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Suspended Droplet Alloying: A New Method for Combinatorial Alloy Synthesis; Nitinol-based Alloys as an Example

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Abstract

A new combinatorial alloy synthesis method (suspended droplet alloying) has been developed as a high-throughput approach for alloy discovery. The method is based on using a laser to melt elemental or alloyed wires fed at a controlled rate to achieve a specific chemistry. In this study, the metallurgical characteristics of alloy buttons created using this technique were assessed for TiNi-based shape memory alloy buttons deposited using pure Ni, Ti, and Cu wires. The microstructural and chemical inhomogeneity was assessed using quantitative electron microscopy and X-ray diffraction. Furthermore, the phase transformation temperatures of the coupons have been compared to cast and heat-treated (reference) samples. In general, the samples displayed a limited local deviation from the target chemistry (± 1 wt.%), while displaying a fairly homogeneous microstructure with the expected phase distribution. Post-process homogenisation heat treatments enhanced the phase transformation response, approaching the response obtained from the reference samples.

Keywords: metals and alloys; laser processing; nitinol; combinatorial synthesis

1. Introduction

Intensive research has been performed on TiNi-based shape memory alloys (SMAs) due to their unique ability to recover a specific shape through a martensite $\leftrightarrow$ austenite phase transformation, which is temperature-induced in the shape memory effect (SME) or deformation-induced in the superelastic (SE) behaviour [1-3]. Certain alloying elements (e.g. Cu, Hf, Pd, Zr, and Pt) are known to strongly influence either the phase transformation

temperature range and/or the magnitude of the reversible/recoverable strain. Nonetheless, it is seldom straightforward to predict the influence of ternary or quaternary additions on the SMAs behaviour. As such, there is a need for an alloy development method that is capable of rapidly producing alloy combinations rapidly to accelerate the discovery of new alloys.

Combinatorial synthesis (CS) describes a high-throughput approach for building material libraries for material development. So far, several combinatorial synthesis processes techniques have been used to develop new SMAs, including continuous composition spread (CCS), combinatorial magnetron sputtering, diffusion couples, and laser ablation [4-8]. However, these processes cannot produce bulk samples for mechanical tests, especially the techniques that produce thin films or compositionally graded samples, which usually display different properties from bulk samples [9]. Research on SMAs development has traditionally been performed mainly using vacuum arc, plasma, or vacuum induction melting, and Self-propagation High-temperature Synthesis (SHS) to create bulk samples [10-14]. For the majority of the melting/re-melting techniques, homogenisation heat treatments are usually required to reduce the gravity segregation associated with the process [10]. Although large samples can be produced, the melting techniques are far from being high-throughput due to the long processing times. SHS can produce large non-segregated samples, but the porosity within these samples limits the application [11, 13, 14]. The development of laser additive manufacturing (AM) technologies provided an approach to produce materials of nominally defined compositions using pre-alloyed powders or of continuously changing compositions by blending and varying the powder chemistry/type (functional-grading). Polanski *et al.* [15] used a direct laser deposition based CS approach using multiple powder feeding systems to produce samples of different compositions. Nonetheless, due to the use of powders, the compositional control for this process is limited to within about ± 3 wt. %. As such, there is a need to develop a high-throughput CS technique that is capable of producing bulk homogeneous samples to accelerate the discovery of new alloy formulations, which is the subject of the present investigation.

2. Experimental Methods & Materials

2.a. Suspended Droplet Alloying process

The propose technique, Suspended Droplet Alloying (SDA), utilises a multiple-wire direct laser deposition CS approach in order to overcome the deviation in chemical composition associated with a powder feed system due to the occasional scatter of the sprayed powders from the meltpool. A prototype SDA machine, equipped with a CO₂ laser (maximum power of 1950 W and spot size of 2 mm) as heat source, and enclosed within a glove box with a controlled Ar atmosphere (≤ 30 ppm oxygen), was used for deposition. The multi-wire feeding system wire is capable of producing alloys from binary to hexabasic alloys if elemental wires are used, nominally to an accuracy of ± 1 wt.% compositional accuracy [16]. Alloy or coated wires can also be used to generate more complex alloy systems. During the process, the wires are fed continuously at a controlled speed (adjusted according to the target chemistry) through a special head (Fig. 1-a) to reach below the laser beam, where they melt and join together, forming a droplet suspended at the tip of wires (Fig. 1-b). The droplet falls to a substrate as soon as it is heavy enough, after which a next droplet start to form and the head moves up 3 to 10mm along z axis. During the formation of the subsequent droplets, the button still gets exposed to the laser beam (Fig. 1-c), which assists in re-melting the top layers, enhancing the homogeneity of the button.

