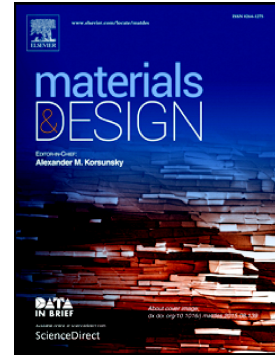


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# Laser Welding of Cu-Al-Be Shape Memory Alloys: microstructure and mechanical properties

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## Abstract

Cu-based shape memory alloys are potential substitutes of NiTi shape memory alloys, owing to their lower production costs and recent increase in their mechanical properties arising from better control of the microstructure. The development of joining technologies for advanced materials is key to expand to the potential applications of any engineering alloy. In this work, laser welding of single crystal-like Cu-Al-Be shape memory alloys was performed. The microstructure and tensile properties were evaluated to understand the effect of laser welding on the microstructural and mechanical features of the welded joints. Cycling tests performed for a wide range of temperatures revealed that the joints possess extraordinary superelastic recovery after joined, with potential applications in damping devices due to the significant amount of energy that can be absorbed during superelastic deformation.

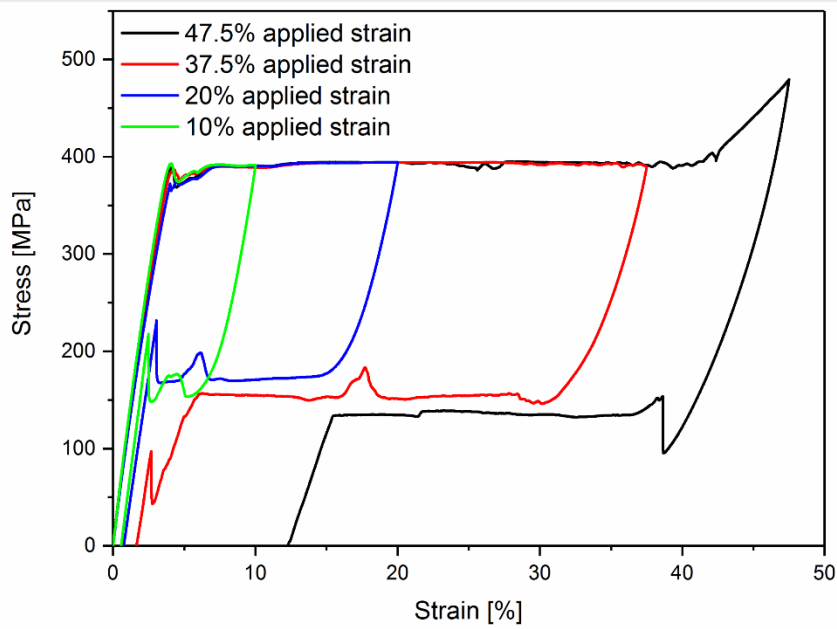
**Keywords:** laser welding; shape memory alloys; characterization; cycling behaviour; superelasticity.

## Highlights

- Successful laser welding of Cu-Al-Be shape memory alloys;
- The joints exhibit excellent superelastic properties;
- Superelasticity is preserved between -40 and 100 °C;
- The joints can be used as energy absorptions devices.

## Graphical Abstract

## Laser welded Cu-Al-Be shape memory alloy



## 1. Introduction

Shape memory alloys have the ability to undergo a reversible thermoelastic phase transformation from the parent phase austenite to a product phase martensite. This particular behaviour is responsible for two main functional properties: the superelasticity and the shape memory effect [1]. In the former one, the martensitic transformation is induced by applied thermomechanical loading of the austenitic phase, leading to important inelastic strains which are recovered upon unloading due to the reverse phase transformation to austenite. Austenite can transform into martensite during mechanical loading, leading to an inelastic deformation that can be recovered spontaneously upon unloading [2]. For the shape memory effect, the material is deformed in the martensitic state, leading to permanent inelastic strains upon unloading. These can be removed by heating up the material to the austenitic phase again: the initial shape is restored triggering the shape memory effect [3].

Cu-based shape memory alloys are considered to be possible substitutes of NiTi, the most used shape memory alloy, owing to their lower production costs and recent improvements on their mechanical properties [4,5]. There are different Cu-based systems, with the most important ones being Cu-Al-Mn [6], Cu-Al-Ni [7] and Cu-Al-Be [8]. The latter one presents, aside from the superelastic and shape memory effects, other interesting properties: strong sound, vibration and mechanical damping capability; high mechanical strength; and resistance to corrosion [9]. These alloys exhibit also a particular technological interest for low and intermediate temperature applications [8]: as a result of the introduction of small amounts of Be, the transformation temperatures decrease drastically, allowing for the occurrence of superelasticity at very low temperatures. In fact, some empirical formulae have been proposed to determine the transformation temperatures in Cu-Al-Be alloys based on their composition [10]. Thus, these alloys can be used in a wide range of temperatures, at ambient temperature or above, but they can be considered also for cryogenic applications [9].

One of the potential applications of Cu-Al-Be alloys is in seismic devices [11] as they combine several properties: high fatigue resistance, coupled with a low sensitivity for changes in the mechanical behaviour for near-ambient temperatures; they are not very sensitive to frequency changes in the 0.1 to 5 Hz regime. Moreover their properties suffer slow degradation due to the surrounding environment [12].

In order to allow for the use of these materials in complex shaped applications, it is often required the use of joining techniques [13]. For shape memory alloys, laser welding is considered as the prime choice owing to its characteristics, such as high precision, reproducibility and reduced extension of the thermally affected regions [14]. Laser welding is the most used technique to join shape memory alloys [15,16]. This technique has been already successfully employed to preserve the functional properties in similar and dissimilar joints of Cu-based shape memory alloys, namely CuAlMn [17,18] and CuAlZn [19]. Furthermore, post-weld processing of the laser welded joint can improve the mechanical properties of the material [20]. Aside from obtain defect-free joints, the main concern after welding of such class of materials is to preserve their functional properties, so that they can be used in a given required application. With the more massive use of the aforementioned Cu-based systems, weldability studies on both similar and dissimilar combinations are necessary to understand the potential of these materials in different applications.

Laser welding of Cu-based material is not easy due to the high reflectivity of these alloys for wavelengths higher than 550 nm [21,22]. Industry-relevant lasers are based on fibre or Nd:YAG, with associated wavelengths of 1064 nm. To make it suitable for industry to join these materials, it is necessary to optimize the process parameters so that these lasers can be used.

