ON THE MECHANICAL PROPERTIES AND DAMPING BEHAVIOUR OF THERMALLY AGED UNMODIFIED AND Ni MODIFIED Cu-Zn-Al SHAPE MEMORY ALLOYS

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ABSTRACT

The effect of thermal age on the mechanical properties and damping behaviour of CuZnAl(x)Ni shape memory alloys (SMAs) (where x = 0, 0.1, 0.3 wt. % Ni), produced via liquid metallurgy processing was investigated. The strength and fracture toughness parameters were observed to increase with increase in Ni concentration and ageing temperatures, while the ductility increased with Ni concentration but decreased with increase in ageing temperature. For the unmodified CuZnAl alloy, damping capacity improved with ageing treatment in comparison with the unaged condition. In contrast, the damping capacity decreased for the Ni modified CuZnAl alloys in the aged condition (0.015 - 0.025 at 250°C and 0.012 - 0.038 at 400°C, for the 0.1Ni modified CuZnAl alloy; and 0.012 - 0.018 at 250°C and 0.016 - 0.0284 at 400°C for the 0.3Ni modified CuZnAl alloy) compared with the unaged condition (0.0376 - 0.050 for unaged 0.1Ni modified CuZnAl alloy, and 0.0428 - 0.062 for the unaged 0.3Ni modified CuZnAl alloy). The results indicate that Ni modification within the range 0.1 - 0.3 wt.% could have a more favourable effect on mechanical properties but could adversely affect the damping capacity of CuZnAl based SMAs in comparison with the unmodified condition.

Keywords: CuZnAl alloy, shape memory alloy, martensite ageing, damping capacity, mechanical behaviour, Ni micro-alloying addition.

INTRODUCTION

Shape memory alloys (SMAs) are a unique class of smart materials that demonstrate the capacity to regain their pre-deformation configuration (that is, the capacity to recover apparent permanent strain) when exposed to an appropriate thermal treatment at a certain temperature [1]. The thermo-responsive properties of SMAs, usually expressed as thermoelasticity and pseudoelasticity, are unique to these class of metallic alloys on account of the martensitic transformation which is characteristic of these alloys. Thus, they are generally applied in sensing devices in pneumatic, biomedical, hydraulic, and robotic systems [2 - 4]. Several alloy systems have been acknowledged to exhibit some degree of shape memory effects (SME); however, Ni Ti, Cu and Fe based SMAs, are considered the most commercially and functionally viable SMA systems [4 - 6]. Cu based SMAs, are well acknowledged to be the most cost and processing sustainable SMA systems for industrial and technological applications. They combine a modest strain recovery (~5 %) which is second only to the NiTi systems (~8 %), with low materials costs and amenability to processing using traditional casting practice [7, 8]. This has made Cu based SMAs top in the consideration list for application in electrical and thermo-responsive industrial and technological systems [9, 10]. Their processing and functional limitations are low ductility,
due to the coarse grain and ordered structures they possess, coupled with their tendency to stabilize the lower transformation phase product (martensite) via precipitation (martensite stabilization) [8, 11]. Efforts to address these limitations have been in the directions of alloy design, thermo-mechanical processing, and heat treatment [12, 13]. However, martensite ageing (also known as martensite stabilization) which occurs during heating towards the reverse transformation temperature for austenite phase formation, has not been thoroughly mitigated in most Cu based SMAs. This has made stable transformation temperatures, which is the core basis for designing thermo-responsive devices difficult to attain in Cu based SMAs [11, 12]. In CuZnAl based SMAs, the martensite phase stabilization is reported to occur by bainite phase precipitation, re-ordering of the β phase, and α (equilibrium) phase decomposition [13, 14]. The use of heat treatment and micro-alloying additions as microstructure modifiers have been successful in addressing issues relating to improving mechanical properties, workability, and damping performance in CuZnAl SMAs, but very sparse information is available on how these modifiers impart on the aging response of the alloys and the consequent influence on the mechanical and damping properties of the alloys. In the present study, the effect of thermal ageing on the mechanical properties and damping behaviour of unmodified and nickel modified CuZnAl SMAs is investigated. From our previous studies, it was reported that Ni microalloying addition resulted in improvement in mechanical and damping characteristics of the SMAs. However, the extent to which these properties are affected by martensite ageing was not covered [15].

