An investigation into the possibility to eliminate the microstructural defects of parts printed using a Ni-rich Ni-Ti elemental powder mixture

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Abstract
Ni-rich Ni-Ti alloys, such as 60NiTi, show a higher hardness and dimensional stability than equiatomic or near-equiatomic NiTi ones. These make them suitable to be employed in structural applications. Laser powder bed fusion technique (LPBF) was used in this research to print parts from a Ni-rich Ni-Ti powder mixture consisting of about 63 wt.% Ni and 37 wt.% Ti. The microstructure of the obtained parts, processed using different parameters, showed inhomogeneity, contained undesirable Ni-rich and Ti-rich regions and a significant amount of cracks. To eliminate these defects, homogenize the microstructure and to obtain the required phases, we applied hot isostatic pressing (HIP) to the printed samples with a selected set of parameters. After HIP at 180 MPa and 1050 °C for 4 h, we observed the formation of a homogeneous microstructure containing mainly NiTi and Ni3Ti phases in the printed samples. However, cracks still persisted in the microstructure of these HIP treated samples. Applying another round of HIP treatment at a temperature just slightly above the melting start temperature of the samples, treated by the elementary HIP procedure, could successfully eliminate the cracks in the microstructure of samples and increase the crystallinity of the existing phases.

1. Introduction
Equiatomic and near-equiatomic NiTi alloys are well known for their shape memory and superelastic properties [1–6]. These virtues are exploited to process parts using these alloys for actuators and in biomedical applications for stents, orthodontic wires, etc [7–9]. However, these grades of Ni-Ti alloys show a relatively low hardness (about 30 HRC) and show lack of dimensional stability, since the austenite-martensite phase transformation occurs at around room temperature in these alloys [7, 9, 10]. As a result, equiatomic and near-equiatomic NiTi alloys are not considered as candidate alloys for structural applications [9, 11].

Based on the equilibrium Ni-Ti phase diagram (figure 1), different stable phases, such as NiTi, Ni7Ti and Ti3Ni, can form amongst Ni and Ti [8]. However, this is just the NiTi phase that shows a reversible austenite-martensite phase transformation and its existence, as the major phase in the microstructure, results in superelastic and shape memory properties in NiTi parts. It is known that increasing Ni content in the composition of the NiTi phase results in a significant drop of the austenite-martensite transformation temperature and also increase in the hardness of the NiTi phase [8, 12].
As an example, 60NiTi, a Ni-rich Ni-Ti alloy having 60 wt.% Ni and 40 wt.% Ti in its composition, shows a high hardness of about 60 HRC. This amount of hardness is about two times higher than that of equiatomic NiTiNol alloys. In addition, the NiTi phase in this alloy, having about 60 wt.% Ni in its composition, is austenitic at room temperatures and does not show austenite-martensite phase transformation till well below room temperature. Consequently, 60NiTi, having good dimensional stability and hardness, is considered as an alloy having the potential to be used for structural applications [7, 13–15]. This grade of Ni-Ti alloys is recently used by National Aeronautics and Space Administration (NASA) for developing hard and resilient rolling bearing components [10, 16–18].

It is expected that other Ni-rich Ni-Ti alloys such as 58NiTi, 59NiTi and etc, with compositions different than 60NiTi, will also exhibit some exploitable promising properties [9].

Printing processes have the potential to manufacture geometrically complex parts reducing the amount of machining needed to obtain the desired final geometry. This can decrease the final processing cost of these alloys. A significant amount of research has been done on the 3D printing of Ni-Ti alloys, specifically NiTiNol, using the prealloyed powders. Effects of different printing processing methods and parameters on the microstructural, chemical, mechanical and phase transformation properties of the developed parts are well investigated and reported [19–25].

However, the research work done on the 3D printing of Ni-Ti alloys, specifically Ni-rich Ni-Ti alloys, using elementally blended powders in not substantial. Printing of the parts using elementally mixed Ni-Ti powders can be considered as a cost-effective method having potential to process Ni-rich Ni-Ti alloys.