In this work the microstructure and mechanical properties of similar laser welded Cu-Al-Be shape memory alloy joint are analysed based on the induced microstructural modifications by the laser/material interaction. This is the first work reporting the effect of laser welding on the mechanical properties of Cu-Al-Be shape memory alloys.

## 2. Materials and Methods

### 2.1 Laser welding

Single crystal-like Cu-11.5Al-0.5Be (wt. %) shape memory alloy wires produced by modified Bridgman growth technique, 1.25 mm in diameter, were used in this investigation. Differential scanning calorimetry measurements of the base material has confirmed that it was fully austenitic at room temperature.

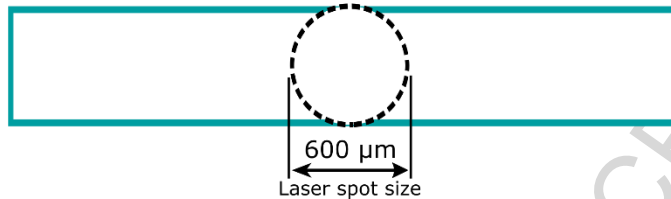
Prior to welding, the oxide layer of the base material wire was gently removed using 2500 fine SiC paper, which lead to a final diameter of 1.24 mm. Acetone and ethanol were used to remove any impurities left in the base material before welding.

Laser welding of the single crystals wires was performed on bead on plate in order to remove joint fit-up as a variable, since this was the first investigation on laser welding of these materials. A Nd:YAG laser (1.064  $\mu\text{m}$  wavelength), from Miyachi Unitek LW50 operating in pulsed mode was used. The laser beam was focused on the surface to a spot diameter of 600  $\mu\text{m}$ . A schematic representation of the welding setup is depicted in Figure 1. The welding process was selected in order to obtain full penetration joints, with minimum heat input. After preliminary tests, a 6 ms pulse profile, which included a 1 ms up and downslope, and a peak power of 5 kW, ensured complete penetration. To avoid oxidation, Ar was inserted at the face and root of the welds at a flow rate of 0.6  $\text{m}^3 \text{h}^{-1}$ .

a) Side view



b) Top view



**Figure 1 – Schematic representation of the experimental setup for laser welding of CuAlBe shape memory alloy (not to scale): a) side view; b) top view. The laser beam was focused on the surface to a spot diameter of 600  $\mu\text{m}$ .**

## 2.2 Microstructural and mechanical characterization

After mechanical polishing, the welded joints were prepared for metallographic observations to reveal the microstructure, using an electrolytical polishing in a solution of 250 ml of phosphoric acid, 5 g of urea, 250 ml of ethanol, 50 ml of isopropanol and 500 ml of distilled water, followed by chemical etching with a solution of 10 ml of hydrochloric acid, iron chloride and 100 ml of distilled water. Optical microscopy and scanning electron microscopy (SEM) were performed in the fusion zone and the base material.

The crystallographic texture was determined by X-ray diffraction using a Seifert XRD 3003 PTS 4-circle goniometer. Measurements were performed with a Cu-K $\alpha$  radiation operating at 40 kV and 40 mA. The phi ( $\Phi$ ) angle was varied between 0 and 360 $^\circ$ , whereas the psi ( $\Psi$ ) angle was varied from 0 to 70 $^\circ$ . For both angles, the incremental step was of 2 $^\circ$ . The  $\beta$  austenitic phase has a complex DO3 cubic structure with a cell parameter  $a_0 = 5.825 \text{ \AA}$  [23]; pole figures were determined for the {440} planes. Local crystallographic orientations were determined using Electron Back-Scattered Diffraction (EBSD) maps with a step size of 2  $\mu\text{m}$  was performed using a JEOL field electron gun SEM



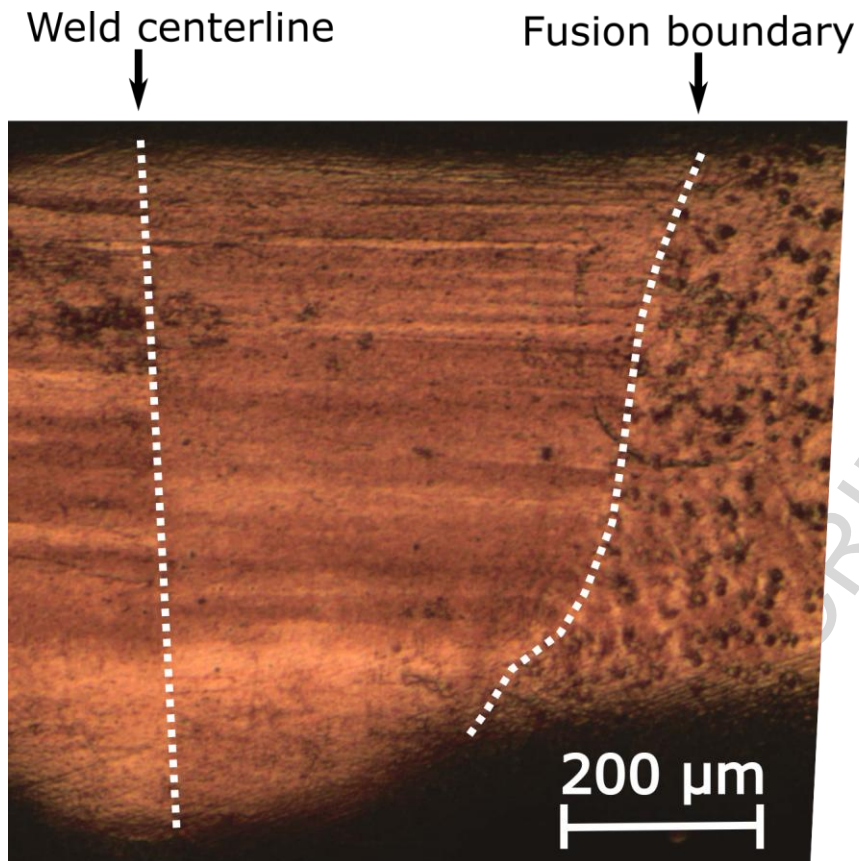
equipped with an Oxford EBSD CCD camera fitted with a FSD detector. EBSD data was treated with the software CHANNEL 5 from Oxford.

Hardness measurements were performed to evaluate the effect of the welding process across the welded joints. A load of 300 gram and a space between indentations of 150  $\mu\text{m}$  were used. Three hardness measurement lines were performed at one third, half and two thirds of the sample height.

