Laser welded superelastic Cu–Al–Mn shape memory alloy wires

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This paper presents the first study on welding of Cu-based shape memory alloys. The superelastic wires used in the investigation had a nominal composition of Cu–17Al–11Mn (at.%). The pulsed Nd:YAG spot welding process altered the original bamboo-like microstructure of the base metal to a fusion zone with fine equiaxed grains. Micro-load-indentation depth analysis revealed that the grain refinement increased the ductility of the fusion zone compared to the base material. Tensile tests did not show any significant difference between base material and welded specimens, with failure occurring far away from the welds in the larger grained base metal. Mechanical cycling and superelastic behavior of the welded joints showed a faster stabilization of the hysteretic response than the base material, which is beneficial for applications where energy absorption is required. The Cu–Al–Mn superelastic alloy had a very high weldability and superior properties compared to other laser welded shape memory alloys, such as NiTi.

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1. Introduction

Shape memory alloys are stimulus-responsive materials which base their properties on a reversible martensitic transformation [1]. Cu-based shape memory alloys (SMAs) have higher thermal and electrical conductivity, good deformability and lower cost than the more widely used NiTi SMAs [2]. These advantages have recently motivated numerous investigations into these alloys. The Cu–Al binary system is the most important of the Cu-based SMAs because of its superior properties [3]. In their investigation of the martensitic transformation of these alloys, Hultgren et al. [4] showed that the ordering reactions β → α′ (CuAl: B2, cubic) → γ (Cu2Al: D0_2, cubic), occur at low temperatures during quenching and are not suppressed by rapid cooling. For a range of compositions, the metastable β phase orders during cooling and undergoes a first-order, diffusionless, structural transition into a more closed packed phase. This is the basis for the martensitic transformation in Cu-based alloys [5]. The addition of Mn to the binary alloy was found to stabilize the bcc phase, widen the single-phase region to lower Al compositions and lower temperatures, and improve the ductility of low Al alloys by decreasing the degree of order of the system. These improvements are the basis for the superior SMA properties of the Mn alloys compared to other Cu-based SMAs [5]. Increasing either Mn or Al decreases the transformation temperatures of the alloy, with a greater sensitivity to changes in the content of the former element [6]. The effect of the Al content on the shape memory effect and superelastic properties was studied by Kainuma et al. [6,7]. Kainuma et al. [7] showed that Cu–Al–Mn SMAs with Al contents below 18 at.% exhibit good ductility and excellent cold-workability due to a lower degree of order in the Heusler (L21) β, γ parent phase. Kainuma et al. [6] studied several alloys including a Cu–Al–Mn alloy with 17 at.% Al, which is similar to the alloy used in the current study. Alloys with lower than 14 at.% Al were found to have two different parent phases: (A2, disordered), and a lower parent phase resulting in more ideal shape memory properties. In these complex Cu–Al–Mn systems, the low temperature phase (martensite) may be of three different types: α’ (3R) forms with low Al content, β (11Mn alloy over NiTi also include

° (18R) forms in an intermediate range

° (2H) is predominant in higher Al content ranges.

The Cu–17Al–11Mn composition has the highest performing superelastic properties among the Cu-based SMAs, and can exceed the recoverable strain achieved in NiTi [8,9]. A comparison of the properties of Cu–17Al–11Mn SMA to the most widely used SMA NiTi is shown in Table 1. Advantages of the Cu–17A–11Mn alloy over NiTi also include a lower stress for inducing the martensite transformation, and greater thermal and electrical conductivities [2,10,11]. In addition to these superior physical properties, Cu-based SMAs are less expensive than NiTi [12]. These advantages may lead to Cu-based SMAs replacing NiTi in suitable applications.