Using the combination of Self-propagating High-temperature Synthesis (SHS) and Selective Laser Sintering (SLS) in the same process, Shishkovsky and Gureev et al [26–28] could successfully obtain different intermetallic phases in Ni–Al, Ti–Al, Ni–Ti and etc systems from the powder mixtures. The optimum laser parameters for maintaining a controlled exothermic reaction to process different intermetallics and obtaining desired phases from the mentioned systems were identified in their research works. In the case of Ni-Ti system, NiTi phase was successfully obtained by employing this engineering process and using a mixture of Ni and Ti powders. However, the developed process results in porous structures and is not suitable to process dense microstructures.

In another research, using directed energy deposition (DED) method, solid NiTiNol parts were successfully fabricated from an equiatomic Ni-Ti powder blend. However, a significant amount of Ti2Ni phases, affecting the superelasticity behavior, were formed in the microstructure of these parts [29].

Laser powder bed fusion (LPBF), also known as selective laser melting (SLM), is one of the most commonly employed 3D printing techniques [19, 22]. It needs to be noted that it is a hard task to control the different exothermic reactions, resulting in the generation of different phases such as NiTi, Ni3Ti, Ni3Ti2 and etc, occurred during the LPBF process of the Ni-Ti blended powder systems. Wang et al [29] reported
inhomogeneity and existence of unwanted Ni$_3$Ti and other unidentifiable secondary phases in LPBF printed parts obtained from an equiatomic blend of Ni-Ti powder. Elahinia et al [19] also explain that the microstructure of the parts obtained from elementally mixed powders suffer from inhomogeneity and is consisted of other undesired intermetallic phases, pure nickel, and pure titanium. Besides, since increasing Ni in NiTi composition results in increased hardness and brittleness in this phase, Ni-rich Ni-Ti parts are more prone to crack formation as compared to less Ni-rich ones during the process of liquid solidification [8]. This can be a challenge during the LPBF process, as the cooling rate is very high once the laser melts the powder, causing the generation of high residual stresses and consequently cracks in the microstructure of the Ni-rich Ni-Ti parts [19].

In this research, at the first stage, an elemental powder mixture was conditioned to consist of about 63 wt.% Ni and 37 wt.% Ti. In the next stage, different sets of LPBF processing parameters were used to fabricate Ni-Ti parts from the processed powder. As this study is mainly focused on the microstructural enhancement, the powder composition was purposefully selected to be extra Ni-rich so that there exist an extensive amount of cracks in the microstructure of the printed samples.

In the next stage, the effect of printing processing parameters on the microstructure and properties of the printed samples was studied. It was also investigated that the used powder shows a better printability with which set of processing parameters. After this stage, post-processing HIP procedures were applied to the samples printed using the identified optimum set of LPBF processing parameters. These HIP procedures were applied to investigate the possibility of obtaining dense, crack-free and homogeneous Ni-rich Ni-Ti parts having a phase structure conforming to that expected based on the binary phase diagram (figure 1) for the used specific composition in this research (63 wt.% Ni and 37 wt.% Ti), i.e. NiTi and Ni$_3$Ti.

The findings obtained in this research help to better understand the properties of LPBF processed Ni-rich Ni-Ti parts fabricated using mixtures of Ni-Ti elemental powder. In addition, this study will provide an insight into the fabrication of other grades of Ni-rich Ni-Ti parts, e.g. 60NiTi, using the LPBF technique and by employing mixed Ni-Ti elemental powders.

2. Experimental, machines used and characterization methods

2.1. Powder characteristics

A Ni-Ti elemental powder mixture, having about 63 wt.% Ni and 37 wt.% Ti, was conditioned from elemental Ni (D$_{90} = 42.1 \ \mu$m) and Ti (D$_{90} = 50.3 \ \mu$m) gas atomized powders having spherical geometries.