Mechanical properties of the base material and welded joints were measured during a tensile test at room temperature using an Instron 5548 micro-tensile tester. The gauge length of the samples was of 20 mm; the displacement rate was set at 0.5 mm/min and the measurement accuracy is of  $\pm 0.5$   $\mu\text{m}$ . Tensile tests were performed on the welded joints. Three samples were tested for reproducibility. Scanning electron microscopy was used to analyse the surface fracture of the joints. Based on the tensile tests performed, the cycling behaviour of the Cu-Al-Be laser welded joints was analysed by performing a total of 10 load/unload cycles. Load/unload cycles up to different maximum strains ranging from 10 to 47.5% were performed at room temperature,  $-40$   $^{\circ}\text{C}$  and  $100$   $^{\circ}\text{C}$  to evaluate the effect of temperature on the cycling response.

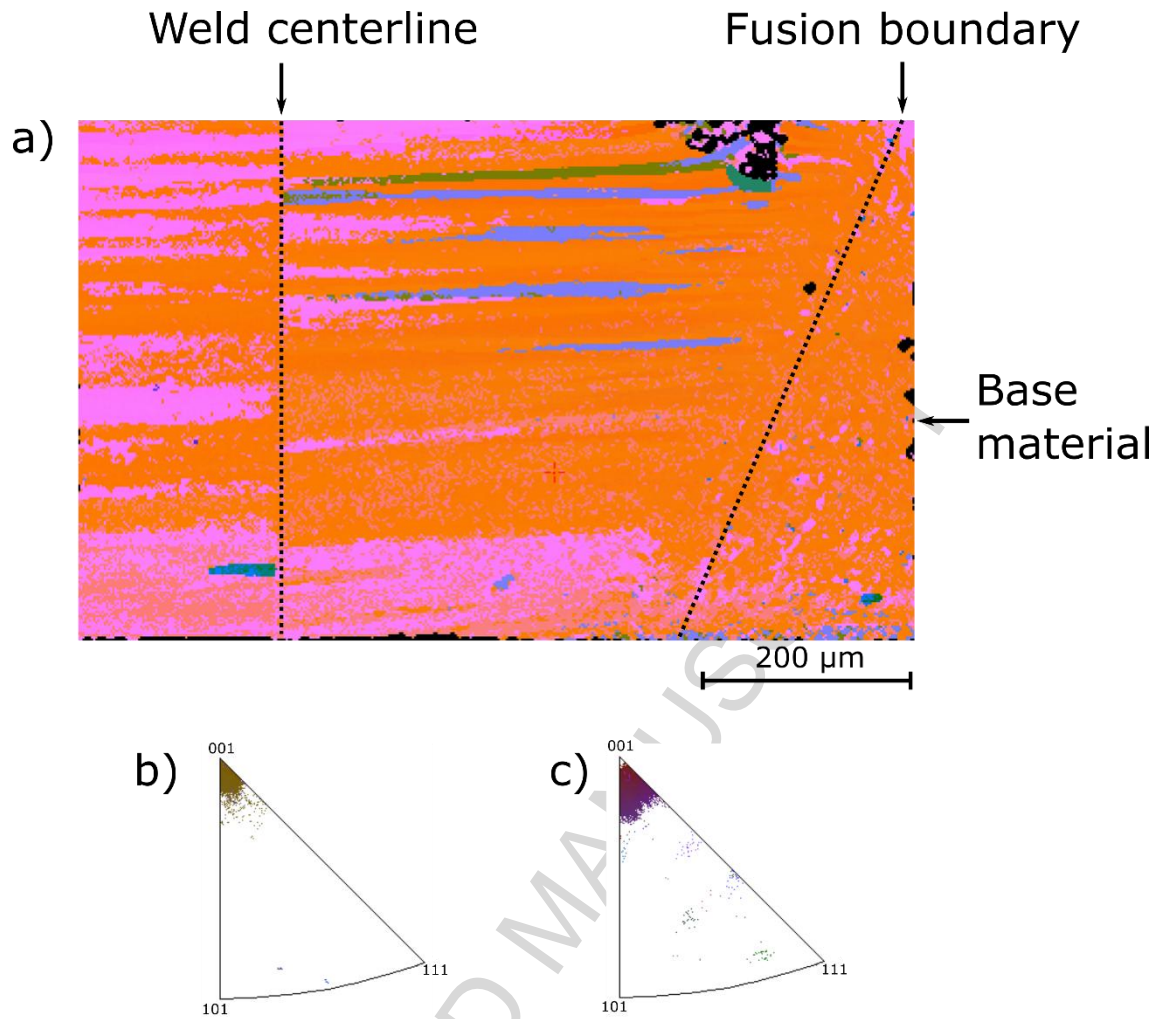
### 3. Results and Discussion

Figure 2 depicts the microstructure of the laser welded joint. No defects, such as pores or cracks are observed within the fusion. A columnar-like subgrain structure is observed in the fusion zone. This large columnar-like subgrain structure, with lengths of nearly 400  $\mu\text{m}$ , develops by epitaxial grain growth starting on solid grains of base material on the fusion line [24] and progresses perpendicular to isothermal lines. The grain growth is larger on the areas subjected to higher temperatures and longer residence times [24].



*Figure 2 – Microstructure of Cu-Al-Be laser welded joint.*

Crystallographic orientations of the base material and the welded joint were deduced from the {440} pole figures measurement: both zones exhibit a strong  $\langle 100 \rangle$  texture in the wire axis. The columnar grains seem to have the same orientation as the initial single crystal. Therefore, the welding process does not contribute to the development of different crystallographic texture within the fusion zone. In order to confirm this result, the welded zone was studied by EBSD (Figure 3).