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Cu-based SMAs are being considered as potential lower cost alternatives to NiTi for seismic and vibrational damping applications [18,19]. After cyclic loading, conventional steel reinforcement bars often have degraded stiffness and strength, experience pinching phenomena, and large cracks form after intense earthquakes [18]. Shrestha et al. [18] showed that Cu–Al–Mn superelastic alloys provided a more stable response under cyclic loading when compared to steel. The viability for the use of the Cu–Al–Mn SMAs as solutions for these problems in structural applications was emphasized recently by Araki et al. [20] and Genkturk et al. [19]. Araki et al. [20] studied the cyclic behavior under different loading frequencies of bars of the same Cu–Al–Mn alloy investigated in the current study. The alloy had a low cyclic hardening of the stress for the martensitic transformation, which makes them promising for biomedical applications and is currently used for ingrown nail correction. However, it was noticed that stable superelasticity required precise control of the grain size and orientation. Similar dependence of the mechanical properties on the grain orientation of other Cu–Al–Mn alloys was also noted in [2,12].

The superelastic Cu–17Al–11Mn SMA is also a primary candidate for biomedical applications and is currently used for ingrown nail correction as it does not present risks to the human health [8]. Both the medical and construction fields would benefit from dissimilar joining of these materials to current alloys in these areas [21]. Thus, a preliminary study envisaged to investigate the weldability of the Cu–Al–Mn alloys. Determining the weldability of the material can also increase the range of potential applications in which complex geometries of Cu–Al–Mn based components can be developed. Minimization of cost would include the minimization of Cu–Al–Mn use in a component, which would result in the weldment being a significant portion of the Cu–Al–Mn in the component. Additionally, it is important to fully characterize the effect of the weld on the superelastic properties of the material so that future components can be successfully designed. Laser welding has produced high quality joints when welding other SMAs, so it was chosen for the current investigation.

So far, no previous attempts of welding any Cu-based SMAs have been reported. In the current work laser welding of a Cu–Al–Mn SMA (superelastic at room temperature) was studied and the joints were characterized and compared to the base material.

### 2. Materials and methods

The Cu–17Al–11.4Mn (at%) alloy was prepared by induction melting under an Ar atmosphere to form an ingot. This ingot was hot forged (superelastic at room temperature) was studied and the joints were characterized and compared to the base material. However, in order to keep the results consistent among themselves, a given wire (named wire 1) was used for the tensile tests and another one (named wire 2) for the mechanical cycling tests. Wire 1 was used for preparing both base material and laser welded samples for the tensile tests and wire 2 was used with the same purpose but for analyzing the cyclic behavior.

#### 2.1. Laser welding

A Miyachi Unitek LW50A pulsed Nd:YAG laser system, with a wavelength of 1064 nm, a top-hat type spatial profile and a spot size of 600 μm was used. Argon was the shielding gas at a flow rate of $0.57 \, \text{m}^3 \, \text{h}^{-1}$ (20 CFH). A pulse profile with duration of 6 ms, including 1 ms upslope and 1 ms downslope was used. The welding process was developed to achieve a full penetration weld with a symmetric contour, with a minimum heat input. Read-on-plate welds were performed with a peak power of 1.5 kW. This geometry was selected to remove the variability of joint fit-up, which was desired because this was the first investigation on the weldability of Cu-based SMAs. An in-house custom built fixture system ensured the wires were straight before welding as shown in Fig. 1.

#### 2.2. Microstructural analysis and hardness measurements

The welded specimens were mounted in epoxy resin, mechanically polished and etched in a solution of FeCl$_3$ (10 g) + HCl (25 ml) + H$_2$O (100 ml) for 5 s. An Olympus BX51M optical microscope was used for microstructural observation.

Scanning Electron Microscopy (SEM) was performed using a JEOL JSM-6460SEM at an acceleration voltage of 20 kV for analyzing the fracture surfaces, while Energy Dispersive Spectroscopy (EDS) was performed with an INCA energy 350 EDS microanalysis system in order to quantify the composition variations along the welded joints for comparison with the base material. Three lines located at 1/3, 1/2 and 2/3 of the wire thickness, with 12 points each, were analyzed.