Inert gas fusion analytical instrument Leco machines were used to determine the amounts of impurities such as O, H, C, S and N existing in the composition of powder. Ni and Ti amounts in the composition of powder were determined using chemical titration methods. These tests were done for three different powder batches and the average results are reported.

A JXA-8100 electron probe micro-analyzer (EPMA) machine equipped with an energy dispersive x-ray spectrometer (EDS) were used to characterize the morphology of the powders (based on the emissions received from the secondary electrons). A laser diffraction particle sizing measurement machine (Malvern Mastersizer 3000) was employed to measure the value of the powder diameters at 10%, 50% and 90% in the cumulative distribution. Hall flowability, apparent density and tap density of the powder was characterized using ASTM B213, ASTM B212 and ASTM B527 standards, respectively [30]. Note that all the tests related to particle size distribution, Hall flowability, apparent density and tap density were done on three different powder batches and the average results are reported.

2.2. LPBF processing and HIP treatment

Cubic samples of 12 mm height with a 6 $\times$ 6 mm square cross-section were designed in a CAD model to be manufactured by a commercially LPBF machine (BLT-A100), using different sets of processing parameters (laser power, scanning velocity, hatch distance, layer thickness). During the sample processing and regardless of the used set of processing parameters, the orientation of hatches was changed by 60° for successive layers. BLT-A100 is equipped with a Yb fiber laser with a wavelength of 1070 nm and a beam spot size of 60 $\mu$m in diameter. The machine worked under the argon/N$_2$ gas atmosphere, keeping the amount of O in the fabrication chamber less than 0.01 wt.%.

In addition, the build platform, which the powder was printed on, was heated to 180 °C. In order to decrease the difference between the thermal expansions of the build platform and the printed parts and consequently decrease the possibility of delamination or cracking caused by the generated thermal stresses, we used a near-equiaxial NiTi plate as the build platform in the mentioned machine. A total of 10 samples were printed by each specific set of processing parameters.

A QIH-15L Quintus HIP machine capable of applying a combined maximum pressure of 200 MPa and temperature of 1400 °C was used to post-process the as-printed samples, processed using a selected specific
optimum set of processing parameters, under Ar protecting atmosphere. Note that the temperature of the machine’s furnace during its operation might show about +2 °C deviation from what it is designed to process the parts. However, the reported temperatures in this manuscript are the actual temperatures which were recorded by the thermocouples existing in the machine’s furnace. After finishing the HIP treatment procedures, the samples were naturally cooled inside the machine.

An STA 409 PC high-temperature differential scanning calorimetry (DSC) machine was used to elucidate phase transformations occurring in the as-printed samples and also determine the melting temperature of the HIP treated samples. In these tests, about 30 mg samples were wire eroded from the bottom side of the samples and were heated from ambient temperature till 1350 °C with a heating rate of 20 °C min⁻¹, while samples were protected under flowing argon gas. The tangent method was used to define the transformation temperatures and the latent heats. Results obtained from these tests helped to better design the temperature for the HIP procedures.

2.3. Processed parts characterization
Dimensional integrity of the as-printed and post HIP processed samples were evaluated by comparing the size of the as-printed samples in different dimensions with what it was initially designed in the CAD file and also comparing the size of the samples before and after the conduction of the HIP procedures. The density of the samples was measured, by the Archimedes method as specified in the ASTMB962 standard [31]. These experiments were done on five different samples, printed using the selected specific optimum set of processing parameters, and the average result is reported. In addition, the chemical analyses and Leco machines mentioned before were used to determine the amount of Ni, Ti and impurities such as O, H, C, S and N existing in the composition of the bottom side of the as-printed samples. These tests were done on three times and the average results are reported.