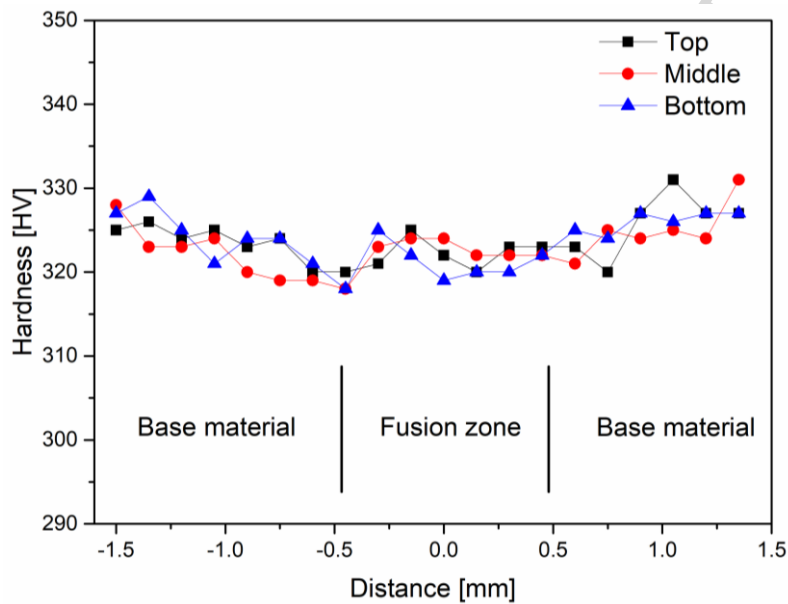
**Figure 3 – a) orientation map determined by EBSD; inverse pole figure in the tensile direction (wire axis) for the initial wire (b) and welded zone (c).**

EBSD observations confirm that the welded zone has the same orientation as the initial crystal.

Misorientation between columnar grains is also very weak: it does not exceed  $3^\circ$ .

In both FCC and BCC metals, the easy growth direction is along the  $\langle 100 \rangle$  direction [24,25]. Two factors contribute for the development of the  $\langle 100 \rangle$  texture in the fusion zone: this is the easy-growth direction for Cu-Al-Be alloys as these have a complex BCC structure [26]; the base material is oriented in that direction and supports the onset for solidification, thus further favouring such crystallographic orientation [27,28].

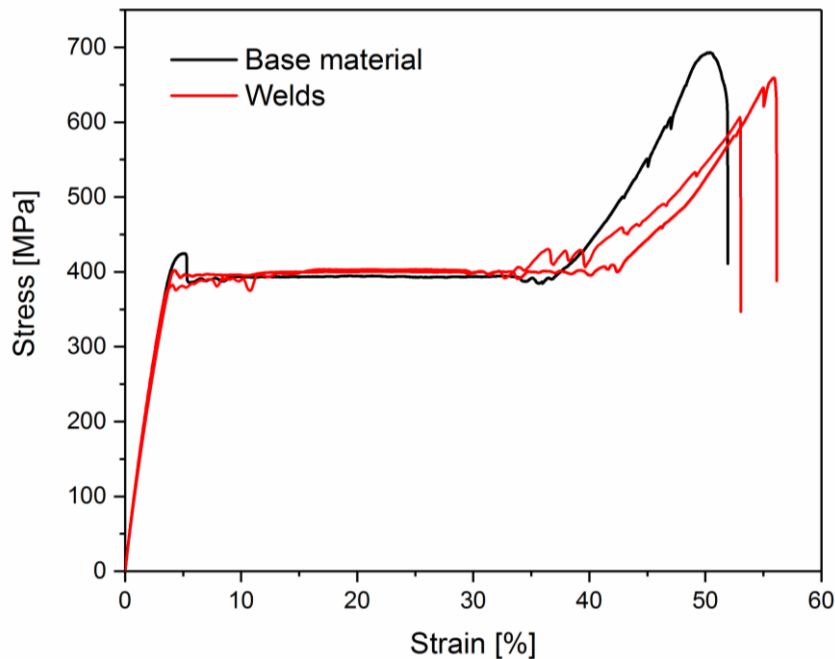
Hardness measurements performed at one third, half and two thirds of the sample height show the fusion zone has the same hardness as the base material (Figure 4), with respectively  $321.6 \pm 2$  HV and  $324.5 \pm 3$  HV. This is in agreement with previous works performed on other laser welding Cu-Al-based alloys where no significant hardness change was found between the fusion zone and the base material [17,20].



**Figure 4 – Hardness measurements results performed at one third (top), half (middle) and two thirds (bottom) of the height of the Cu-Al-Be laser welded joint.**

The tensile behaviour of both base material and welded joints is depicted Figure 5. It can be observed that the tensile strength of the base material is slightly higher than that of the welded joints ( $686 \pm 8$  MPa vs  $631 \pm 19$  MPa, respectively). On the other hand, the fracture strain of the joints is higher ( $50.8 \pm 0.2$  % vs  $54.1 \pm 1.2$  %). Fracture of the joints occurred in the fusion zone. The higher fracture strain of the welds is probably due to fact that with the refined grain structure of the fusion zone any crack that initiates there will not propagate straightforward along the wire diameter (as it would occur in the single crystal base material), hence allowing the material to deform more. It is interesting to note that the overall tensile properties of the welded joints do not differ significantly from those of the base material, which appears to be a common feature for welded joints of Cu-

based shape memory alloys (CuAlMn) [17] but not for NiTi [15,29–31], as the most studied alloy of this class.

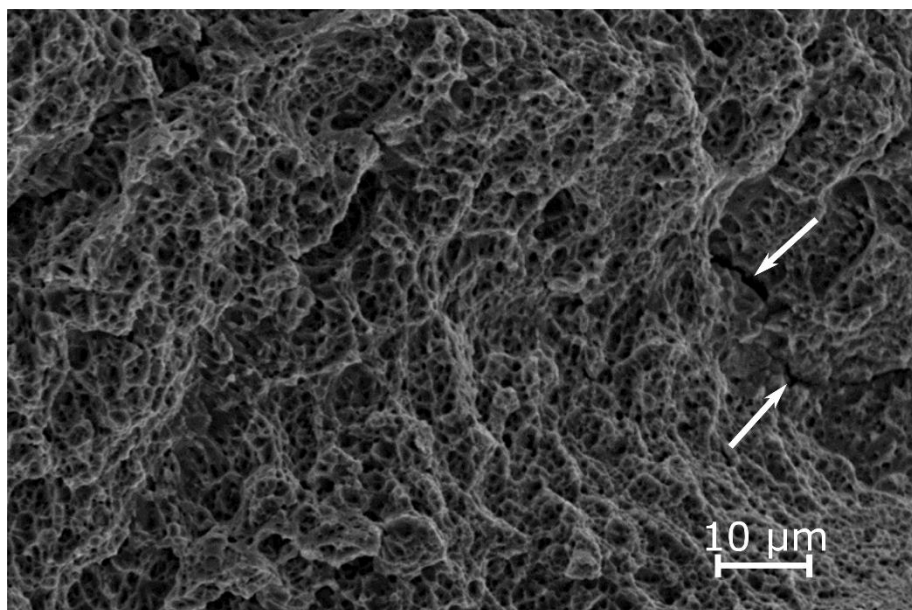


*Figure 5 – Tensile behaviour of the Cu-Al-Be base material and laser welded joints.*

From Figure 5 it can also be observed that the stress onset for the martensitic transformation is similar for both base material and welded joints: approximately 400 MPa. Although it is known that Cu-Al-Be shape memory alloys have a dependence between grain size and the stress for the onset of the superelastic plateau (the higher the grain size, the lower the stress onset) [32], the volume fraction of the welded region, compared to the remaining base material during tensile testing, is not enough to promote any significant change in respect to this mechanical property.