Figure 1. The suspended droplet alloying process: (a) fire-feeding system displaying a picture of the produced alloy button, (b) and (c) droplet formation.

The multi-wire feeding system has a number of advantages over a powder-based system. First, the capture rate of the sprayed powders into the meltpool during deposition hardly achieves 50-70% [17, 18], meaning that the chemistry is likely to be affected multiple powder types are being used, whereas the wires and the molten droplets fall entirely into the melt pool. Second, the melting behaviour of the wires can be adjusted easily by changing the wire diameters to account for evaporation. Third, the feed rate of each wire can be controlled independently and precisely during deposition based on the target composition. Finally, the cost of the wires is considerably lower than that of the powders for most elements. Nonetheless, it is not always possible to find wires of specific elements, whereas powders can be atomised from various elements.

In this study, SDA was used for binary TiNi and ternary TiNiCu alloys, with an aim to assess the utility of the method in producing homogeneous alloy buttons, which are characterised for their microstructural/chemical homogeneity and shape memory behaviour.

2.b. Materials

Commercial purity 1 mm diameter wires (e.g. Ti wire with 99.8 wt.% purity, Ni wire with 99.55 wt.% purity and Cu wire with 99.9 wt.% purity) were used to build a number of binary and ternary TiNi-based alloy buttons, as listed in Table 1 (composition in at. % throughout the paper).

Table 1 Sample code, composition (at.%) and size.

Sample name	Ti	Ni	Cu	Size (mm)
Ti ₅₀ Ni ₅₀	50	50	-	Φ10 × 20
Ti ₅₂ Ni ₄₈	52	48	-	Φ10 × 20
Ti ₄₈ Ni ₅₂	48	52	-	Φ14 × 45
Ti ₅₀ Ni ₂₅ Cu ₂₅	50	25	25	Φ14 × 25
Ti ₅₂ Ni ₃₈ Cu ₁₀	52	38	10	Φ15 × 24

The metallurgical coordinate system for the buttons is shown in Fig. 1-a, with the z-direction being the build direction. The samples were deposited using 800 W to 1300W laser power, 5

to 8 mm/s wire feed rate for Ti, and 3 to 3.5 mm/s for Ni. Since the laser power needed to be changed continuously during the deposition. The specific laser power was varied generally between 500 W to 1300 W. Following deposition, the samples were sectioned using Electric Discharge Machining (EDM), mechanically polished, and etched using Kroll's reagent (100 ml H₂O + 2 ml HF + 5 ml HNO₃). The button microstructure was characterised using a Leica DMRX Polarised Optical Microscope (POM). A Philips XL30 Scanning Electron Microscope (SEM), equipped with Oxford Inca Energy-Dispersive X-ray Spectroscopy (EDS) system and HKL Channel 5 Electron Backscattered Diffraction (EBSD) systems, was used to assess the chemical inhomogeneity, and quantify the grain size and texture development. X-ray Diffraction (XRD) was used for phase identification and analysis using a Philips X'Pert system, equipped with a Cu K α anode, operated at 35 kV.

Post-SDA homogenisation heat treatment was performed at 1273 K in sealed silica tubes, followed by water quenching. A Mettler Toledo DSC500 Differential Scanning Calorimeter (DSC) system was used to characterise the characteristic temperatures of the martensite $\leftrightarrow$ austenite transformation (M_s : martensite start, M_f : martensite finish, A_s : austenite start, A_f : austenite finish). A commercially produced (cast, homogenised, and hot-rolled) TiNi sample with 50.6 at.% Ti content was used as a reference sample for comparison with the Ti₅₀Ni₅₀ sample produced by SDA.

3. Results and Discussion

3.a. Coupon Microstructure

Optical micrographs of the XY section of SDA-built Ti₅₀Ni₅₀ sample are shown in Fig. 2. The microstructure shows a ringed microstructure, with clear grain bands making the concentric rings (rings 1, 2 and 3), which surround three zones between them (zones A, B and C). The ringed microstructure is characteristic of this technique, as the molten droplet falls on a previously solidified drop. The different rings show different grain sizes (Fig. 2-a), with the central ring displaying a coarser grain structure, and finer grains in the outer ring due to the

faster cooling in the external regions. The rings also demonstrated bands of intermetallic particles (appearing as annular clusters of fine grey particles), as shown in Fig. 2-b. The interface between the particle-rich and particle-free bands can be seen later in Fig. 3-b in a different sample.