The EPMA machine, a LEICA DMI 3000M optical microscope and a RIGAKU high-resolution x-ray diffractometer (XRD) machine, using a copper Kα radiation, were employed to obtain images (SEM images were based on the emissions received from the secondary electrons) and conduct phase analysis of the as-printed and HIP treated samples. Note that these tests were done from the cross-section of the samples prepared in parallel to the building direction. Samples were ground and polished before conducting the XRD phase analysis. The sample preparation procedure done to obtain microstructural images consisted of using P220, P500 and P1200 SiC papers at 300 rpm for grinding the samples. Vibratory polishing with 9 μm, 3 μm and 1 μm diamond paste solutions were applied in the next step and the polishing procedure was finalized by applying 0.4 μm colloidal silica suspension. Finally, to help better distinguish phases in the microstructural and elemental distribution studies, the ground and polished samples were swab-etched with a room temperature aqueous solution of 1 vol.% HF and 10 vol.% HNO₃ for 90 s [32].

Since all phases existing in NiTi exhibit diffraction peaks very close to each other, XRD analysis alone is not sufficient to identify the phases existing in NiTi compounds and their identification is difficult [33–35]. To confidently identify the phases existing in the samples, the EDS system was used to provide information on elemental distribution and determine the elemental ratio of different precipitates from different spots and regions of the samples (the same ones used for microstructural studies). These ratios were used to determine different phases based on the Ni/Ti atomic ratio categories reported for each specific phase in the literature [36]. Note that the EDS measurements are semi-quantitative only. Nevertheless, the semi-quantitative analysis is sufficient for the purpose of this study, as this research is mostly focused on the Ni–Ti atomic ratio.

3. Results and discussion

3.1. Powder characterization
Figure 2 shows the microstructural images of the Ni–Ti elemental powder mixture used to print the samples. As seen, the powder particles have a fine and spherical geometry and some small satellites are also formed on the surface of the particles.

Tables 1 and 2 report some specific physical characteristics, such as particle size distribution, Hall flowability, apparent density and tap density, and amounts of different elements and impurities of the conditioned powder, respectively.

As seen, the powder particles, other than having a spherical geometry, contain a low amount of impurity (about 0.120 wt.%) and show a particle size distribution having D90 < 50 μm. As a result, the processed powder can be considered suitable for the LPBF process.
3.2. Processing of the as-printed parts

As seen in table 3, a wide range of processing parameters was employed in this research to print the samples. This includes using laser powers ranging from 50 to 150 watts and scanning velocities of 100 to 500 mm s$^{-1}$. The hatch spacing was varied from 0.06 to 0.16 mm for samples prepared under the laser power of 50 watts and from 0.08 to 0.24 mm for the ones processed by that of 100 watts. For other sets of parameters having laser powers of 70 and 150 watts, the hatch spacing was kept constant for 0.12 mm. The layer thickness in all different processing sets was kept constant for 0.03 mm. These resulted in laser energy inputs spanning from 39.68 to 185.18 J mm$^{-3}$ in the processing of printed samples.

Note that different exothermic reactions might occur during the synthesis process of the intermetallic materials from the blended powder systems. This means that, other than the external laser energy input provided by the laser, there is an additional energy input from the chemical reactions that occurs between the elemental materials and different phases during the process. Depending on the synthesis conditions and the used processing parameters, some predicted phase transformations may occur and some others might not. As a result, the amount of additional energy input might be different depending on the employed processing parameters. This study does not provide an analysis on this matter and just identifies the optimum set of processing parameters and the resulted energy inputs excluding the internal energies generated during the process.

Amongst all the employed processing sets, just the sets 6, 7, 8 and 9 (as highlighted in table 3), having the laser power of 50 watts, led to the print of cubic samples. The used powder did not show printability with any other employed set of parameters having laser powers over 50 watts. This is interesting, as sets having similar laser energy inputs (namely processing sets 14, 15 and 21) to those of sets 6 and 8 (having laser energy inputs of 55.55 and 46.29, respectively) were not successful to print the used powder. These processing sets have different laser powers than the one (50 watts) used in sets 6 and 8. In addition, this is just the laser power (70 watts) that is different in processing set 14 than that of (50 watts) processing set 9.