Fracture analysis of the welded joints was performed using scanning electron microscopy (Figure 6). Typical ductile-like fracture, characterized by the massive presence of dimples, can be observed. Additionally, it can be detected the presence of minor cracks (marked with white arrows). The presence of those cracks in the fusion zone justifies the higher deformation until fracture of the welds: while in the single crystal base material any crack that form will propagate without any

impingement, such as grain boundaries, the same does not occur in the welded joints, as the refined grain structure can delay crack propagation and also enables to accommodate stress.

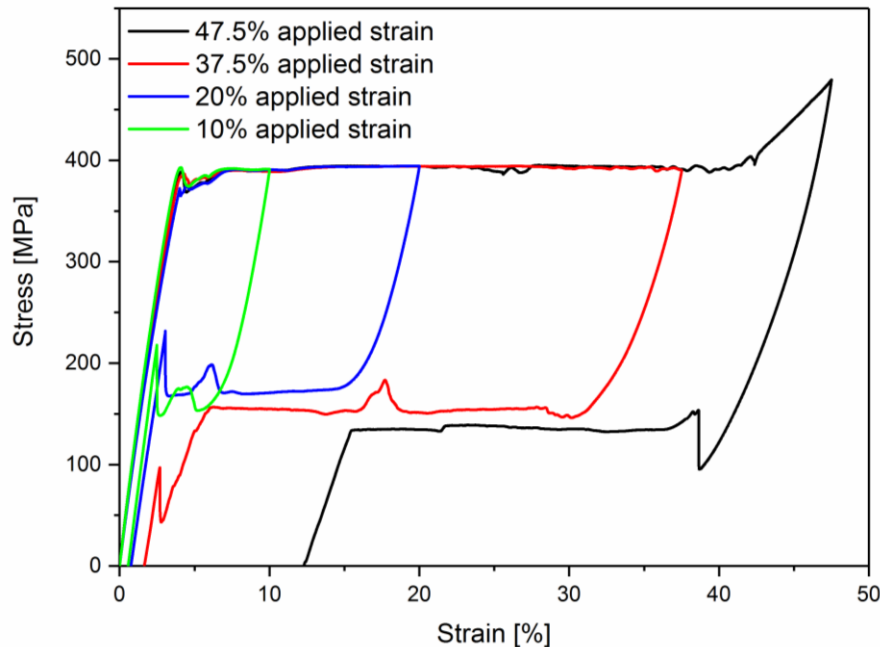


*Figure 6 – Fracture surface of the fusion zone the welded joint. The white arrows show other cracks which developed inside the fusion zone.*

Due to their lower production costs when compared with NiTi alloys, Cu-based shape memory alloys can be used in energy-absorption devices [5]. For such applications, it is required that the materials in use are able to absorb significant amounts of energy. For shape memory alloys, such dissipation is usually performed in the superelastic regime so that the imposed external deformation can be (ideally) totally restored. For this reason, is important to understand the load/unload cycling behaviour of the welded joints in order to assess the feasibility of their use in such applications.

Based on the tensile behaviour of the welded joints, their cycling behaviour was analysed by a load/unload cycle up to different maximum strains: 10, 20, 37.5 and 47.5 % (Figure 7). It can be observed that the superelastic plateau extends up to about 40 % strain, as a result of the unique characteristics of the single crystal base material. This means that the transformation strain of the welded joints (the length of the superelastic plateau) is of nearly 35 %. Such high transformation strains were also reported in Cu-based alloys [33], but also in the Ni-Ti-Hf system [34]. After the end

of the superelastic plateau (corresponding to the applied strain of 47.5 %) an increasing stress is required to proceed with deformation, where detwinned martensite is first elastically deformed and, subsequently, plastic deformation occurs [35].