XRD pattern in Fig. 2-c identified the presence of B19' martensite phase, in addition to Ti_2Ni intermetallic phase [19]. Neither, TiNi_3 nor Ti_3Ni_4 precipitates were identified, which is expected in equilibrium for an equi-atomic TiNi alloy, based on the phase diagram [3]. To quantify the Ti_2Ni fraction, optical and SEM backscattered (BSe) micrographs were taken from the various regions in the build and analysed using ImageJ (within $\pm 3\%$ error). It was found that the microstructure showed considerable amounts of Ti_2Ni , which suggests the presence of significant Ti-segregation within the microstructure. The area fraction of the Ti_2Ni particles was found to vary locally between 0.03 to 0.21, with a total average area fraction of 0.09, as summarised in Table 2.

Figure 2. (a) and (b) Optical micrographs for the cross-section of etched $\text{Ti}_{50}\text{Ni}_{50}$ sample, showing (a) the three microstructural zones, (b) the distribution of Ti_2Ni (fine dark spots), and (c) XRD pattern for the same sample showing the phases present in the microstructure (B19' and Ti_2Ni).

Table 2 Area fractions of the microstructural zones and precipitates in $\text{Ti}_{50}\text{Ni}_{50}$ sample.

Zones/Bands	A	Ring 1	B	Ring 2	C	Ring 3	Total/Average
Area fraction of regions	0.133	0.017	0.397	0.049	0.245	0.162	1
Precipitate fraction	0.11	0.06	0.11	0.21	0.09	0.03	0.1

There was some microstructural inhomogeneity in both the grain size and precipitates from edge to centre, as shown in the rings and areas marked in Fig. 2-a. Ring 1 (external) showed a limited fraction of Ti_2Ni precipitates and some fine elongated grains between ring 1 and the edge of the sample, which is likely to be due to the rapid cooling at the external surface of the sample. Ring 2 had the highest Ti_2Ni area percentage, while the central zone (ring 3) again showed a limited fraction of Ti_2Ni . In terms of the grain size, ring 1 contained 100~200 μm grains elongated towards the periphery of the coupon, while zone A showed coarse (around 1 mm) equiaxed grains. However, ring 2 contained fine equiaxed grains up to 100 μm . In general, the grain size and morphology changed from columnar to equiaxed, and coarse to fine across the button cross-section. The observed microstructural inhomogeneity suggests that further post-process homogenisation will help in dissolving the intermetallic particles, in order to reduce the chemical segregation within the build. Furthermore, these findings suggest that the produced coupons may require further thermomechanical deformation to reduce the grain size inhomogeneity, in order to be useful for the development of structural materials, which are typically homogenised and/or forged.

Similar observations were found in the Ti-rich coupons built using SDA. The inhomogeneities (ringed structures) were also observed along XZ-section in the $\text{Ti}_{52}\text{Ni}_{48}$ sample in Fig. 3. The microstructure was predominantly columnar along the build direction, with most the columnar grains inclined slightly to the build direction (towards the direction of the maximum heat flux), whereas the columnar grains in the centre are aligned vertically, Fig. 3-a. Furthermore, the spatial variation in the Ti_2Ni precipitates was found to be rather sharp over a fine length-scale (Fig. 3-b). On the other hand, some remelted regions were observed, as shown in Fig. 3-c and 3-d. These regions are also commonly observed in Laser Engineered Net-Shaping (LENS) processes or Direct Laser Deposition (DLD) [20], along the deposition direction, due to the extension of the meltpool beyond the deposited layer, resulting in the occurrence of remelting in the previously solidified layers, repeating every $\sim 800 \mu\text{m}$ (Fig. 3-c).

Figure 3. The microstructural development in SDA $\text{Ti}_{52}\text{Ni}_{48}$ sample, showing (a) the spatial variation in the columnar grain orientation along the build direction, (b) BSE micrograph for the Ti_2Ni -segregated regions in the XY plane, (c) SE micrograph showing the remelted zone in XZ plane, and (d) the dendritic structure surrounded by Ti_2Ni precipitates.

The microstructure in SDA obtains its unique characteristics from the way that the process operates. The process differs from the LENS process in the fact that the laser is stationary, meaning that the build and the uppermost meltpool get continuously heated throughout the process by the laser beam. The substrate acts as a heat sink, transferring the heat to the platform, which results in the formation of columnar grains aligned along the build direction in the centre of the button, and slightly inclined at the edges due to the convective cooling by the argon gas flow around the build in the radial direction. Due to the rapid cooling rates at the surface, fine columnar grains form, with the dendrites surrounded by Ti_2Ni intermetallic phase.