### Table 1. Some physical properties of the processed powder.

| Particle size distribution ($\mu$m) | Hall flowability (s/50 g) | Apparent density (g cm$^{-3}$) | Tap density (g cm$^{-3}$) |
|-----------------------------------|---------------------------|-------------------------------|--------------------------|
| D90 = 45.40                       |                           |                               |                          |
| D50 = 31.20                       | 16.13                     | 4.07                          | 4.42                     |
| D10 = 20.8                        |                           |                               |                          |

### Table 2. Amounts of different elements and impurities of the processed powder.

| Ni (wt.%) | Ti (wt.%) | O (wt.%) | N (wt.%) | S (wt.%) | C (wt.%) | H (wt.%) |
|-----------|-----------|----------|----------|----------|----------|----------|
| 62.960    | 36.920    | 0.091    | 0.007    | 0 < 0.01 | 0.005    | 0.017    |

Figure 2. Ni-Ti powder mixture.
This means that laser power is the primary factor ruling the successful printing of the cubic samples from the used Ni-Ti elemental powder mixture. On the other hand, it is noted that the powder could not be printed using sets 1 to 5, despite having a laser power of 50 watts, and just sets 6 to 9 having laser power of 50 watts and laser energy inputs \( 55.55 \text{ J mm}^{-3} \) were successful to print the cubic samples. This means that the laser energy input plays the secondary role in printability of the used powder in this research, after the laser power playing the primary role.

In essence, the powder could not be printed using the employed processing sets having laser powers above 50 watts. Moreover, for the sets of processing parameters having a laser power of 50 watts, the lower the used laser energy input the higher the number of printed cubic samples (out of 10). No sample could be printed for

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**Table 3. Different sets of LPBF processing parameters used to print the cubic samples.**

| Processing sets | Laser power (W) | Scanning velocity (mm s\(^{-1}\)) | Hatch spacing (mm) | Layer thickness (mm) | Laser energy input (J mm\(^{-3}\)) | Number of printed samples (out of 10) |
|-----------------|----------------|-----------------------------------|-------------------|---------------------|------------------------------------|-------------------------------------|
| 1               | 50             | 100                               | 0.12              | 0.03                | 138.88                             | 0                                   |
| 2               | 50             | 150                               | 0.12              | 0.03                | 92.59                              | 0                                   |
| 3               | 50             | 200                               | 0.12              | 0.03                | 69.44                              | 0                                   |
| 4               | 50             | 250                               | 0.06              | 0.03                | 111.11                             | 0                                   |
| 5               | 50             | 250                               | 0.08              | 0.0.3               | 83.33                              | 0                                   |
| 6               | 50             | 250                               | 0.12              | 0.03                | 55.55                              | 2                                   |
| 7               | 50             | 250                               | 0.16              | 0.03                | 41.66                              | 7                                   |
| 8               | 50             | 300                               | 0.12              | 0.03                | 46.29                              | 7                                   |
| 9               | 50             | 350                               | 0.12              | 0.03                | 39.68                              | 10                                  |
| 10              | 70             | 150                               | 0.12              | 0.03                | 129.62                             | 0                                   |
| 11              | 70             | 200                               | 0.12              | 0.03                | 97.22                              | 0                                   |
| 12              | 70             | 250                               | 0.12              | 0.03                | 77.77                              | 0                                   |
| 13              | 70             | 300                               | 0.12              | 0.03                | 64.81                              | 0                                   |
| 14              | 70             | 350                               | 0.12              | 0.03                | 55.55                              | 0                                   |
| 15              | 70             | 400                               | 0.12              | 0.03                | 48.61                              | 0                                   |
| 16              | 100            | 150                               | 0.12              | 0.03                | 185.18                             | 0                                   |
| 17              | 100            | 200                               | 0.12              | 0.03                | 138.88                             | 0                                   |
| 18              | 100            | 250                               | 0.08              | 0.03                | 166.66                             | 0                                   |
| 19              | 100            | 250                               | 0.12              | 0.03                | 111.11                             | 0                                   |
| 20              | 100            | 250                               | 0.16              | 0.03                | 83.33                              | 0                                   |
| 21              | 100            | 250                               | 0.24              | 0.03                | 55.55                              | 0                                   |
| 22              | 100            | 300                               | 0.12              | 0.03                | 92.59                              | 0                                   |
| 23              | 100            | 350                               | 0.12              | 0.03                | 79.36                              | 0                                   |
| 24              | 100            | 400                               | 0.12              | 0.03                | 69.44                              | 0                                   |
| 25              | 150            | 250                               | 0.12              | 0.03                | 166.66                             | 0                                   |
| 26              | 150            | 300                               | 0.12              | 0.03                | 138.88                             | 0                                   |
| 27              | 150            | 350                               | 0.12              | 0.03                | 119.04                             | 0                                   |
| 28              | 150            | 400                               | 0.12              | 0.03                | 104.16                             | 0                                   |
| 29              | 150            | 450                               | 0.12              | 0.03                | 92.59                              | 0                                   |
| 30              | 150            | 500                               | 0.12              | 0.03                | 83.13                              | 0                                   |

