Wire and arc additive manufacturing of a Ni-rich NiTi shape memory alloy: microstructure and mechanical properties

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Abstract: Wire and Arc Additive Manufacturing (WAAM) was used for fabrication of NiTi parts using a commercially available Ni-rich NiTi wire as the feedstock material. The as-built parts are near fully austenitic at room temperature as confirmed by differential scanning calorimetry, X-ray diffraction and superelastic cycling. The as-built microstructure changed from columnar, in the first deposited layers, to equiaxed in the last deposited ones as a result of the different thermal cycle conditions. This is the

first work where WAAM NiTi parts exhibit superelastic behavior under tensile conditions, highlighting the potential use of the technique for the creation of parts shaped in a complex manner based on this material and process. The potential to use WAAM for deposition of advanced functional materials is demonstrated.

Keywords: NiTi shape memory alloy; Wire and arc additive manufacturing; Phase transformation; Microstructure; Digital image correlation

1. Introduction

NiTi shape memory alloys (SMAs) are used in multiple industries (e.g. automotive, aerospace, robotic, and biomedical), as a result of their shape memory and superelastic properties [1]. Both properties occur due to a thermodynamic and crystallographic reversible martensitic transformation [2]. Although NiTi SMA research has taken place for nearly six decades now, and has been implemented in several applications, SMAs applications are still limited to simple geometries processed by laser [3-5], Tungsten Inert Gas (TIG) [6], electrical resistance [7] or ultrasounds [8].

With the advent of additive manufacturing, complex parts which could not be obtained by conventional manufacturing routes are now possible [9]. The majority of SMAs research work conducted to date has focused on powder-bed systems using a laser [10, 11] or an electron beam [12-14] as the heat source. The application of multiple additive manufacturing techniques to create NiTi parts have been extensively described by Elahinia et al. [15, 16].

NiTi parts created by selective laser melting (SLM) can exhibit superelastic properties in the as-built condition [17] or after appropriate post-process heat treatments [18, 19] which incorporate compression techniques. A multi-scale shape memory effect in SLM NiTi parts was also observed by Hamilton et al. [20] and this can be attributed to a gradient of microstructures along the as-built part due to the thermal cycle imposed during production [21]. Additionally, owing to the typically fast thermal cycles during SLM, nanoscale precipitates such as Ni_4Ti_3 can be formed [22].

Some of the shortfalls of laser and electron beam powder-based additive

manufacturing techniques include the high costs of equipment and powder feedstock, as well as slow production rates. Despite these limitations, these processes are still extremely common due to no other fusion-based additive manufacturing technique being capable of replicating the precision and accuracy of these processes at this time. Another critical issue often found during SLM of NiTi parts is the lack of evaluation of the part's mechanical properties under tensile conditions. Such can be attributed to the high probability of defects, such as lack of fusion or porosity, that may occur in powder-bed systems.

Wire and arc additive manufacturing (WAAM), which is an alternative additive manufacturing technique, is capable of achieving high production rates at the expense of geometrical tolerance. Here, a wire acts as the feedstock material while an arc-based heat source promotes its deposition onto a substrate. As a result, three dimensional parts can be created by the deposition of multiple layers similar to SLM. The use of WAAM for the creation of metallic parts is often associated with a low number of defects, provided that the process parameters are optimized [23]. As a result, parts created by WAAM can be evaluated under compression [24] but also under tension conditions [25, 26], which further expands the potential application of this technique for more demanding applications. The potential of WAAM to create large complex-shaped parts with short delivery times has attracted the attention of the aerospace industry in this technology. In fact, WAAM has been already successfully applied to the fabrication of different metallic components, such as aluminum [27-30], titanium [31, 32] and steel [33].

A preliminary investigation into the use of WAAM to create NiTi parts was recently presented by Wang et al. [34]. The authors were able to create walls using Ni and Ti wires, fed into the weld pool separately. The as-built parts were mechanically characterized, and the fracture strain ranged between 4.1% and 5.5%. No evaluation of the superelastic response was performed, which is fundamental to understand the feasibility of the WAAM technique to preserve this important functional property. It is also noted the NiTi walls were created with a tandem-like system using two feedstock wires. This option is technically more challenging than using only one feedstock wire

and may pose potential problems to control the composition of the as-built material, which for NiTi shape memory alloys must be very precise [35].

Since there is commercially available NiTi wire, it is possible to use it as the feedstock material. This solution has the advantage of using the exact composition desired for the as-built parts, since most of NiTi wires available can be selected in advance. Therefore, if desired, is it possible to select Ti-rich NiTi wire for parts to be martensitic at room temperature, or Ni-rich NiTi to be austenitic at room temperature. In this work, a commercially available Ni-rich NiTi wire was used to create walls with WAAM technology. The microstructural evolution along the as-built part was studied by means of microscopy techniques, differential scanning calorimetry and high energy synchrotron X-ray diffraction. Additionally, the mechanical properties were evaluated using tensile testing until fracture, and superelastic cycling. This is the first work on WAAM of NiTi SMAs reporting the existence of superelastic behavior in the as-built parts under tensile testing conditions. These results open the door for WAAM to provide a new way of producing complex shaped parts based on NiTi shape memory alloys.