Moreover, the subsequent solidification of the molten droplets results in the ringed microstructural zones. The previously solidified surface enhances the cooling rate when a new droplet falls into, which enhances the nucleation, resulting in the fine columnar grains observed in ring 2 in the XY plane (Fig. 2-a). The central region, however, experiences an extended heating period by the laser beam between the subsequent droplets, which results in melting in the central area, until a new droplet forms and blocks the laser beam. As this area was continuously exposed to the laser for a long time during the process, coarse grain (close to 1 mm) can be found in this area. Remelting occurs when a new droplet drops on the pre-solidified build, which could result in chemical segregation.

According to the Ti-Ni phase diagram, Ti_2Ni forms below 1237 K while TiNi solidifies at 1583 K [3]. Ti_2Ni only forms at the edge of the TiNi solidifying dendrites due to solute rejection and segregation. With the continuous heating to temperatures >1273 K, Ti_2Ni may dissolve and change its morphology to a finer, discontinuous, and more rounded phase, as shown in Fig. 3-b. This does not mean that the repeated heating fully homogenises the microstructure, as interdendritic Ti_2Ni still remains in some regions at the end of the process.

Comparing the microstructure of the SDA TiNi with vacuum arc melted and induction melted TiNi samples [21], the microstructure appears to be similar, which suggests that the cooling rates are similar in both processes. The grain size of the SDA sample is relatively finer, but heterogeneous in size distribution compared to the arc melting samples. Since neither eutectic morphology nor Ti_2NiO_x were found in the SDA samples, the microstructural inhomogeneities and oxygen pick-up are still lower in the SDA process, compared with the other button melting techniques. SDA also builds a sample at a much faster speed (e.g. 10 mm dia. $\times$ 20 mm button in 3 minutes). Comparing to the microstructure of TiNi built by DLD from powder [22], the fraction of Ti_2Ni is similar, whereas the grain size in SDA samples are larger due to the continuous (static) exposure to the laser beam during processing (there is no X-Y movement), resulting in a higher heat input per volume in SDA.

In order to assess the crystallographic orientation in SDA samples, a $\text{Ti}_{48}\text{Ni}_{52}$ sample (with the B2 (TiNi) austenitic phase at room temperature) was EBSD mapped along the XY-plane, Fig. 4. The presence of a fine grain zone with a random texture towards the edge of the sample, associated with rapid cooling, was evident. Generally, the grain size increases from the edge to the centre, with an infrequent presence for fine grain bands associated with the ringed microstructure in SDA samples. Additionally, the $\{100\}$ pole figure was constructed for the entire sample, as shown in Fig. 4. It shows a strong texture mainly in the $\{100\}$ direction, which is the preferred growth orientation of the B2 (cubic) phase during solidification [1].

Figure 4. (a) EBSD map of the XY plane for the $\text{Ti}_{48}\text{Ni}_{52}$ SDA sample, and (b) $\{100\}$ pole figure of the whole sample, showing a relatively strong texture in the $\{100\}$ direction.

3.b. Chemical composition

TiNi-based alloys are very sensitive to slight variations in the chemical composition, especially the oxygen content, which is known to reduce the transformation temperatures (TTs) and shape memory performance [23]. The oxygen content in the $\text{Ti}_{50}\text{Ni}_{50}$ SDA sample was 0.06 wt.% (measured using X-ray fluorescence [24]). The oxygen content in the Ti-wire was 1200 ppm, while the Ni-wire was 10 ppm (supplier's data). So, assuming no pick-up during the process, the total oxygen content was expected to be 0.0534 wt. %. As such, the oxygen pick-up during SDA was only 0.00664 wt.%, which is expected to influence the M_s

by ~ 1 K [23]. The total oxygen pick up in SDA process was estimated to create a 5.5 K reduction in the M_S , which is a reasonable range for alloy development [23]. Following a homogenisation heat treatment for 3 hours at 1273 K, the oxygen content in the sample reached 0.174 wt.%, which was calculated to decrease the M_S by 16 K.