### EXPERIMENTAL

#### Materials

Pure grade copper, zinc, aluminum billets were utilized as the parent materials for the development of the Cu-Zn-Al based shape memory alloys, while analytical pure grade nickel particles were selected as the micro alloying addition. The Cu, Zn, Al, and Ni materials were sourced locally from licensed vendors.

#### Alloy Design and Production

Three compositions, Cu-18Zn-7Al, Cu-18Zn-7Al-0.1Ni and Cu-18Zn-7Al-0.3Ni were of interest in the present investigation. In order to achieve these alloy compositions, charge calculations and alloy development procedures were adopted in the study in accordance with Alaneme and Umar, [15]. Utilizing conventional melting and casting practice, the three compositions of the alloys were produced using a gas-fired crucible furnace with sand moulds for casting of the melts. The cast samples were retrieved and fettled, and were subsequently machined into various test samples for mechanical, damping and microstructural characterization. Thereafter, selected samples from the alloys were artificially aged at two different temperatures of 250°C and 400°C for 2 h and were air-cooled. The compositions and treatment conditions of the alloys with corresponding sample designations, are presented in Table 1.

#### Microstructural Characterization

The microstructures of the Cu-Zn-Al alloys produced were examined using a Zeiss optical microscope. Series of grinding and polishing operations were used to prepare the sample surfaces to mirror-like metallographic finish, before they were etched using 5 g FeCl₂, 10 mL HCl, and 95 mL ethanol solution. The samples were subsequently examined using the microscope.

#### Mechanical Testing

##### Hardness Measurement

The hardness of the as-cast and thermally aged CuZnAl(x)Ni alloys (where x is 0, 0.1, and 0.3 wt. %) was determined with the aid of a hardness testing machine. The samples were prepared by sectioning and

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Alloy compositions &amp; Treatment</th>
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<tbody>
<tr>
<td>CZ1</td>
<td>Cu-Zn-Al</td>
</tr>
<tr>
<td>CZ2</td>
<td>Cu-Zn-Al Aged at 250°C</td>
</tr>
<tr>
<td>CZ3</td>
<td>Cu-Zn-Al Aged at 400°C</td>
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<tr>
<td>CZ4</td>
<td>Cu-Zn-Al-0.1Ni</td>
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<tr>
<td>CZ5</td>
<td>Cu-Zn-Al-0.1Ni Aged at 250°C</td>
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<tr>
<td>CZ6</td>
<td>Cu-Zn-Al-0.1Ni Aged at 400°C</td>
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<td>CZ7</td>
<td>Cu-Zn-Al-0.3Ni</td>
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<tr>
<td>CZ8</td>
<td>Cu-Zn-Al-0.3Ni Aged at 250°C</td>
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<tr>
<td>CZ9</td>
<td>Cu-Zn-Al-0.3Ni Aged at 400°C</td>
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polishing to achieve a fine polished, plan parallel surface. The testing was performed with the use of 30 kgf load for sample indentation, applied for 10 s (dwell time). The testing was conducted following the recommendations of ASTM E92 standard, with five repeat tests conducted and the statistical average recorded as the hardness value of the respective samples [16].

**Tensile Testing**

The tensile properties of the as-cast and aged Cu-Zn-Al alloys were evaluated by tensile testing with the use of a universal testing machine. The test samples were machined to cylindrical rod specifications of 5 mm and 30 mm, diameter and gauge length, respectively. A quasi-static strain rate of 10^-3/s was utilized for tensile loading to fracture, while three repeat tests were conducted for each test case to assure for the consistency of test results. The recommendations of ASTM E8/E8M standard was utilized for the conduct of the test [17].