2. Experimental procedure

In this investigation, 0.7 mm diameter Ni-rich (50.5 at.%) NiTi wire was deposited onto a NiTi baseplate using a conventional TIG torch as the WAAM heat source. The setup is depicted in Fig.1. A direct current (75 A) combined with an ultra-high frequency pulse (current: 50 A, frequency: 20 kHz, duty cycle: 50%) was selected as the current mode of the arc. A local Ar (99.99% pure) shielding device was used to minimize oxidization. To create thin walls, the travel speed of the torch, wire feed speed, and the Ar flow rate were set at 0.2 m/min, 0.9 m/min, and 15 L/min respectively. An appropriate inter-layer cooling time can be fundamental to improve the forming quality of WAAM thin walls [36]. In this work, the idle time between subsequent depositions was set at 1 minute. Before deposition of the first NiTi layer, the substrate was pre-heated with the TIG torch using a travel speed of 0.3 mm/s and a current of

75 A, while Ar at a flow of 1.5 L/min was also used. The pre-heating of the substrate aims at improving the adherence of the first deposited layers which can be hampered by a cold substrate. Additionally, the use of pre-heating decreases the cooling rate which, in turn, decreases cracking susceptibility. It must be noticed that owing to high costs and low availability of the NiTi feedstock material, the process parameters were optimized to obtain defect-free parts, hence only one set of process parameters is analyzed in this work.

Fig. 1. Experimental setup of the WAAM process

Metallographic specimens were cut vertically to the deposited height. For microstructural observation, these specimens were prepared using conventional metallographic techniques. Then, the WAAM specimens were etched using a $\text{H}_2\text{O}:\text{HNO}_3:\text{HF}$ solution for 5 to 10 seconds. The as-built microstructure was examined using an Olympus optical microscope, a JSM-6490LV scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) system. Vickers micro-hardness measurements along the sample height was performed with a series of 100 g indents, held for 15 seconds.

The transformation temperatures were characterized by Differential Scanning

Calorimetry (DSC) following the ASTM F2004-05 standard. The heating/cooling rate was set at 10°C/min. The transformation temperatures were determined as described in the literature [37].

Synchrotron X-ray diffraction was used to determine the existing phases in the as-built samples. These experiments were performed at P07 High Energy Materials Science beamline in DESY. Working in transmission mode with an energy of 87.1 keV (0.14235 Å), a beam spot size of 0.5 x 0.5 mm hit the sample and the corresponding Debye-Scherrer rings were captured by a 2D Perkin Elmer 2D set at 1389 mm from the sample. The raw diffraction data was treated with Fit2D (XXX) with full and partial integrations along the azimuthal angle, φ , as described in XXX. Fig. 2 depicts the reference system relative to the definition of the azimuthal angle.

Fig. 2. Schematic representation of the Debye-Scherrer or diffraction rings, and of the azimuthal and scattering angles.

Parts for tensile testing were obtained by wire cutting from the deposited layers along the horizontal direction (X-Y in Fig. 3a) with 40 mm length and 1 mm thickness, shown in Fig. 3b. An Instron 5548 micro-tensile tester was used to assess the as-built mechanical properties of three samples at a strain rate of 0.4%/s at room temperature ($\approx 25^\circ\text{C}$). Digital image correlation (DIC) was used during the tensile tests with a resolution of 4000 x 3000 pixels and a focal length of 50 mm, to evaluate local changes in the mechanical properties of the parts. The fracture surfaces after tensile testing

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were analyzed by SEM. The superelastic behavior under tensile conditions was evaluated by loading up to 6% strain and then unloading to a zero-stress condition. 10 load/unload cycles were imposed to the as-built WAAM NiTi parts. The accumulated irrecoverable strain after each cycle was determined [38].

3. Results and Discussion

3.1 Microstructure, hardness and chemical composition

Fig.3a depicts the top bead appearance of the as-deposited NiTi parts. It can be seen that the deposited beads are uniform throughout the deposition without evidence of discontinuities. Additionally, the as-built wall is characterized by a bright silver color, which indicates that no evidence of surface oxidation is present. This is of special importance for NiTi, due to high susceptibility to oxidation at elevated temperatures, which is known to degrade the mechanical and functional properties of the material [39].

Fig.3c depicts the X-Z cross-section view of 5 deposited layers. Each layer was marked using dashed red lines. Equiaxed grains are visible on the Ni-rich substrate and these will support the formation of columnar crystals in the first deposited layer.

Fig. 3. a) Macroscopic appearance of the WAAM NiTi specimens; b) Samples extracted from the wall; c) Microstructure of the as-built part

The high cooling rate of the first deposited layer is enhanced by the large substrate which rapidly dissipates heat, further influencing a columnar-like microstructure to

form in this region, highlighted in Fig.4a. It can be observed that the columnar grains in the first deposited layer present an inclination in the growth direction towards the center of the fusion zone. These elongated grains occur as a result of the heat source movement and of the large local heat flux from the center of the fusion zone pool to the end of the weld pool tail [40]. With subsequent depositions, the thermal gradient is reduced due to the intrinsically low thermal conductivity of this class of alloys and lower cooling rates of the deposited material due to previous depositions, which creates a pre-heating effect. As a result, the columnar grain inclination is limited as additional WAAM deposits are made. Partial remelting of the already solidified grain occurs on the following deposition. Then, the existing equiaxed grains at the top of the fusion zone grow by epitaxy, contrary to the direction of heat extraction. As a result, needle-like grains are formed, and these are observed at the interface of subsequent deposited layers shown in Fig.4b.

