause grain refinement. Grain refinement observed in Cu–based alloys has been attributed to changes in solidification conditions of the material as a result of micro-alloying elements addition reducing the coarseness of the microstructure [31,33]. The grain size increase observed in this study can be related to results observed elsewhere. Some micro-alloying elements such as Ti–B have been reported to delay nucleation of certain phases while enhancing grain growth simultaneously [34]. The formation of martensite in the forward transformation has been reported to be as a result of nucleation and grain growth in the parent phase; hence the rate of nucleation influences the type and morphology of martensite formed [35].

3.2. Analysis of X-ray diffraction

The X-ray diffraction analysis of selected alloy compositions is presented in Fig. 9. Cu–Zn and Cu–Al were identified as the crystalline phases present in the alloy. The Cu–Zn phase was
determined to be fcc structure from analysing the pattern of the diffracting crystal planes for the entire 2θ diffraction angles [36]. The Cu–Al phase was determined to have bcc structure following similar basis. The predominance of Cu–Zn peaks in the alloys analysed was in agreement with EDS results (Fig. 7c), and XRD patterns of Cu–Zn–Al alloys reported in literature [37]. The crystalline phases identified are typical of Cu–Zn–Al alloys with shape memory capacity. Guerioune et al. [9] reported that the Cu–Zn phase in Cu–Zn–Al alloy is a metastable phase which exhibits shape memory effect and the Cu–Al forms as a result of the affinity of Cu for Al. The micro-alloying elements had no effect on the XRD peaks as diffractions by the same crystal planes are observed to occur with the same intensity and diffraction angles (2θ).

3.3. Mechanical behaviour of the Cu–Zn–Al alloys

3.3.1. Hardness

The hardness values of the unmodified and modified Cu–Zn–Al alloys are presented in Fig. 10. It is observed that the hardness of the unmodified Cu–Zn–Al alloy is higher than that of the modified alloys with reductions in hardness ranging between 32.4 and 51.5%. The modified Cu–Zn–Al alloy compositions, is observed to have a significant decrease in hardness with increase in B concentration. However, the Fe modified Cu–Zn–Al alloy grade had marginal increase in hardness with increase in Fe concentration. It is also noted that the Cu–Zn–Al alloys modified with Fe–B had the highest hardness values in comparison with other modified Cu–Zn–Al alloy compositions. The variation in hardness can be attributed to the variation in grain size and morphology of the alloys as observed from Figs. 1 to 8. The hardness trend is also observed to correlate well with the transverse grain size determined for all the Cu–Zn–Al alloy grades produced. In this regards, the hardness increase with decrease in the grain size determined (Table 2). The fine lath martensite structure is principally responsible for the high hardness of the unmodified alloys as indentation resistance improves with finer grain size [25].

3.3.2. Ultimate tensile strength

The ultimate tensile strength results of the unmodified and modified Cu–Zn–Al alloys are presented in Fig. 11. The tensile strength of the unmodified alloy is observed to be significantly lower than that of the modified alloy grades. Tensile strength increase within the range of 28.37–52.74% was observed with the use of Fe, B and Fe–B as micro-alloying elements for the Cu–Zn–Al alloy. The low tensile strength of the unmodified alloy is attributed to the fine lath martensite structure. The edges of the needle like lath structure serve as sites for stress concentration and triaxial stress state in the microstructure. Stress concentration and triaxial stress state constrains yielding of the material and facilitates micro-crack nucleation and propagation which culminates in fracture even when the nominal applied stress on the material is relatively low [31].

Fig. 7 – Back scattered electron images of (a) 0.05Fe modified Cu–Zn–Al alloy, (b) 0.1Fe modified Cu–Zn–Al alloy, and (c) representative EDS profile of the 0.1Fe modified Cu–Zn–Al alloy.
Improved tensile strength in the modified compositions is as a result of the change in the grain morphology despite the obvious increase in grain size. The round/elliptical grain edges reduce the tendency to act as stress concentrators, and thus necessitate the application of a relatively higher stress to facilitate yielding and increase maximum stress bearing capacity. This implies that the stress applied to the modified alloy is more uniformly distributed in contrast to the unmodified alloy where higher stress concentration occurs at the lath edges (tips).