To assess the chemical homogeneity of the samples, EDS was used to map the compositional variation in the XY-plane of the $Ti_{50}Ni_{50}$, XZ-planes of the $Ti_{52}Ni_{48}$ sample and $Ti_{50}Ni_{25}Cu_{25}$ samples, using $1\text{ mm} \times 1\text{ mm}$ area maps (error ± 1 at.%). It was found that the Ti-content varied from 49.0 at. % to 50.7 at. % (± 0.5 at.%) across the $Ti_{50}Ni_{50}$ SDA sample, with only the periphery of the sample showing a higher Ti-content within a limited area towards ring 1/region A and another peripheral region with a lower Ti-content, Fig. 5-a. It is important to note that the samples are normally extracted from the button core to avoid any surface or chemical inhomogeneity. The central region also showed a slightly high Ti-content (50.3 at.%). Nonetheless, the average Ti-composition for the whole section was ~ 49.9 at. %, which is only 0.1 at. % lower than the target composition. In the $Ti_{52}Ni_{48}$ sample (Fig. 5-b), the Ti-composition was also very close to target (52 at.%), and was fairly homogeneous apart from the central part of the build, where it varied from 51.4 at.% to 53.8 at.%.

Since the melting point of Ti is 1941 K, which is 213K higher than the melting point of Ni, Ti-segregation could be induced in the molten droplet. By analysing a solidified droplet attached to the wires (i.e. prior to falling onto the substrate), it was found that the Ti wire melted more slowly than the Ni wire. This means that Ti stays relatively concentrated on the upper part of the droplet, rather than distribute homogeneously within the droplet. This is because Ni has a higher density and lower melting point than the Ti. Still, it is possible that the fall of the molten droplet onto the melt pool, as well as the exposure of the top part of the build to the laser beam before the next droplet lands, help in mixing the alloying elements.

Unlike gravity segregation in arc melting or induction melting, this fine-scale segregation between the layers or within the button could be reduced by a heat treatment at 1273 K for 3 hours, as shown in Fig. 5-c and 5-d. It is clear that the central segregation (re-melt zone) in SDA samples can be reduced by homogenisation. The Ti₂Ni area fraction in the heat-treated sample varied from 0.03 to 0.09, with an overall average of 0.054. Since obtaining a homogenous chemical composition is necessary for the characterisation of the shape memory behaviour, SDA has the advantage that they required less time for homogenisation as the chemical segregation from the process is lower than that observed in other processes.

In the ternary system (Fig. 5-d), the variation in Ti-content was relatively larger (49.7 at.% to 55.5 at.%). Nonetheless, typically the variation does not exceed ± 2 at. % from the target content, except for local variations towards the edge of the samples. The SDA system can be used to produce complex alloys, with highly reflective elements (e.g. Cu). However, it is advisable to perform a homogenisation treatment to eliminate any chemical inhomogeneity in the samples [25], especially when limited chemical variations can influence the performance.

Figure 5. The chemical composition map (Ti-content) for the SDA samples measured using EDS (± 1 at.%): (a) the XY-section of the $\text{Ti}_{50}\text{Ni}_{50}$ sample, showing rings of chemical segregation notably towards the edge, (b) the XZ-section of the $\text{Ti}_{52}\text{Ni}_{48}$ sample with the remelt pattern in the centre and segregation at the edge, (c) the chemical composition map of (b) after a homogenisation treatment, and (d) the XY section of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ternary sample.

3.c. Phase Transformations

Since the chemical composition is critical to the SME, especially in the Ti-Ni system [1, 26], DSC was applied to identify the TTs for the as-built SDA $\text{Ti}_{50}\text{Ni}_{50}$ specimen (actual average chemical composition is $\text{Ti}_{49.9}\text{Ni}_{50.1}$, slightly deviating from the target chemistry), compared to a homogenised (heat-treated) sample from the same button, and a reference (cast, homogenised, and hot rolled) $\text{Ti}_{50}\text{Ni}_{50}$ sample (which was the target composition). As shown in Figure , the TTs and the DSC trace for the as-built SDA alloy was found to match the TTs in the $\text{Ti}_{49}\text{Ni}_{51}$ samples produced by the arc melting method in the literature, with a A_s of $\sim 60^\circ\text{C}$ and M_f of $\sim 30^\circ\text{C}$ [26, 27]. As the DSC test sample is extracted as a $4\text{ mm} \times 4\text{ mm} \times 2\text{ mm}$ disk from the centre of the button, the Ni-rich area at the edge is not included. The heat of martensitic transformation in $\text{Ti}_{50}\text{Ni}_{50}$ SDA sample was 26.5 J/g while the heat of reference sample was 23.4 J/g . The $\text{Ti}_{52}\text{Ni}_{48}$ sample had similar transformation behaviour, in terms of the TTs and peak width as the reference sample, but the total transformation heat is varied due to the higher Ti-content and Ti_2Ni fraction. The temperature hysteresis slightly reduced from 70°C to 60°C . The A_f and M_s also become close to the reference sample after the heat treatment, which is due to dissolution of the Ti_2Ni particles, resulting in less segregation within the TiNi-matrix.