For the following depositions and with more deposited layers, the cooling rates decreases due to a pre-heating effect of previous depositions [41]. As a consequence, the as-solidified microstructures change to an equiaxed morphology (see Fig.4c). Additionally, compared with the microstructure in the first deposited layers, a noteworthy decrease in the grain size occurs in the last deposited layer. This is related to the fact that no subsequent depositions were made. As such, in the last deposited layer, the time and temperature necessary for grain growth to occur does not happen. In summary, the microstructural differences in terms of grain morphology occur due to the different thermal cycle conditions experienced, namely the decrease of the cooling rate, with consecutive depositions of material, except for the last deposited layer of NiTi.

During the WAAM process, an ultra-high frequency pulse (20 kHz) power was applied. The high-frequency pulse can refine the grain structure and improve the joint performance when compared to conventional TIG torches [42, 43]. Future work will analyze the influence of different TIG torches (conventional vs high-frequency ones) on the grain morphology and material performance.

Fig. 4. Microstructure of the NiTi WAAM parts cross section: a) magnified microstructure of zone D; b) magnified microstructure of zone E; c) magnified microstructure of zone F; d) magnified microstructure of zone G). Zones D to G are all marked in Fig. 3.

According to EDS analysis, the Ni chemical composition in zones E, F and G of Fig. 2c is of 50.15, 50.08 and 50.02 at%. Minor changes in the Ni content can be attributed to local segregation upon solidification [12], precipitation or preferential evaporation. From the EDS analysis it can be concluded that the material composition is homogenous throughout its height. Following the Ni-Ti equilibrium phase diagram, for a Ni content of 53.5 at%, the expected stable phases below 400 °C are NiTi and Ni₃Ti [44]. Other metastable phases, such as Ni₄Ti₂ and Ni₂Ti₂, can precipitate and decompose to Ni₃Ti after long periods at critical temperatures [34, 39, 40, 45]. The non-equilibrium solidification conditions that occur during WAAM prevented the formation of Ni₃Ti precipitates [35, 46].

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For WAAM, the pre- and post-heating caused by subsequent depositions, can drastically impact the as-solidified microstructure and solid-state transformations of the as-built parts. In opposition to welding, where columnar grains are typically prevalent due to the fast cooling, which often lead to a deterioration of mechanical

properties in the fusion zone, in the NiTi WAAM parts these columnar grains only formed in the first deposited layer. It must be noticed that some micro-pores were observed in the last deposited layer. These are probably formed as a result of entrapped gas during the solidification process or due to some instability in the shielding gas flow [47].

The microhardness measurements performed in the centreline along the as-built wall (Z direction in Fig. 3c) are depicted in Fig. 5. The first and second layers exhibited lower hardness, from 228 to 236 HV, while the third and subsequent layers kept a relatively constant hardness at 245 HV. The lower hardness in the first deposited layers can be attributed to the different grain morphologies obtained: while for the first layers the existence of columnar grains decreases the hardness, in the top layers the equiaxed morphology is responsible for an increase in hardness [48, 49]. It must be noticed that unlike other materials that exhibit a martensitic transformation, such as steels, the cooling rates do not highly impact the resulting hardness.

Fig. 5. Microhardness along the NiTi WAAM specimen

2433.2 Phase transformation characteristics

The phase transformation characteristics of the as-received NiTi wire and as-built

WAAM part were analyzed by DSC and the results are depicted in Fig. 6. A summary of the transformation temperatures is presented in Table 1. M and A are related to the martensite and austenite phases, while subscripts s and f refer to the start and finish of the transformations, respectively.

Table 1. Transformation temperatures (°C) of the WAAM specimen and as-received NiTi wires.

Materials	A _s	A _f	M _s	M _f
As-received NiTi wire	3.6	16.2	12.5	-2.8
WAAM specimen	-23.4	30.6	-30.4	-62.9

At room temperature, the as-received NiTi wire is fully austenitic. The onset temperatures of the as-built part for both M_s and A_f were -30.4°C and 30.6°C, respectively, with a wider transformational range and hysteresis comparing to the as-received NiTi wire, which was measured to be 12.5°C and 16.2°C. This change in the transformation temperatures can be related to the differences in grain size and development of residual stresses, which are known to influence the martensitic transformation in NiTi SMAs [50]. Similar results were presented in ref. [34], where the transformation temperatures were all below room temperature.

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For Ni-rich NiTi, a decrease of the Ni matrix content by 1 at. % can drastically increase the M_s temperature by more than 100 °C [35]. There are multiple factors that can justify the differences in the transformation behavior of the WAAM part compared to the feedstock material. First, the feedstock material, from a microstructural point of view, i.e. grain size, composition and residual stresses, is expected to be homogenous along its length. The same does not occur in the WAAM specimen. As observed before, the grain size changes from the first to the last deposited layer of the as-built part. Differences in grain size have been seen to influence the martensitic transformation for NiTi alloys [51, 52]. For the WAAM part, there also is the development of residual stresses which will not be uniform throughout the part height owing to the different thermal cycle conditions. As exemplified in [53], significant differences in the

transformation behavior may occur in NiTi when processed with localized heat sources, as in WAAM or SLM, due to the development of thermally induced residual stresses. In addition, nanoscale precipitation, in this case Ni_4Ti_3 , may also change the matrix chemical composition, which will modify the transformation temperatures. Previous work on SLM of NiTi reported the formation of nanoscale Ni_4Ti_3 [22]. In SLM, the thermal cycle available for Ni_4Ti_3 precipitation is rather small, compared to WAAM. Additionally, during WAAM, as a result of the heat accumulation, it is expected that more favorable conditions for Ni_4Ti_3 precipitation occur as the part is being built. Nonetheless, in WAAM, the time available for precipitation of this phase is within the order of a few seconds, though the volume fraction is expected to be low [54].