Conventional hardness was performed with a micro-Vickers hardness tester, from Shimadzu Corporation, along a cross-section of the weld in order to characterize the base material and the fusion zone. A load of 300 g was used and the hold time was kept at 20 s. A total of 18 indentions were performed.

Indentation load vs indentation depth analysis was made with a Nanovue M1 hardness tester. Three sets of loads (20, 30 and 38 N) were applied in the fusion zone and in the base material. The loading/ unloading rates were kept at 60, 85 and 120 N/min for 20, 30 and 38 N loads, respectively. A flat tip head with 100 μm diameter was used.

![Fig. 1. Schematics of fixture, laser and shielding gas position for the welding experimental setup.](Image)

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|-------------------|-----------------------|---------------------------------------------|--------------------|---------------------------|-----------------------|
2.3. Mechanical testing

Tensile testing was performed at room temperature using an Instron model 5548 micro-tensile tester at a displacement rate of 0.5 mm/min and a measurement accuracy of ±0.5 μm, following the ASTM F2516-07 standard. The overall gauge length of the tested specimens, both base and welded material, was of 20 mm. The peak stress was measured from the tensile curves as the maximum stress achieved during the tensile test. Three samples were tested for each condition. Scanning Electron Microscopy of the fracture surfaces was observed using a Zeiss Leo 1550 Field Emission SEM with an accelerating voltage of 10 kV.

Cycling behavior of the base metal and of the welds was also analyzed. A total of 10 mechanical load/unload cycles at 5% strain were performed at a rate of 0.5 mm/min, similarly to the tensile tests.

3. Results and discussion

3.1. Microstructural and hardness characterization

The base material had a bamboo-like microstructure, with a grain size ranging from 1 to 2 mm in length (Fig. 2). This microstructure re-solidified into fine columnar and equiaxed grains in the fusion zone (Figs. 3, 4) due to the high cooling rate characteristic of laser welding [22]. The grain size in the fusion zone ranged between 15 and 80 μm (Fig. 4) which was significantly smaller than the original base material grain size. The changes in shade of the microstructure along the base material and within the fusion zone have previously been identified to be related to differences in grain orientation [11].

The high cooling rates ensured that no α-precipitates formed in the fusion zone, thereby, preserving the superelastic properties of this region. The α-precipitates do not exhibit superelasticity and their presence is known to degrade the superelastic properties of the alloy. No heat affected zone was identified in optical microscopy because the base material had previously been subjected to high temperature annealing heat treatments that resulted in a very large grain size compared to the fusion zone.

Hardness measurements were performed on a line through the base material and fusion zone as depicted in Fig. 3. A large scatter of hardness values was observed with no significant difference from the fusion zone to the base material. The Cu-Al-Mn base material average hardness was 263.9 ± 6.5 HV, while in the fusion zone this was 258.4 ± 8.1 HV. These values fall within the expected hardness range for this alloy [23]. They also confirm that there is no heat affected zone. This inability to detect a heat affected zone by either optical or hardness measurements has been previously observed by Schlobmacher et al. [24] and Hsu et al. [25] during laser welding of NiTi. This lack of heat affected zone was attributed to the effect of annealing heat treatments performed on the base material prior to welding, so the weld thermal cycle had a minimal change on the base material and no heat affected zone was noticeable.

EDS was performed on the welded joint to characterize the compositional variations along the welds and through the wire thickness, as shown in Fig. 3. No significant compositional changes were observed in the EDS results. The average compositional change in the fusion zone did not differ significantly from the base material nominal composition, as depicted in Table 2. Laser welding can change the composition of a material through vaporization, as reported for NiTi SMAs [26]; however, the parameters and single pulse used in the current process were insufficient to have any significant change on the composition of the wires.

Fig. 2. Optical micrograph of the original base material.