**Fracture Toughness Testing**

Tensile testing of circumferential notch cylindrical rod samples was used to generate the primary data used for the evaluation of the fracture toughness of the samples [18]. The specimens were machined with gauge length and diameter of 30 mm and 6 mm, respectively, with gauge diameter to notch diameter ratio of 1.33 and notch angle of 60°. The samples were loaded in tension to fracture at a quasi-static strain rate of 10^-3/s, and repeat tests were performed for consistency of generated results to be certified. The fracture toughness and validity of results were established using equations (1) and (2) [19].

\[
K_{IC} = \frac{P_f}{d^{\frac{3}{2}}} \left[1.72 \left( \frac{D}{d} \right) - 1.27 \right], \tag{1}
\]

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

where, where \( K_{IC} \), \( P_f \), \( D \) and \( d \), are the fracture toughness, fracture load, specimen diameter, and notch diameter, respectively.

**Damping Test**

The damping properties of the unaged and aged CuZnAl(x)Ni alloys (where x is 0, 0.1, and 0.3 wt. %), were studied within the temperature range of 30°C to 250°C using a dynamic mechanical analyzer. The testing was performed in three-point bending deformation mode using rectangular bar specimens with dimensions 40 mm x 5 mm x 0.9 mm. The test parameters: strain amplitude (\( \varepsilon \)), vibration frequency (f), and heating rate (T), were fixed at 10 mm, 1 Hz, and 5°C/min, respectively; and the testing was performed in line with ASTM E756-05 recommendations [20]. The loss tangent (tan \( \delta \)), which is a measure of damping capacity, was evaluated using equation 3 [15]:

\[
\tan \delta = \frac{E''}{E'} \tag{3}
\]

where \( E'' \) and \( E' \) are the loss modulus and the storage modulus determined directly from the test.

**RESULTS AND DISCUSSION**

**Microstructure**

Representative optical micrographs of the Cu-Zn-Al alloys are presented in Figs. 1-3. The micrographs show differences in microstructural features for the varied compositions and ageing treatment. However, higher resolving microscopic analysis is required for proper delineation of precipitates and other microstructural features. This would form part of further studies to be performed on the Cu based SMAs by the authors.

**Mechanical Properties**

**Hardness**

The hardness of the unmodified and Ni-modified Cu-Zn-Al alloys in the unaged and aged conditions are presented in Fig. 4. The hardness values are observed to increase with Ni concentration and ageing temperature. For the unaged condition, hardness increase of 8.6 % and 67.2 % were attained in the alloys when 0.1 and 0.3 wt. % Ni, respectively, are used as alloying addition. The improvement in the hardness observed in the Ni modified Cu-Zn-Al alloys has been reported by Alaneme et al. to be linked to grain shape and width modification which occurs in the alloys with Ni micro alloying addition within the range 0.1 - 0.3 wt. % [15]. This grain morphological changes and relatively finer sizes result in increased hardness due to increased boundary strengthening effect (more boundaries serving as barriers to dislocation motion) [21, 22].

For the alloys subjected to ageing treatment, it is noted that the hardness increases with ageing temperature increase from 250°C to 400°C. The enhanced hardness
Fig. 1. Representative Micrograph of CuZnAl alloy: (a) as-cast structure, (b) subjected to ageing treatment at 250°C, and (c) subjected to ageing treatment at 400°C.

Fig. 2. Representative Micrograph of 0.1 wt. % Ni modified CuZnAl alloy: (a) as-cast structure, (b) subjected to ageing treatment at 250°C, and (c) subjected to ageing treatment at 400°C.
observed in the aged samples can be linked to the presence of precipitates which serve as barriers to the motion of dislocations. The increased hardness at 400°C in comparison with 250°C, can be attributed to increase precipitation which result in the availability of harder phase and barriers to dislocation motion values.