As described above, there are multiple possibilities to explain the differences in the transformation characteristic of the WAAM NiTi parts compared to the as-received feedstock material. Further research work is in progress to isolate how each one of the aforementioned microstructural features contributed to the change in the transformation temperatures.

Fig. 6. Phase transformation of as-received materials and as-built NiTi WAAM part

Synchrotron X-ray diffraction was performed to evaluate existing phases in the as-built material at room temperature. The diffractogram of the as-built sample obtained after full integration along the azimuthal angle is depicted in Fig. 7. Austenite, martensite, R-phase and Ni_4Ti_3 are identified. These results are in good agreement

with the DSC analysis which suggested the presence of all austenite, martensite, R-phase phases at room temperature.

The presence of Ni_4Ti_3 precipitates can be related to the continuous reheating and cooling experienced by the already deposited layers. It is known that for Ni_4Ti_3 precipitation to occur only a few seconds in the 500 to 300 °C temperature range are required [55]. The existence of R-phase is then favoured by presence of these precipitates as comprehensively described in [56, 57]. Finally, the presence of Ni_4Ti_3 in the as-built parts promotes a Ni depletion from the matrix, thus justifying the increased transformation temperatures of the WAAM deposited material as described above, as increase in hardness along the wall height.

Fig. 7. X-ray diffraction pattern of the as-built NiTi WAAM part obtained after full integration along the azimuthal angle

Fusion-based additive manufacturing techniques are known to promote strong texture in the as-built material. This qualitative evaluation of texture can be seen in Fig. 8a, where the peak position of different phases varies along the azimuthal angle (refer to image 2). The (110) austenite peak, located at $2\theta \approx 3.84^\circ$, is predominant over all other diffraction peaks. Note that the R-phase and Ni_4Ti_3 peaks are not clearly visible in Fig. 8a owing to their relatively low intensity, thus their peak positions were not marked.

What can be perceived from Fig. 8a is the existence of minor intensity

reinforcements at specific azimuthal angles. These reinforcements can originate from one of the previously identified phases in Fig. 7. At that specific angles a sufficiently high number of grains of these low volume fraction phases was in diffraction condition, which was captured by the 2D detector. This crystallographic dependence is clearly observed when comparing the diffraction patterns obtained upon integration along the azimuthal angles of 0 and 90° (Fig. and Fig. 8c, respectively). For example, the diffraction peaks corresponding to Ni_4Ti_3 are clearly observed when the φ angle is of 0°, but not for $\varphi = 90^\circ$. The same occurs for R-phase, where its diffraction peaks are clearly depicted for $\varphi = 90^\circ$ and not for $\varphi = 0^\circ$. Also, note that the relative intensity of the austenite and martensite peaks varies for different azimuthal angles, which again occurs due to the highly direction solidification conditions imposed during WAAM.

Fig.8 a. Dependence of austenite and martensite diffraction peak positions with the azimuthal angle; b and c. diffraction patterns obtained with integration along the azimuthal angles of 0 and 90°, respectively.

These results also emphasize the need to correlate the X-ray diffraction results with DSC, in order to fully understand the existing phases, especially at temperatures where the material is not in a single-phase region. Here, it is shown that the full integration of the synchrotron X-ray diffraction raw data along the azimuthal data can hinder low volume fraction phases, thus highlighting the need to analyse the azimuthal dependence of all potential phases of the NiTi system. Finally, our results also clearly evidence the potentialities of synchrotron X-ray diffraction data: the very high signal

to noise ratio allows to clearly detect minority phases, which would require extensive (if even possible) counting times when using conventional laboratory sources.

3.3 Mechanical properties

To evaluate the mechanical properties of the NiTi WAAM parts conventional tensile testing until fracture was performed. Three samples were analyzed and the typical stress-strain curve of the as-built wall is depicted in Fig. 9. The stress induced transformation from austenite to martensite was seen to occur at 352.8 ± 16.2 MPa and the tensile strength of the parts was of 571.4 ± 18.6 MPa with a corresponding fracture strain of $16.8 \pm 2.4\%$.

The analysis of Fig. 9 reveals the mechanical behaviour of a near fully austenitic NiTi SMA: first, elastic deformation of austenite occurs; then, at around 350 MPa the stress-induced transformation to martensite takes places and proceeds at a near-constant applied stress. At the same time, detwinning of martensite is occurring [44]. The next inflection point, at $\approx 10\%$ strain, denotes the onset for elastic deformation of detwinned martensite, which eventually started to deform plastically, and then fracture occurs at $\approx 17\%$. The excellent tensile properties are evidenced by these mechanical tests, and the existence of small pores in the last deposited layers does not significantly affect the overall performance of the as-built walls.