Note: the highlighted rows show the processing sets being successful to print the used powder.

This means that laser power is the primary factor ruling the successful printing of the cubic samples from the used Ni-Ti elemental powder mixture. On the other hand, it is noted that the powder could not be printed using sets 1 to 5, despite having a laser power of 50 watts, and just sets 6 to 9 having laser power of 50 watts and laser energy inputs \( \leq 55.55 \text{ J mm}^{-3} \) were successful to print the cubic samples. This means that the laser energy input plays the secondary role in printability of the used powder in this research, after the laser power playing the primary role.

In essence, the powder could not be printed using the employed processing sets having laser powers above 50 watts. Moreover, for the sets of processing parameters having a laser power of 50 watts, the lower the used laser energy input the higher the number of printed cubic samples (out of 10). No sample could be printed for
the processing sets having laser energy inputs above 55.55 J mm$^{-3}$ and the number of cubic samples which were printed successfully increased from 2 in set 6 (having a laser energy input of 55.55 J mm$^{-3}$) to 10 in set 9 (having a laser energy input of 39.68 J mm$^{-3}$).

These might have roots in residual stresses which are generated in the samples during the printing process. In fact, the effect of the generated residual stresses is clear in the geometry of the printed samples. As observed in figure 3, the samples show warping effect (i.e., separation of the sample from the build platform) which is caused by the high residual stresses that are formed in the first layers of the printing process. These residual stresses are mainly attributed to the high gradient temperatures formed during the fabrication of the first layers of the samples and also the mismatch between the thermal expansion of the printed parts and the build platform. Note that phase transformations occurred in the samples during the processing can be another source of residual stress generation in the samples. As mentioned, different sets of processing parameters might lead to different phase transformations in the processed parts. In addition, the amount of generated phases might differ amongst samples processed using different sets of processing parameters. This factor is neglected in this study and its effects are not analyzed [19, 22, 37].

Figure 4 shows the optical images obtained from the outer surface of the bottom regions of the samples processed using sets 6 and 9. As seen, the warping effect is more pronounced in the samples processed using set 6 than the ones fabricated by set 9. The bottom of these samples is curvier than the ones prepared by set 9 and cracks are clearly observed in the bottom part of these samples. These show that the level of residual stresses are significantly higher in samples processed by set 6 than the ones processed by set 9 [22].
Both laser power and laser energy input are factors playing role in the level of the generated residual stresses. It is estimated that the lower are these factors, the lower will be the temperature of the melt pool. This results in a smaller difference between the temperature of melt pool and the plate where samples are printed on, causing the generation of lower amounts of residual stresses in the printed samples. This is as compared to the conditions where higher laser powers and laser energy inputs are used and consequently the melt pool has a higher temperature and a larger thermal gradient is generated between that and the plate