Fig. 3. a) Optical micrograph of the welded joint showing the position of EDS scan lines and hardness measurements. Three EDS line scans were performed across the cross section of the base material and fusion zone (total of 12 analyzed spots per line scan). b) Corresponding hardness values for the different regions of the welded material (total of 18 analyzed spots).

Fig. 4. Magnified view of the microstructure of the base metal and fusion zone at the fusion boundary.
3.2. Local mechanical behavior

In order to obtain separate mechanical characterization of the fusion zone and the base material, load–displacement indentation tests were conducted. Fig. 5 depicts the plots of Load vs. Penetration depth in these regions for three sets of maximum applied loads (20, 30 and 38 N). The indenter size was 100 μm which captured either multiple grains in the fusion zone or a portion of the large base material grain in each indentation.

For applied loads of 20 and 30 N both the base material and the fusion zone exhibited the same behavior. However, for the maximum applied load of 38 N, the fusion zone had a higher penetration when compared to the base material. This increase in ductility resulted from the reduction in grain size from the bamboo-like grained base material to the fine grained fusion zone.

3.3. Tensile failure and fracture analysis

Fig. 6 depicts stress–strain curves for both base material and welded wire. The tensile curves of the welds were very similar to the base material, with both materials requiring the same average stress for inducing the martensitic transformation. When welding NiTi, the most studied SMA, a decrease of the mechanical properties has been observed due to grain growth [25]. However, in the case of this Cu–Al–Mn SMA, the intentionally massive grain size of the base metal was unaffected by the welding process as previously discussed, so no significant difference was observed in the tensile behavior of the welded versus base material wires.

In superelastic Cu–Al–Mn alloys, the large grains improve the stress–strain response [11]. The superelastic strain increases with the increase of grain size (d) relative to the wire diameter (D). When d/D increases, the free surface grain boundary area also increases, which drastically reduces the constraining strain imposed by the surrounding grains [11]. In the fusion zone the amount of grains was considerably higher than that in the base material, leading to an increase in the constraint of strain. However, this did not lead to any changes in the tensile properties of the welded wires.

Necking occurred in the fusion zone because of the higher ductility of this region compared to the base material. However, fracture did not occur at this necking, instead it always occurred in the coarse grained base material far away from any influence of the weld. SEM analysis of the fracture surfaces of the specimens revealed ductile fracture depicted by the dimples as shown in Fig. 7, for the welded sample. No influence of the welding process was observed on the fracture surface. Fracture along the grain boundary in the base material of the welded specimens occurred as shown in Fig. 8.

In the NiTi welds fracture occurred in the thermal affected regions [25,27,28] due to the localization of strain in the softened material. In this Cu–Al–Mn alloy, the isolation of the grain boundaries in the bamboo-like wires made them prone to localized deformation. In comparison, the fusion zone contained many grains that hindered

<table>
<thead>
<tr>
<th>Region</th>
<th>Cu [at.%]</th>
<th>Al [at.%]</th>
<th>Mn [at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base material</td>
<td>72.48 ± 2.21</td>
<td>16.16 ± 1.89</td>
<td>11.37 ± 1.31</td>
</tr>
<tr>
<td>Fusion zone</td>
<td>71.92 ± 2.65</td>
<td>16.44 ± 2.31</td>
<td>11.64 ± 1.73</td>
</tr>
</tbody>
</table>

Fig. 5. Indentation curves in the fusion zone and in the base material for different applied loads.

Fig. 6. Tensile tests for the base material and welded specimens.
dislocation motion during plastic deformation. The smaller grain sizes accommodated the load such that failure did not occur in the fusion zone but rather in the base material at the isolated grain boundary.

3.4. Cyclic tensile behavior

The existence of a high density of mobile twins in the martensitic phase and mobile interfaces between the parent phase and martensite leads to internal friction \cite{10} and a significant amount of energy can be absorbed due to this effect giving rise to high damping in SMAs. As these alloys are intended to be used in systems subjected to load variations (e.g. seismic structural applications, or medical components which move with the body) it is fundamental to understand their behavior under cyclic loading/unloading.