Fig. 9. Representative tensile stress-strain curve of a NiTi WAAM specimen

During tensile testing, DIC was used for the analysis of the local mechanical behavior of the specimen at given representative applied stresses. These DIC contours are shown in Fig. 10a to Fig. 10e. In region 1 which corresponds to low (≈ 50 MPa) applied external stress no significant strain localization occurs. When the stress onset for the martensitic transformation (≈ 350 MPa for these NiTi WAAM parts) is reached, the martensite bands start to nucleate as shown in the red box of Fig. 10b, which corresponds to region 2 of Fig. 9. These Lüders/transformation bands are highly mobile and occur at an angle of approximately 55° relative to the load direction in order to fulfill the requirements for macroscopic strain compatibility (least additional elastic deformation) between the undeformed and deformed regions [58, 59].

In region 3, corresponding to the onset for elastic deformation of detwinned martensite, there is some evidence of Lüders bands on the top of the tested specimens (marked with a red rectangle in Fig. 10 c). At this point there is significant strain localization at one region of the sample surpassing 9 % strain. This strain concentration may arise from a local microstructural heterogeneity, such as a pore, that can act as a stress concentrator. This strain localization is even more noticeable prior to failure (region 4 in Fig.9 and Fig. 10 d) reaching a local strain of 17%. At this moment no evidence of transformation bands exist in the tested sample. The region where strain localization has occurred is where fracture occurs, which takes places for an external applied stress of ≈ 570 MPa and a corresponding fracture strain of $\approx 17\%$.

Fig. 10. Local mechanical properties of WAAM specimens measured using digital image correlation: a. strain distribution at 50 MPa; b. strain distribution at 350 MPa; c. strain distribution at 420 MPa; d. strain distribution at 550 MPa; e fracture

SEM imaging of the fracture surfaces was performed after tensile testing (Fig. 11). A ductile-like fracture surface is clearly observed, as evidenced by the existence of

dimples, which is in excellent agreement with the large elongation to fracture of the WAAM NiTi parts. There are no signs of cleavage on the fracture surface. It is noted that nucleation of voids, growth and coalescence are known to start on microcracks or precipitates. Some micro-cracks along the equiaxed grains boundaries can be observed in the high magnification image of Fig. 11b. These cracks can serve as preferential sites for fracture initiation and propagation. The propagation of secondary microcracks occurs as a result of the continuous changes in the local stress state during deformation [60].

Fig. 11. Fracture surface after tensile test (a. macro-structure b. magnified microstructures of zone B in Fig.9a)

Aside from the tensile properties to failure, the cycling behavior of the as-built NiTi parts was also evaluated. The graph in Fig. 12a depicts a total of 10 load/unload cycles to a maximum of 6% tensile strain, followed by unloading to a zero-stress condition. It can be seen that the WAAM specimens exhibit good superelastic properties, evidenced by a low irrecoverable strain of 1.13% upon unloading in the first cycle. The plastic strain increased during the first 7 cycles, and reached nearly a constant value of 2.73% (Fig.12b). For NiTi SMAs, the strain recovery due to the superelastic effect can be as high as 10% [61]. However, there are several aspects that may impair a complete superelastic recovery of the material. These include the testing temperature, the applied strain and strain rate, any thermal and/or mechanical treatment, as well as the grain size of the tested sample [38]. In this investigation, the incomplete recovery of the initially imposed deformation can arise from the microstructural modifications, i.e. significant differences in grain size induced by the

WAAM process [62]. In fact, the existence of a non-homogeneous microstructure, as evidenced by the simultaneous presence of columnar and equiaxed grains, can promote distinct local mechanical behavior. That is, regions with coarse grain size are expected to be easily deformed, when compared to smaller grain sizes, and, therefore, martensite stabilization and subsequent loss of superelasticity can occur [63]. Therefore, the different microstructures, i.e. columnar at the bottom and equiaxed at the top along the height of the WAAM part can explain the irrecoverable strain of the as-built part [64]. Additionally, the material is not fully austenitic at the testing temperature ($\approx 25^\circ\text{C}$) as shown by both DSC and synchrotron X-ray diffraction experiments, thus part of the irrecoverable strain can also be attributed to presence of martensite prior to any imposed deformation.

Fig. 12. load/unload functional fatigue curve of NiTi WAAM specimen (a. load/unload fatigue stress-strain curve, b. accumulated residual strain)

As described in the experimental procedure section, in this investigation only one set of parameters was used to create the WAAM NiTi parts. Future work will focus on the effect of different process parameters on the grain structure, mechanical and functional properties of the WAAM NiTi parts.

4. Conclusions

Wire and Arc Additive Manufacturing was used to create NiTi shape memory alloy walls, using commercially available Ni-rich NiTi wires as the feedstock material. The following main conclusions can be drawn:

- 1) A columnar grain structure was observed in the first deposited layers, while towards the top of the wall fine equiaxed grains were formed. This is related to the thermal cycle conditions in both regions.
- 2) The as-built walls are near fully austenitic at room temperature as suggested by stress-strain and superelastic cycling results.
- 3) The as-built parts exhibit superelasticity under tensile conditions and a stable mechanical response is obtained after 7 load/unload cycles.
- 4) The viability to deposit advanced functional materials such as NiTi shape memory alloys by WAAM using a TIG heat source was demonstrated. This opens new doors for this additive manufacturing technique to be applied for the production of large parts based on these materials.