**Tensile Properties**

The tensile strength results of the unmodified and Ni modified Cu-Zn-Al alloys in the unaged and aged conditions are presented in Fig. 5. The tensile strength values are observed to increase as both Ni concentration and ageing temperature increases. For the unaged Cu-Zn-Al alloys, an increase of 2.73 % and 42.5 % was recorded with the use of 0.1 and 0.3 wt. % Ni, respectively, as alloying addition. The improvement in the tensile strength could be connected with the modification of the sharp and elongated grains edge morphology to a roundish/elliptical grain edge shape for the Ni modified Cu-Zn-Al alloy grades. The sharp grain edge morphology, serves as sites for localized stress amplification, which results in the lowering of the maximum stress bearing capacity of the alloy. Conversely, with the use of Ni as alloying addition, less stress amplification within the grain edge vicinity results, allowing for more even stress distribution, consequently improved strength is achieved [15, 23]. For the aged alloys, the tensile strength increased with increased ageing temperatures due to increased precipitate formation at 400°C than 250°C, which implies more precipitates serving as barriers to dislocation motion [24]. This point has been acknowledged already as
responsible for the improved hardness noted in the artificially age-hardened Cu-Zn-Al alloys discussed earlier. The percentage elongation of the unmodified and Ni modified Cu-Zn-Al alloys are presented in Fig. 6. The elongation values of the un-aged Cu-Zn-Al alloy are noted to be higher than that of the alloys subjected to ageing treatment. The tensile elongation was however, relatively higher for Ni modified CuZnAl alloy samples subjected to ageing treatment then the aged unmodified CuZnAl alloy grade. There was also apparent decrease in tensile elongation for samples aged at 400°C in comparison to those aged at 250°C.

Fracture Toughness
The fracture toughness results of the unmodified and modified Cu-Zn-Al alloys subjected to ageing treatment are presented in Fig. 7. The fracture toughness, which is a crack propagation resistance parameter, is also observed to increase with increase in the Ni concentration and ageing temperatures. For the unaged alloys, the fracture toughness values increased by 11.42 % to 25.18 %. This has been reported to be due to the modification of the sharp and elongated tips of the Cu-Zn-Al alloys, which results in the reduction of the stress concentration within the grain tip vicinity. The impact this has is to mitigate the potential tri-axial stress state created by the sharp grain tips, which facilitate brittle fracture [25, 26]. The improved fracture toughness with ageing temperature may be rationalized to be on account of the precipitates which act as crack arresters/crack branching facilitators that serve to slow the crack propagation rate, thereby resulting in improved fracture toughness [27].

Damping Properties
The damping properties of the unmodified and modified Cu-Zn-Al alloy subjected to ageing treatment are presented in Figs. 8 - 10. From Fig. 8(a), it is observed that the storage modulus improved with ageing treatment for the unmodified CuZnAl alloy. The sample aged at 400°C is observed to have relatively higher storage modulus values within the test temperature range of 30°C - 200°C. This is followed by the sample aged at 250°C, while the unaged samples had the least storage modulus values. Storage modulus is a measure of the dynamic stiffness of a material and is consistent with atomic and interface bond strength/rigidity [15, 28]. The implication is that the aged samples have a higher...
mechanical energy absorption capacity in comparison to the unaged sample. This is however, in sharp contrast with the trend observed in the Ni modified CuZnAl alloys (Fig. 8(b), (c)), where it is seen that ageing, particularly at 400°C, resulted in a sharp drop in the storage modulus of the CuZnAl alloys. Higher resolution microscopy characterization would perhaps be required to provide answers as to why this sharp contrast was observed for both Ni modified CuZnAl alloy compositions. This is expected to be addressed in future studies we intend to carry out on the SMA system.