3.3.3. Percent elongation
The percent elongation of the Cu–Zn–Al alloys was observed to increase with the addition of the micro-alloying elements (Fig. 12). This implies that the ductility of the alloys improved with B, Fe, and Fe–B addition. The elongation is also observed to be sensitive to the concentration of the microelement as reduction in percentage elongation occurred with increase in the concentration of the respective micro-alloying elements (B, Fe and Fe–B). The Fe and Fe–B modified Cu–Zn–Al alloy compositions were observed to have higher elongation values. The unmodified alloy had the lowest elongation (6.7%) compared to 12.6% and 11.7% for 0.05Fe and 0.05Fe–0.05B modified alloys, respectively. Improvement in ductility due to additions of Fe and B to Cu–Zn–Al alloys has been reported by Alaneme [25] and Ferreira et al. [23]. This improvement is an indicator of improved plasticity and hence the workability of the Cu–Zn–Al alloy.

3.3.4. Fracture toughness
The fracture toughness values of the unmodified and modified Cu–Zn–Al alloys are presented in Fig. 13. It is observed that the fracture toughness of the Cu–Zn–Al alloy increased within the range of 10–23% with the use of Fe, B, and Fe–B as micro-alloying additions. The Fe modified Cu–Zn–Al alloy compositions were observed to have the highest improvement (~23% increase) of all the modified Cu–Zn–Al alloys produced. In essence, this implies that the resistance of Cu–Zn–Al alloys to crack propagation is improved. The grain modification from lath martensite (needle-like) grain edges to round/elliptical grain edge morphology for the modified Cu–Zn–Al alloys is responsible for the improved fracture toughness. The elliptical grain edge morphology helps reduce stress concentration which reduces tendency for crack nucleation and propagation [38].

3.3.5. Fracture surface observation
Fig. 14 shows representative secondary electron images of the tensile fracture surfaces of the unmodified and modified Cu–Zn–Al alloys investigated. The fracture features are

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**Fig. 8** Back scattered electron images of (a) 0.05Fe–0.05B modified Cu–Zn–Al alloy, and (b) 0.025Fe–0.075B modified Cu–Zn–Al alloy.

**Fig. 9** X-ray diffraction analysis of the unmodified alloy (A) and three modified alloy compositions (0.05B modified Cu–Zn–Al alloy) (B), (0.05Fe modified Cu–Zn–Al alloy) (D) and (0.05Fe–0.05B modified Cu–Zn–Al alloy) (F).
indicative of a fibrous micro-mechanism to crack initiation, propagation and fracture characterised by the prevalence of dimpled rupture particularly for the modified alloy compositions (Fig. 14(b) and (c)). A combination of spherical dimples and grain facets were observed on the fracture surface of the unmodified Cu–Zn–Al alloy, indicating mixed fracture modes. The fractographic features observed are in agreement with fracture surface characteristics of Cu–Zn–Al alloys modified with micro-alloying elements reported by other authors [24,33].
4. Conclusion

The microstructure, phase characteristics and mechanical behaviour of Cu–18Zn–6Al alloys containing two different weight percent each (0.05 wt.% and 0.1 wt.%) of Fe and B, and two other compositions which have mixtures of Fe and B (0.05 wt.% B and 0.05 wt.% Fe) (0.025 wt.% Fe and 0.075 wt.% B) were investigated. The results show that:

1. Needle-like lath martensite structure with sharp grain edges observed for the unmodified Cu–Zn–Al alloy was transformed to grains with significantly larger transverse grain size and curved/near elliptical grain shape for the Fe, B, and Fe–B modified Cu–Zn–Al alloys.
2. Cu–Zn with fcc structure was the predominant crystalline phase identified in the alloys while Cu–Al with bcc structure was the second phase observed.
3. The crystalline phases identified are typical of Cu–Zn–Al alloys with shape memory capacity.
4. The hardness of the unmodified Cu–Zn–Al alloy was higher than that of the modified alloys with reductions in hardness ranging between 32.4 and 51.5%.
5. The tensile strength of the unmodified Cu–Zn–Al alloy was significantly lower than that of the modified alloy grades. The percent elongation and fracture toughness of the modified alloy were higher than that of the unmodified alloy grade.
6. The modified Cu–Zn–Al alloys mostly exhibited fracture features indicative of a fibrous micro-mechanism of crack initiation and propagation characterised by the prevalence of dimpled rupture.

Conflicts of interest
The authors declare no conflicts of interest.

REFERENCES