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References

- [1] A. Mitchell, U. Lafont, M. Hołyńska, C. Semprimoschnig, Additive manufacturing -A review of 4D printing and future applications, *Additive Manufacturing*, 2018, 24: 606-626.
- [2] M.J. Jani, M. Leary, A. Subic, M.A. Gibson, A review of shape memory alloy research, applications and opportunities, *Materials & Design*. 2014, 56: 1078–113.
- [3] H. Gugel, A. Schuermann, W. Theisen, Laser welding of NiTi wires, *Materials Science & Engineering A*. 2008, 481-482: 668-671.
- [4] Z. Zeng, B. Panton, J.P. Oliveira, A. Han, Y. Zhou, Dissimilar laser welding of NiTi shape memory alloy and copper, *Smart Materials and Structures*. 2015, 24(12): 125036.
- [5] S. Himanshu, R. Harrison, C. Carpenter, A. Bandyopadhyay, Stainless steel to titanium bimetallic structure using LENS™, *Additive Manufacturing*, 2015, 5: 1-8.
- [6] D.T. Waghmare, C.K. Padhee, R. Prasad, M. Masanta, NiTi coating on Ti-6Al-4V alloy by TIG cladding process for improvement of wear resistance: Microstructure evolution and mechanical performances, *Journal of Materials Processing Technology*, 2018, 262:551-561.
- [7] B. Tam, A. Pequegnat, M. Khan, Y. Zhou, Resistance Microwelding of Ti-55.8 wt pct Ni Nitinol Wires and the Effects of Pseudoelasticity, *Metallurgical and Materials Transactions A*, 2012, 43:2969-2978.
- [8] W. Zhang, S. Ao, J.P. Oliveira, Z. Zeng, Z. Luo, Z. Hao, Effect of ultrasonic spot welding on the mechanical behaviour of NiTi shape memory alloys, *Smart Materials and Structures*. 2018 27, 085020.
- [9] M. Jacob, B. Zhang, D. Hartl, A. Elwany, Effect of process parameters and electropolishing on the surface roughness of interior channels in additively manufactured nickel-titanium shape memory alloy actuators, *Additive Manufacturing*, 2019, 27: 565-575.
- [10] T.A. Mohsen, S. Saedi, A.S. Turabi, M.R. Karamooz, M. Elahinia, Mechanical and shape memory properties of porous Ni50.1Ti49.9 alloys manufactured by

selective laser melting, *Journal of the Mechanical Behavior of Biomedical Materials*, 2017, 68:224-231.

[11] B. Zhang, W. Meng, S. Shao, N. Phan, N. Shamsaei, Effect of Heat Treatments on the Morphology of Pores in Laser Additive Manufactured Parts, *Manufacturing Letters*, <https://doi.org/10.1016/j.mfglet.2019.06.005>.

[12] K.F. Ayarkwa, S.W. Williams, J. Ding, Assessing the effect of TIG alternating current time cycle on aluminium wire+arc additive manufacture, *Additive Manufacturing*, 2017, 18: 186-193.

[13] M. Dinovitzer, X. Chen, J. Laliberte, X. Huang, H. Frei, Effect of wire and arc additive manufacturing (WAAM) process parameters on bead geometry and microstructure, *Additive Manufacturing*, 2019, 26: 138-146.

[14] X. Xu, J. Ding, S. Ganguly, S. Williams, Investigation of process factors affecting mechanical properties of INCONEL 718 superalloy in wire + arc additive manufacture process, *Journal of Materials Processing Technology*, 2019, 265:201-209.

[15] M.H. Elahinia, M. Hashemi, M. Tabesh, S.B. Bhaduri, Manufacturing and processing of NiTi implants: A review, *Progress in Materials Science*. 2012, 57(5): 911-946.

[16] M. Elahinia, M.N. Shayesteh, M.T. Andani, A. Amerinatanzi, R.F. Hamilton, Fabrication of NiTi through additive manufacturing: A review, *Progress in Materials Science*, 2016, 83: 630-663.

[17] N.S. Moghaddam, S. Saedi, A. Amerinatanzi, A. Hinojos, A. Ramazani, J. Kundi, M.J. Mills, H. Karaca, M. Elahinia, Achieving superelasticity in additively manufactured NiTi in compression without post-process heat treatment, *Scientific Reports*, 2019, 9: 41.

[18] S. Saedi, A.S. Turabi, M.T. Andani, C. Haberland, H. Karaca, M. Elahinia, The influence of heat treatment on the thermomechanical response of Ni-rich NiTi alloys manufactured by selective laser melting, *Journal of Alloys and Compounds*, 2016, 677:204-210.

[19] S. Saedi, A.S. Turabi, M.T. Andani, N.S. Moghaddam, M. Elahinia, H.E. Karaca,

Texture, aging, and superelasticity of selective laser melting fabricated Ni-rich NiTi alloys, *Materials Science and Engineering: A*, 2017, 686:1-10.

[20] R.F. Hamilton, B.A. Bimbera, A.M. Taheri, M. Elahinia, Multi-scale shape memory effect recovery in NiTi alloys additive manufactured by selective laser melting and laser directed energy deposition, *Journal of Materials Processing Technology*, 2017, 250:55-64.