The cycling behavior of both base material and welded wires are shown in Fig. 9 a) and b), respectively. In these figures the start of the martensitic transformation had higher values than those in the previous tensile tests. As discussed in the experimental section, a different set of wires was used for the tensile failure, and cyclic tensile specimens. These wires may have very small variations in their composition or in the heat treatment that impacted their mechanical properties. The stress to induce the martensitic transformation is dependent on the ratio of grain size to wire diameter, and the crystallographic orientation of the grains \cite{11}. In Cu–Al–Mn SMA alloys the transformation strain is highly dependent on the crystallographic orientation of the grains \cite{2, 11}, which affects the critical stress level for inducing the transformation following the Clausius–Clapeyron relationship \cite{29}.

Smart design based on the superelastic effect requires that cycling behavior along a given load/unload path is stabilized for a given number of cycles which depends on the application \cite{30}. The stabilization of the superelastic effect occurs in SMAs as the microstructure evolves to inhibit dislocation motion \cite{31}. The most significant differences between the cycling behavior of the welded and base material specimens was the evolution of the irrecoverable strain after each cycle, and the hysteretic loop which gives a measure of the absorbed energy per cycle.

The irreversible strain after the first cycle for the base material was close to 0.5%, which is within the range of values expected from the work performed by Kainuma et al. \cite{6}. For the welded specimens a slightly higher value for the irreversible strain after the first cycle was observed and this was 1.1%. The larger irreversible strain in the welded specimen is due to the fine grained fusion zone, which had a d/D ratio smaller than the base metal, which reduced the superelastic recovery after unloading \cite{11}. This small d/D ratio resulted in a greater constriction of transformation which explains the larger plastic strain observed.

![Fig. 7. Fracture surface of the welded specimen, which occurred in the base material as indicated in Fig. 8.](image)

![Fig. 8. Schema of the fracture along a grain boundary in the base material (not to scale).](image)

![Fig. 9. Mechanical cycling behavior of: a) the base material; and b) the welded specimen.](image)
After the first cycle, the superelastic hysteretic response started to stabilize both in the base material and in the welded sample. This effect can be observed in Fig. 10 which presents the accumulation of irrecoverable strain and the energy absorbed per cycle.

Both the base metal and welded specimens converged to a stabilized superelastic response after a low number of cycles, with the latter being faster to converge than the former. This observation is of major interest when planning to design a structure using such a welded joint because it will not need a high number of mechanical cycles prior to its effective use in structural applications. The stabilized hysteretic response is obtained earlier in the welded specimen than in the base material because of the faster plastic buildup related to the constrictio of transformation by the surrounding grains.

The polycrystalline wires used in this investigation had a similar cyclic deformation behavior as single crystal material studied by Kato et al. [32]. The convergence of the hysteretic response occurred in a low number of cycles, the majority of the plastic strain occurred in the first cycle and stabilized in a low number of cycles, and the critical stress for martensite formation decreased with each cycle.

4. Conclusions

This study was the first investigation of laser welding superelastic Cu–Al–Mn wire. The microstructures, hardness values and mechanical properties of welded and base metal samples were analyzed to determine the effects of welding on these shape memory alloys.

- The Cu–Al–Mn alloy had excellent weldability, which may open new possibilities for its use in civil structures and other damping applications.
- Micro-indentation load vs depth analysis showed that the finer grained fusion zone was more ductile than the bamboo-like grained base material.
- No degradation of the overall tensile properties of the welded specimens was observed when compared to the base material.
- Fracture of the welded specimens always occurred away from the fine grained fusion zone in a ductile mode in the coarse grained base material.
- Irrecoverable strains after the first mechanical cycle were 1.1% for the welded wire and 0.5% for the base material. After the first cycle, the irrecoverable strains of both materials quickly reduced to a stabilized value.

- The pseudoelastic hysteresis response of the welded wires rapidly converged, while the base material response converged after some additional cycles.

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References