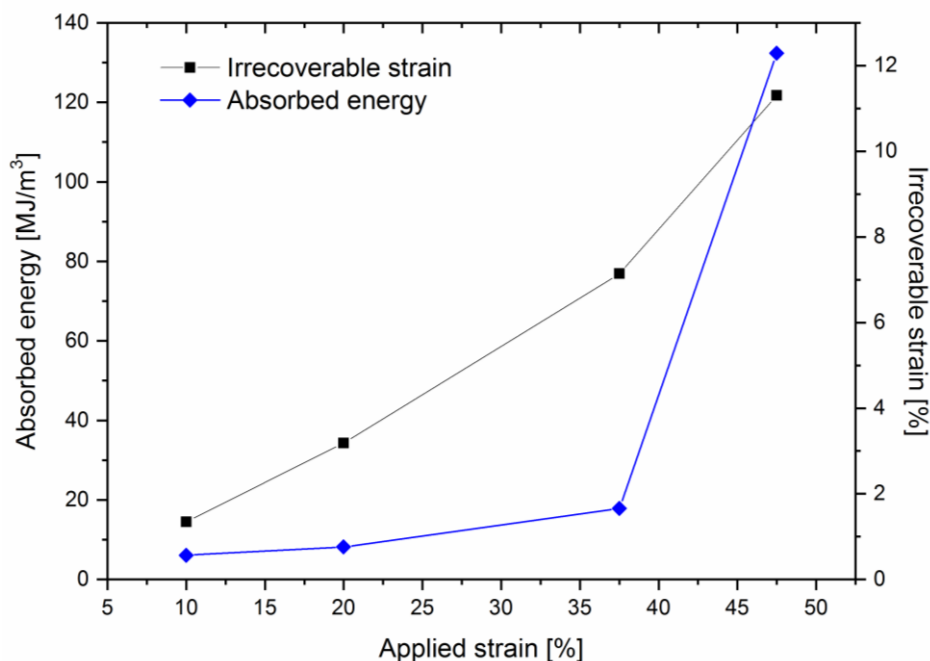


*Figure 7 – Load/unload cycling behaviour of the welded joints.*

From the load/unload behaviour of the joints it is possible to determine the evolution of irrecoverable strain and absorbed energy of the Cu-Al-Be welds as a function of the applied strain, as depicted in Figure 8. These results were obtained only for the first load/unload mechanical cycle. The very high superelastic recovery of the welds is clearly demonstrated with only 0.6, 0.8 and 1.6% of irrecoverable strain for maximum applied strains of 10, 20 and 37.5%, respectively. The increase of irrecoverable strain with applied strain within the superelastic plateau, may be due to the unfavourable microstructure of the fusion zone of the welds, when compared to the single crystal base material. That is, the slight misorientation of the fusion zone compared to the crystallographic orientation of the base material can account for part of the irrecoverable strain. Ideally, in any deformation performed within the superelastic plateau, the irrecoverable strain, upon unloading, would be null. However, the presence of a refined grain structure in the fusion zone may inhibit part

of the reverse transformation from martensite to austenite during unloading, thus promoting a non-ideal superelastic behaviour, as evidenced in Cu-Al-Be shape memory alloys [36]. However, during the stress induced transformation it is possible that some grains exceed locally the stress for slip to occur [37], which will result in an irrecoverable strain upon unloading [38]. It must be pointed though, that these results are the best, in terms of superelastic recovery during mechanical cycling, for any welded shape memory alloy, when compared to the available literature on the subject [3,39,40].

When the applied strain is increased to 47.5 %, the irrecoverable strain increases significantly to 12.3 % as a result of mechanical stabilization of martensite, which is known to occur after the superelastic plateau as results of plastic deformation of martensite [35]. Nonetheless, even for this maximum applied strain, the welded joints were able to recover more than 35 %, which is a remarkable result as far as the superelastic behaviour of these joints.

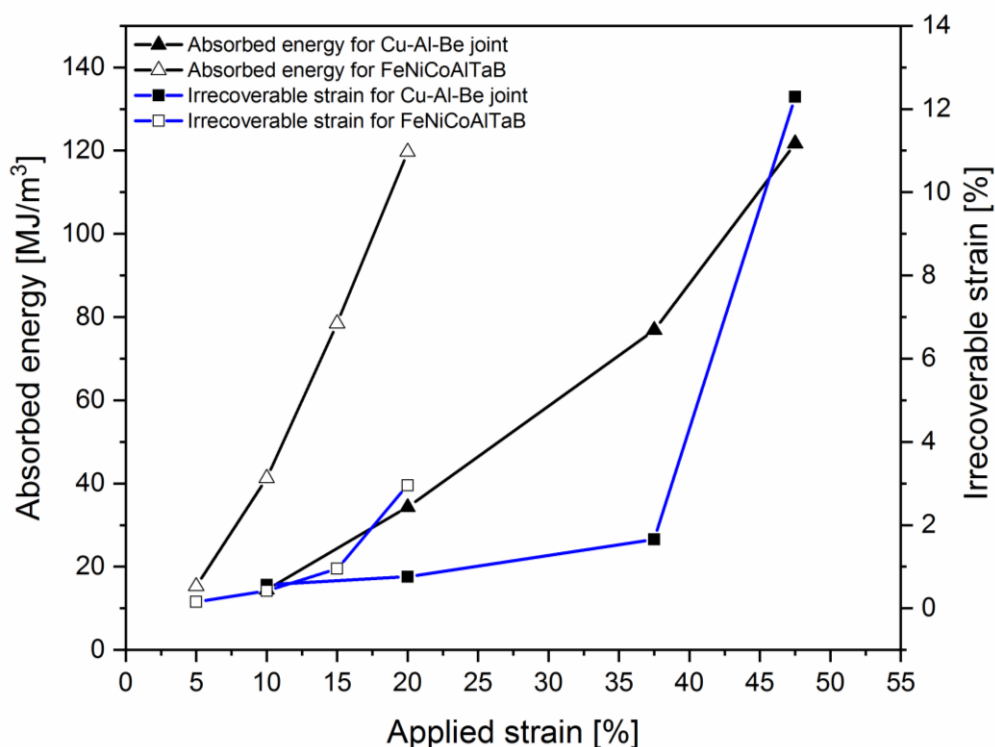


**Figure 8 – Irrecoverable strain and absorbed energy as a function of applied strain during one load/unload cycle for the welded joint.**



Recently, a new textured Fe<sub>28</sub>Ni<sub>17</sub>Co<sub>11.5</sub>Al<sub>2.5</sub>Ta<sub>0.05</sub>B (at. %) shape memory alloy was found to absorb a significantly high amount of energy during a hysteric load/unload cycle [41], which would be very useful in damping applications, for example. The impressive results presented in [41] are due to the very high onset stress for the beginning of the stress induced transformation and the high mechanical hysteresis between the forward and reverse transformations. In order to compare the absorption behaviour of both the Fe-based shape memory alloy and of the Cu-Al-Be laser welded joint the evolution of the absorbed energy and irrecoverable strain as a function of the applied strain were determined and are presented Figure 9. The selection of this Fe-based shape memory alloy for comparison with the experimental results obtained for the welded joints is related to the fact that, to the best of the author's knowledge, no other shape memory alloy is known to exhibit such significant energy absorption.

The very high transformation strain of the Cu-Al-Be laser welded joint can exceed the already high absorbed energy of the Fe-based shape memory alloy. However, this high energy absorption capability of the Cu-Al-Be weld comes at an expense of a slight irrecoverable strain, when compared to the Fe-based shape memory alloy. Nonetheless, these cycling results show the potential for such laser welded joints to be used in energy-absorption applications, such as seismic devices, where large amount of energy need to be absorbed.



**Figure 9 – Evolution of the absorbed energy and irrecoverable strain as a function of the applied strain during superelasticity cycling: comparison between the Cu-Al-Be laser welded joint and the Fe<sub>28</sub>Ni<sub>17</sub>Co<sub>11.5</sub>Al<sub>2.5</sub>Ta<sub>0.05</sub>B (at. %), noted as FeNiCoAlTaB, shape memory alloy [41].**

Cu-based shape memory alloys have potential applications as seismic devices for energy absorption [42,43]. However, for these materials to be used in such applications it is necessary that the superelastic behaviour is stable for a wide range of temperatures [44], below -10 °C and up to 50 °C, ideally.