[21] J.P. Oliveira, A.J. Cavaleiro, N. Schell, A. Stark, R.M. Miranda, J.L. Ocana, F.M. Braz Fernandes, Effects of laser processing on the transformation characteristics of NiTi: A contribute to additive manufacturing, *Scripta Materialia*, 2017, 152:122-126.

[22] J. Ma, B. Franco, G. Tapia, K. Karayagiz, L. Johnson, J. Liu, R. Arroyave, I. Karaman, A. Elwany, Spatial Control of Functional Response in 4D-Printed Active Metallic Structures, *Scientific Reports*, 2017, 7: 46707.

[23] T.A. Rodrigues, V. Duarte, J.A. Avila, T.G. Santos, R.M. Miranda, J.P. Oliveira, Wire and arc additive manufacturing of HSLA steel: Effect of thermal cycles on microstructure and mechanical properties, *Additive Manufacturing*. 2019.27: 440-450.

[24] K.S. Derekar, A review of wire arc additive manufacturing and advances in wire arc additive manufacturing of aluminium, *Materials Science and Technology*. 2018, 34(8): 895-916.

[25] C.V. Haden, G. Zeng, F.M. Carter, C. Ruhl, B.A. Krick, D.G. Harlow, Wire and arc additive manufactured steel: Tensile and wear properties, *Additive Manufacturing*. 2017.16: 115-123.

[26] H. Geng, J. Li, J. Xiong, X. Lin, F. Zhang, Geometric limitation and tensile properties of wire and arc additive manufacturing 5A06 aluminum alloy parts, *Journal of Materials Engineering and Performance*. 2017, 26(2): 621-629.

[27] B. Cong, J. Ding, S. Williams, Effect of arc mode in cold metal transfer process on porosity of additively manufactured Al-6.3% Cu alloy, *The International Journal of Advanced Manufacturing Technology*, 2015, 76: 1593–1606.

[28] Z. Qi, B. Cong, B. Qi, H. Sun, G. Zhao, J. Ding, Microstructure and mechanical

properties of double-wire + arc additively manufactured Al-Cu-Mg alloys, *Journal of Materials Processing Technology*, 2018, 255: 347–353.

[29] Z. Qi, B. Cong, B. Qi, G. Zhao, J. Ding, Properties of wire + arc additively manufactured 2024 aluminum alloy with different solution treatment temperature, *Materials Letter*, 2018, 230: 275–278.

[30] Z. Qi, B. Qi, B. Cong, H. Sun, G. Zhao, J. Ding, Microstructure and mechanical properties of wire+ arc additively manufactured 2024 aluminum alloy components: As-deposited and post heat-treated, *Journal of Manufacturing Processes*, 2019, 40: 27-36.

[31] F. Wang, S. Williams, P. Colegrove, A. Antonysamy, Microstructure and mechanical properties of wire and arc additive manufactured Ti-6Al-4V, *Metallurgical and Materials Transactions A*, 2013, 44: 968–977.

[32] F. Martina, J. Mehnen, S. Williams, P. Colegrove, F. Wang, Investigation of the benefits of plasma deposition for the additive layer manufacture of Ti-6Al-4V, *Journal of Materials Processing Technology*, 2012, 212: 1377.

[33] D. Herzog, V. Seyda, E. Wycisk, C. Emmelmann, Additive manufacturing of metals, *Acta Materialia*, 2016, 117: 371–392.

[34] J. Wang, Z. Pan, G. Yang, J. Han, X. Chen, H. Li, Location dependence of microstructure, phase transformation temperature and mechanical properties on Ni-rich NiTi alloy fabricated by wire arc additive manufacturing, *Materials Science and Engineering: A*, 2019, 749:218-222.

[35] M.I. Khan, A. Pequegnat, Y.N. Zhou, Multiple Memory Shape Memory Alloys, *Advanced Engineering Materials*, 2013, 15: 386–393.

[36] D. Yang, G. Wang, G. Zhang, Thermal analysis for single-pass multi-layer gmaw based additive manufacturing using infrared thermography, *Journal of Materials Processing Technology*, 2017, 244:215-224.

[37] Z. Zeng, M. Yang, J.P. Oliveira, D. Song, B. Peng, Laser welding of NiTi shape memory alloy wires and tubes for multi-functional design applications, *Smart Materials and Structures*, 2016, 25(8):1-10.

[38] J.P. Oliveira, R.M. Miranda, N. Schell, F.M. Braz Fernandes, High strain and long

duration cycling behavior of laser welded NiTi sheets, *International Journal of Fatigue*, 2016, 83(2): 195-200.

[39] J.P. Oliveira, D. Barbosa, F.M. Braz Fernandes, R.M. Miranda, Tungsten inert gas (TIG) welding of Ni-rich NiTi plates: functional behavior, *Smart Materials and Structures*, 2016, 25(3): 1-7

[40] X. Wan, Y. Feng, X. Lin, H. Tan, Large superelastic recovery and elastocaloric effect in as-deposited additive manufactured Ni_{50.8}Ti_{49.2} alloy, *Applied Physics Letters*, 2019, 114(22): 1-5

[41] S.M. Kelly, S.L. Kampe, Microstructural evolution in laser-deposited multilayer Ti-6Al-4V builds: Part II. Thermal modeling, 2004, 35(6):1869-1879.

[42] H. Yuan, C. Yang, W. Xie, S. Lin, C. Fan, Application of power ultrasonic in arc welding, *Hot Working Technology*, 2015, 44(09): 6-10.