The loss modulus of the unmodified and Ni modified CuZnAl alloys (Fig. 9) also follows a contrasting trend. It is noted that for the unmodified CuZnAl alloys, ageing treatment improved the energy dissipation capacity (loss modulus). Specifically, ageing at 400°C, resulted in a relatively higher loss modulus compared with when ageing was performed at 250°C while unaged sample exhibited the least loss modulus. Energy dissipation in SMAs normally occurs by martensite interface and boundary sliding which the precipitates do not appear to restrain. The implication however, of the results is that ageing of the unmodified CuZnAl alloy improves its energy dissipation capability. For the Ni modified CuZnAl alloys, it is observed that ageing resulted in a significant drop in the loss modulus of the 0.1 Ni modified CuZnAl alloys. In SMAs, capacity for energy dissipation is very high due to martensite and interface boundary mobility/sliding effect. This is however, constrained during precipitation as the precipitates pin/hinder interface boundary sliding. This same trend is observed for the 0.3 Ni modified SMA alloys where ageing is observed to result in significant drop in the loss modulus of the alloys. Close observation shows that the loss modulus at 400°C is slightly higher than that at 250°C.

The damping capacity results are presented in Fig. 10, it is observed that the use of Ni as alloying addition to the CuZnAl alloy, resulted in improvement in the damping capacity, which is noted to improve with increase in the Ni concentration from 0.1 wt. % to 0.3 wt. %. This improvement in damping capacity may be linked to the grain structure refinement induced by the Ni addition, which contributes to the creation of more boundaries and interfaces [29]. The mobility of the martensite variants and interfaces is responsible for the generally high damping capacity exhibited by SMAs.
Fig. 9. Loss modulus of: (a) aged and unaged CuZnAl shape memory alloys, (b) aged and unaged 0.1 wt. % Ni modified CuZnAl shape memory alloys, and (c) aged and unaged 0.3 wt. % Ni modified CuZnAl shape memory alloys.

Fig. 10. Damping capacity of: (a) aged and unaged CuZnAl shape memory alloys, (b) aged and unaged 0.1 wt. % Ni modified CuZnAl shape memory alloys, and (c) aged and unaged 0.3 wt. % Ni modified CuZnAl shape memory alloys.
Thus, the higher the number of boundaries and interfaces (from higher number of grains), the higher the damping effect from higher number of mobility centres within the grain structure. The damping capacity trends of the SMAs on ageing (Fig. 10) are observed to follow trends consistent with the loss modulus (Fig. 9). For the unmodified CuZnAl alloys, ageing resulted in increase in the damping capacity of the alloys in comparison with the unaged alloy. This implies that in applications where damping capacity is of primary interest, the ageing due to exposure to operating temperature environments may not have an adverse effect on the damping capacity/capacity to mitigate vibration. For the Ni modified CuZnAl alloys, damping capacity is noted to be lower for the samples subjected to ageing than in the unaged conditions. In SMAs, damping capacity - measure of capacity to convert mechanical/vibration energy to a safe mode in form of heat - is realised through martensite variants and interfaces movement and reorientation [15, 30]. This process is apparently constricted with the presence of precipitates which pin the boundaries/interfaces making the process of martensite movement/reorientation more cumbersome.

CONCLUSIONS

The effect of thermal ageing on the mechanical properties and damping behaviour of unmodified and nickel modified CuZnAl SMAs was investigated. The results show that:

- The hardness, tensile strength, and fracture toughness values improved with increase in Ni concentration and ageing temperatures, while the percentage elongation increased with Ni concentration but decreased with increase in ageing temperature.
- For the unmodified CuZnAl alloy, damping capacity improved with ageing treatment (0.03 - 0.0375 at 250°C and 0.025 - 0.034 at 400°C) in comparison with the unaged condition (0.014 - 0.029).
- In contrast, the damping capacity decreased for the Ni modified CuZnAl alloys in the aged condition (0.015 - 0.025 at 250°C and 0.012 - 0.038 at 400°C, for the 0.1Ni modified CuZnAl alloy; and 0.012 - 0.018 at 250°C and 0.016 - 0.0284 at 400°C for the 0.3 Ni modified CuZnAl alloy) compared with the unaged condition (0.0376 - 0.050 for unaged 0.1Ni modified CuZnAl alloy, and 0.0428 - 0.062 for the unaged 0.3 Ni modified CuZnAl alloy).
- Ni modification within the range 0.1 - 0.3 wt. % could have a more favourable effect on mechanical properties but could adversely affect the damping capacity of CuZnAl based SMAs in comparison with the unmodified condition.

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