The laser welded Cu-Al-Be joints were also subjected to a total of 10 load/unload cycles up to 37.5 % strain at -40 °C, 23 °C (room temperature) and 100 °C. These results are depicted in Figure 10, showing only the 1<sup>st</sup>, 5<sup>th</sup> and 10<sup>th</sup> cycles for clarify purposes.

One of the most remarkable features observed from these cycling tests at different temperatures is the double step plateau which occurred at -40 °C (Figure 10 a). However, this two-step plateau is not observed in the cycling tests performed at both room temperature and 100 °C. Cu-Al-Be shape memory alloys have their stress induced martensitic transformation occurring in the following

sequence:  $\beta$  austenite  $\rightarrow$  18R martensite  $\rightarrow$  6R martensite. However, the presence of the two-step plateau is evidenced or not depending on the test temperature. In [45], the authors performed load/unload testing on Cu-Al-Be shape memory alloys at different temperatures and observed that at lower testing temperatures the two step plateaus were clearly distinguished. With temperature increase, the first martensitic transformation ( $\beta \rightarrow$  18R) starts at significantly higher stress levels, whereas the second martensitic transformation (18R  $\rightarrow$  6R) starts at a lower stress level. Further increase of the testing temperature would cause for both plateaus to occur at the same stress level. Similar observations were performed in fundamental studies on the mechanical behaviour of CuAlBe shape memory alloys [45].

Of special relevance on the martensitic transformations of Cu-Al-Be shape memory alloys is the dependence of both transformations,  $\beta \rightarrow$  18R and 18R  $\rightarrow$  6R, with temperature: the  $\beta \rightarrow$  18R has a positive Clausius–Clapeyron relation of 1.86 MPa/K, while for the 18R  $\rightarrow$  6R transformation the relation is of -0.28 MPa/K. This means that the temperature effect on the stress onset for the start of the martensitic transformation on Cu-Al-Be shape memory alloys is extremely important for the  $\beta \rightarrow$  18R transformation, whereas in the 18R  $\rightarrow$  6R transformation the temperature effect is almost negligible and tends to decrease the stress onset for the transformation to occur.

In the cycling tests performed at 23 °C and 100 °C only a unique plateau is visible meaning that overlapping between the two stress induced transformation has occurred at these temperatures.

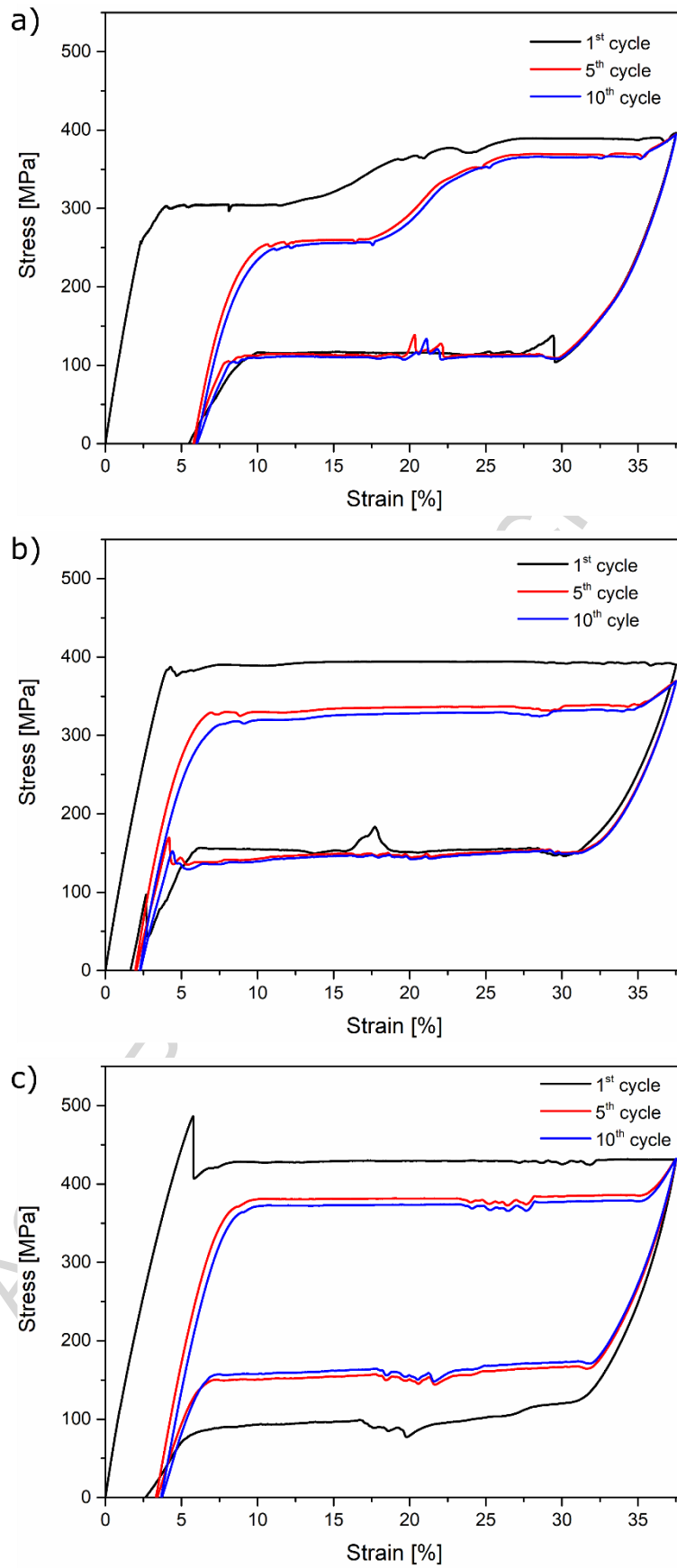
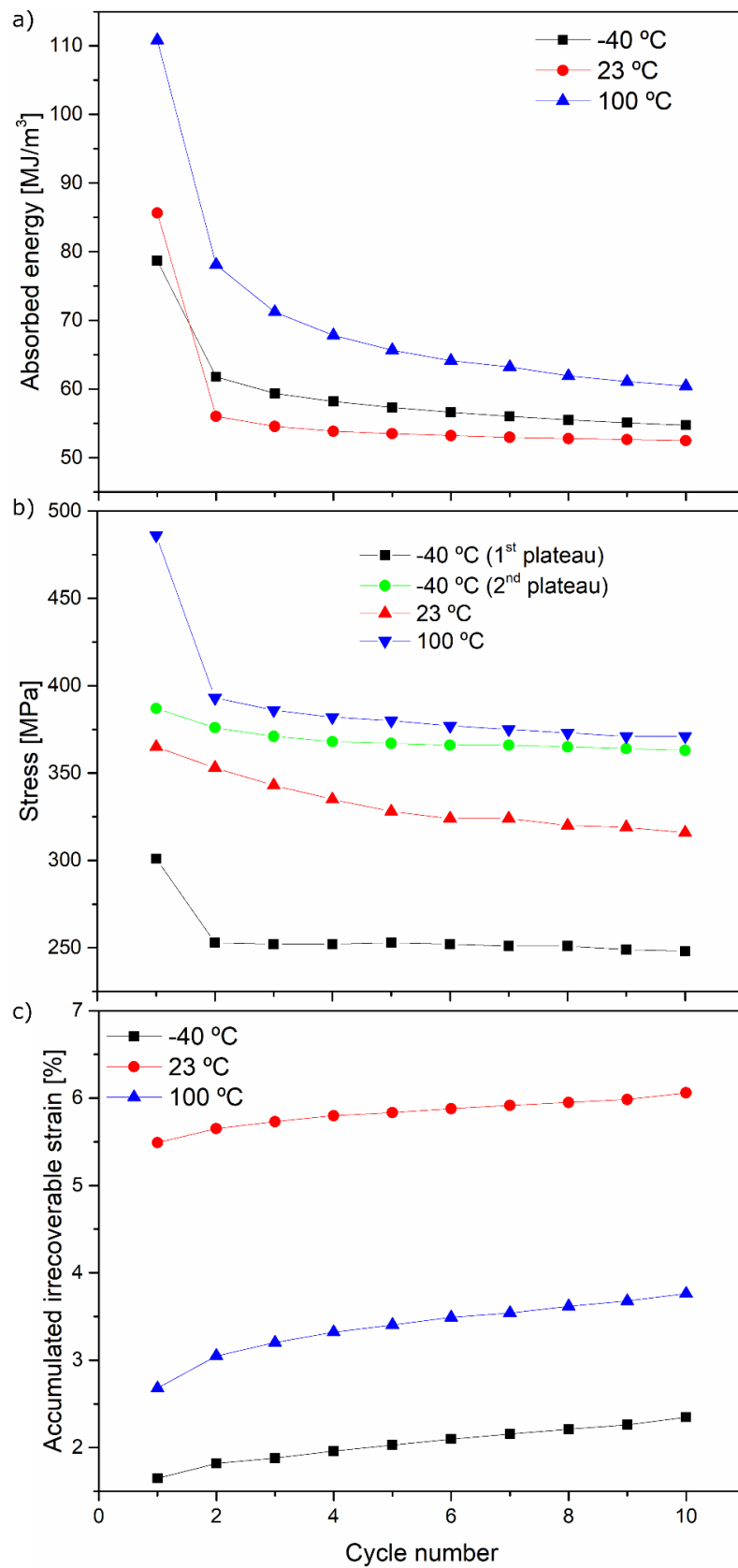