[43] M. Yang, B. Qi, B. Cong, F. Liu, Z. Yang, Effect of pulse frequency on microstructure and properties of Ti-6Al-4V by ultrahigh-frequency pulse gas tungsten arc welding, *International Journal of Advanced Manufacturing Technology*, 2013, 68:19-31.

[44] K. Otsuka, X. Ren, Physical metallurgy of Ti-Ni-based shape memory alloys, *Progress in Materials Science*. 2005, 50 (5): 511-678.

[45] D. Gu, C. Ma, In-situ formation of Ni₄Ti₃ precipitate and its effect on pseudoelasticity in selective laser melting additive manufactured NiTi-based composites, *Applied Surface Science*. 2018, 441: 862-870.

[46] A. Falvo, F.M. Furguele, C. Maletta, Laser welding of a NiTi alloy: Mechanical and shape memory behaviour, *Materials Science & Engineering A*, 2005, 412: 235-240.

[47] A. Bagheria, M.J. Mahtabia, N. Shamsaeib, Fatigue behavior and cyclic deformation of additive manufactured NiTi, *Journal of Materials Processing Technology*. 2018, 252: 440-453.

[48] Z. Qi, B. Qi, B. Cong, H. Sun, G. Zhao, J. Ding, Microstructure and mechanical properties of wire plus arc additively manufactured 2024 aluminum alloy components: As-deposited and post heat-treated, *Journal of Manufacturing Process*. 2019, 40: 27-36.

[49] L. Wang, J. Xue, Q. Wang, Correlation between arc mode, microstructure, and

mechanical properties during wire arc additive manufacturing of 316L stainless steel, *Materials Science and Engineering A*. 2019, 751: 183-190.

[50] Y. Zheng, F. Jiang, L. Li, H. Yang, Y. Liu, Effect of ageing treatment on the transformation behaviour of Ti-50.9at.% Ni alloy", *Acta Materialia*, 2008, 56: 736-745.

[51] A. Ahadi, Q. Sun, Effects of grain size on the rate-dependent thermomechanical responses of nanostructured superelastic NiTi, *Acta Materialia*, 2014, 76: 186-197.

[52] F.J. Gil, J.M. Manero, J.A. Planell, Effect of grain size on the martensitic transformation in NiTi alloy, *Journal of Materials Science*, 1995, 30(10): 2526-2530.

[53] J.P. Oliveira, F.M. Braz Fernandes, R.M. Miranda, N. Schell, J.L. Ocaña, Effect of laser welding parameters on the austenite and martensite phase fractions of NiTi, *Materials Characterization*, 2016, 119: 148-151.

[54] J.P. Oliveira, F.M. Braz Fernandes, R.M. Miranda, N. Schell, On the Mechanisms for Martensite Formation in YAG Laser Welded Austenitic NiTi, *Shape Memory and Superelasticity*, 2016, 2: 114-120.

[55] A.R. Pelton, J. DiCello, S. Miyazaki, Optimisation of processing and properties of medical grade Nitinol wire, *Minimally Invasive Therapy and Allied Technologies*, 2000, 9: 107-118.

[56] J. Khalil-Allafi, A. Dlouhy, G. Eggeler, Ni₄Ti₃-precipitation during aging of NiTi shape memory alloys and its influence on martensitic phase transformations, *Acta Materialia*, 2002, 50(17):4255-4274.

[57] X. Wang, S. Kustov, B. Verlinden, J.V. Humbeeck, Fundamental development on utilizing the r-phase transformation in NiTi shape memory alloys. *Shape Memory and Superelasticity*, 2015, 1(2):231-239.

[58] L. Dong, R. Zhou, X. Wang, G. Hu, Q. Sun, On interfacial energy of macroscopic domains in polycrystalline NiTi shape memory alloys, *International Journal of Solids and Structures*, 2016, 80: 445-455.

[59] P. Sedmák, J. Pilch, L. Heller, J. Kopeček, J. Wright, P. Sedlák, M. Frost, P. Šittner,

636 Grain-resolved analysis of localized deformation in nickel-titanium wire under
637 tensile load, *Science*, 2016, 353: 6299.

638 [60] F. Jiang, S.V. Kenneth, Fracture of Nitinol under quasistatic and dynamic loading,
639 *Metallurgical and Materials Transactions A*, 2007, 38: 2907-2915.

640 [61] Y. Xiao, P. Zeng, L. Lei, Y. Zhang, In situ observation on temperature dependence
641 of martensitic transformation and plastic deformation in superelastic NiTi shape
642 memory alloy, *Materials & Design*, 2017, 134:111-120.

643 [62] Z. Zeng, J.P. Oliveira, M. Yang, D. Song, B. Peng, Functional fatigue behavior of NiTi-
644 Cu dissimilar laser welds, *Materials & Design*. 2017, 114(15): 282-287.

645 [63] J.P. Oliveira, F.M. Braz Fernandes, N. Schell, R.M. Miranda, Martensite stabilization
646 during superelastic cycling of laser welded NiTi plates, *Materials Letters*, 2016,
647 171: 273-276.

648 [64] J.P. Oliveira, T.G. Santos, R.M. Miranda, Revisiting fundamental welding concepts
649 to improve additive manufacturing: From theory to practice, *Progress in*
650 *Materials Science*, 2019, 107:100590.

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