In order to assess the properties of SDA-built ternary alloys, a $\text{Ti}_{52}\text{Ni}_{38}\text{Cu}_{10}$ ternary alloy was built and compared with the reference hot rolled $\text{Ti}_{50.4}\text{Ni}_{39.6}\text{Cu}_{10}$ sample. The DSC curves of

these samples, shown in Fig. 6, revealed that the transformation behaviour of ternary alloys matched the reference sample without homogenisation, especially as the chemical composition is beyond the range when the TTs are very sensitive to slight chemical variations. The higher transformation energy per weight in the reference sample (21.34 J/g) than SDA sample (12.63 J/g) is due to the lower $\text{Ti}(\text{Ni}, \text{Cu})_2$ precipitates in this sample. It is expected that the transformation energy can be matched following a homogenisation treatment, as the energy proportional to the TiNi phase fraction.

Figure 6. DSC trace for hot-rolled reference sample (solid), as-built $\text{Ti}_{50}\text{Ni}_{50}$ (red), 6 hours heat treated $\text{Ti}_{50}\text{Ni}_{50}$ (blue), $\text{Ti}_{50.4}\text{Ni}_{39.6}\text{Cu}_{10}$ hot-rolled reference sample (green), and SDA-built $\text{Ti}_{52}\text{Ni}_{38}\text{Cu}_{10}$ sample (magenta), showing the phase transformation behaviour.

3.d. Influence of Heat Treatment

In order to investigate the influence of heat treatment on SME and the chemical homogeneity of the SDA samples, a 70 mm long $\text{Ti}_{50.4}\text{Ni}_{49.6}$ sample was built and cut into 7 sections for heat treatment at different times. The samples were sealed in a steel tube, evacuated 10^{-5} MPa and put into muffle furnace at 1273 K for 0 hours, 3 hours, 6 hours, 24 hours, 48 hours and

100 hours. As shown in Fig. 7, because of its heterogeneity, the as-built sample showed a lower TTs ($M_S = 327$ K, $A_f = 366$ K, hysteresis = 39 K) compared with the $Ti_{50.6}Ni_{49.4}$ reference (cast, homogenised, and hot rolled) sample ($M_S = 348$ K, $A_f = 384$ K, hysteresis = 36 K). The heat of transformation was 26 J/g in the as-built condition, increasing to 29 J/g after a 3 hours homogenisation heat treatment, and slightly increased to 30 J/g after a 100 hours heat treatment.

Increasing the heat treatment time (from 6 hours to 100 hours) did not significantly affect the TTs. As increasing the heat treatment time could potentially increase the oxygen content or the Ti_2Ni particles size and distribution, and therefore affect the shape memory properties, it was found that 6 hours of heat treatment was sufficient for the SDA built samples in order to achieve the expected TTs (compared with the reference SMA sample).

Figure 7. Influence of the heat treatment time on the TTs and peak height, in comparison to the reference $Ti_{50.4}Ni_{49.6}$ sample (marked as reference on the left of the figure). The as-built sample has lower TTs due to chemical inhomogeneity, while the heat-treated samples have TTs similar to the reference sample. The error in temperature measurement was $\sim \pm 1^\circ\text{C}$.

4. Conclusions and further work

SDA is a new alloy development process, which is based on multi-wire laser deposition. The process was developed and used to deposit TiNi-based SMAs. The samples were studied to assess their microstructural homogeneity, with respect to the grain structure, Ti₂Ni precipitate distribution, chemical composition, and texture.

1. Local variations were observed in terms of the grain structure size and morphology, and the Ti₂Ni precipitate fraction, due to different cooling rates and the segregation associated with the process mechanism. The texture and grain size of SDA sample was generally similar to that produced by arc-melting.
2. On average, the chemical composition approached the target composition (± 1 at.%), despite some local variations (especially in the external surface or within the centre). Fine scale segregation was associated with the differences in the melting point and density between the various alloying elements.
3. Homogenisation heat treatment at 1273 K for 6 hours improved the homogeneity of the samples, resulting in shape memory behaviour similar to commercial TiNi-based alloys that are typically homogenised following casting.

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