Figure 10 – Cycling tests up to 37.5% strain at different temperatures: a) -40 °C; b) room temperature (23 °C); c) 100 °C.

The irrecoverable strain upon unloading in the first load/unload cycle varies with no apparent influence of the temperature. This is related to the fact that during the first superelastic cycles at which shape memory alloys are subject material accommodation occurs. In this case only one load/unload cycle is required for the following cycling tests to present a stabilized behaviour, that is, the irrecoverable strain and mechanical hysteresis between consecutive load/unload cycles is minimal. In fact, the evolution of the accumulated irrecoverable strain and the stress onset for the forward martensitic transformation do not vary significantly after the first load/unload cycle.

Cycling behaviour analysis in laser welded NiTi shape memory alloys showed an increase in the accumulated irrecoverable strain due to introduction of dislocations that stabilize martensite, preventing the transformation to austenite upon unloading, thus not participating further in the superelastic behaviour [40,46]. Additionally, the introduction of internal residual stresses during superelastic cycling of shape memory alloys justifies the decreasing external stress required for the martensitic transformation to occur [47], as depicted in Figure 11 b).



*Figure 11 – a) Evolution of the accumulated irrecoverable strain with the number of load/unload cycling tests; b) Evolution of the stress onset for the forward martensitic transformation with the number of load/unload cycling tests; c) Evolution of the absorbed energy with the number of load/unload cycling tests.*

The temperature effect on the necessary stress for the martensitic transformation to occur is clearly observed in Figure 11 b): with increasing temperature, higher stress is required for the transformation to occur, which correlated well with a positive Clausius–Clapeyron relation when the  $\beta \rightarrow 18R$  transformation occurs.

The evolution of the energy absorbed as function of the number of load/unload cycles at the different testing temperatures is depicted in Figure 11 c). It can be observed that the first cycle has the higher absorbed energy for all testing temperatures. This is related to the fact that in the following cycles the a given irrecoverable strain has already occurs which reduces the total superelastic strain of the welded joint. At 100 °C, the absorbed energy is slightly higher than at the other two testing temperatures. This is related to the Clausius–Clapeyron effects which rises the stress onset for the stress induced transformation, which translates into a higher capacity for energy absorption. At -40 °C and room temperature the absorbed energy does not vary significantly, despite the two step plateau observed at -40 °C.

## 4. Conclusions

Defect-free joints were obtained when laser welding of Cu-Al-Be shape memory alloys and this study shows the potential to use such high energy density welding process for joining these alloys. The following major conclusions can be drawn:

- The crystallographic texture of the fusion zone was not modified by the welding processes, following the same orientation as the base material;
- No significant hardness changes were determined between the fusion zone and base material;

- The tensile strength of the laser welded joints is slightly lower than the base material (686 vs 631 MPa), whereas the tensile strain was higher for the welds (50.8 vs 54.1 %). This was attributed to the microstructure in the fusion zone, which sustain a higher amount of deformation owing to the presence of obstacles that oppose to crack propagation.

- Superelastic behaviour of the welded joints was preserved with associated high energy absorption capabilities and transformation strain. Moreover, at both -40 and 100 °C, the laser welded joint exhibit superelastic behaviour. These features make these joints potential candidates for applications requiring large damping capabilities, such as in seismic systems.

## 5. Acknowledgements

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Data availability: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.



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