It is estimated that the level of warping effect, and the consequent separation of the samples from the build platform caused by the generation of residual stresses, was that high for samples processed by sets other than 6 to 9 that the printed bulk parts, after few layers of formation, were hit and removed from the build platform by the movement of blade depositing the next layer of powder. As a result, no sample could be fabricated using these sets of parameters. On the other hand, samples fabricated by set 9, processed by the lowest amount of laser power and laser energy input and subsequently having the least amount of generated residual stresses amongst all other samples, showed less warping effect than sets 1 to 8. Consequently, more numbers of samples (10 out of 10) were successfully processed using this set of parameters than other sets (6 to 8) having the identical amount of laser power but higher laser energy inputs (table 3).

Dimensional integrity of the printing process was evaluated by comparing the size of the printed samples, using set 9, with what it was initially designed in the CAD file (cubic samples of 12 mm height with a 6 × 6 mm square cross-section). It is noted that the printed samples have a square cross-section with an average size of 6.19 × 6.28 mm (figure 3). However, as discussed before and shown in figure 4(b), the samples have a curvy geometry in their bottom part. These fabricated parts have an average density of 6.68 g cm⁻³.

3.3. Characterization of the as-printed parts

Many cracks, parallel to the building direction, were seen in the microstructure of samples processed using sets 6–9. Note that for the sake of brevity, just the microstructure (figures 5 and 6) of samples processed by sets 6 and 9, causing respectively the highest (55.55 J mm⁻³) and lowest (39.68 J mm⁻³) laser energy inputs in printing of the samples, are shown here. As discussed before, these cracks are expected to be formed due to the generation of significant amounts of residual stresses in the printed samples. In addition to these cracks, small amounts of micropores are also seen in the microstructure of these samples. As Cai et al [39] explain, these spherical pores might have been generated due to the gases trapped within the molten pool formed during the printing process or have roots in the consolidation of powder.

Based on the equilibrium Ni-Ti binary phase diagram and for the specific composition (about 63 wt.% Ni and 37 wt.% Ti) used in this research, Ni₃Ti and NiTi are the stable phases that are expected to exist in the sample (figure 1) [8]. However, results obtained from EDS studies and elemental dot mapping (figure 7) clearly show that the printing process did not result in a complete reaction between the elemental Ni and Ti existing in the powder mixture. The obtained results clearly show the existence of Ni-rich and Ti-rich areas in the processed samples. In fact, dark regions in the Ni map are bright regions in the Ti map showing the existence of Ti-rich phases and vice versa. Elemental ratios obtained from EDS analysis showed that the brightest areas were Ni-rich, containing about 1–3 wt.% Ti, suggesting the formation of Ni. On the other hand, Ti-rich areas contain about 7 wt.% Ni, suggesting the formation of Ti. These regions are darkest under the SEM images (figure 6). These areas seem to be respectively the original cores of the Ti and Ni elemental particles, used in the powder mixture.
to print the samples. Based on the results obtained from EDS analysis and interpreting the elemental ratios [36], the region between these two extreme areas are filled with other phases in a gradient way. Areas attributed to elemental Ti were surrounded by Ti-rich Ti<sub>2</sub>Ni and elemental Ni areas were next to Ni-rich Ni<sub>3</sub>Ti with Ni<sub>3</sub>Ti<sub>2</sub> and NiTi phases in the middle of these areas (figure 7(b)).

These results comply with the ones done other researchers reporting that the microstructure of the printed samples obtained from elementally blended powders consists of other undesired intermetallic phases, pure nickel, and pure titanium [21].

Table 4 reports the amounts of different elements and impurities of the as-printed samples fabricated using different processing sets.
As seen in Table 4, the amount of impurities in the printed samples did not change significantly as compared to those existing in the powder (Table 2). Specifically, the amount of O in the printed samples is just about 0.01 wt.% higher than that of the used powder. This is because the amount of O in the fabrication chamber was kept less than 0.01 wt.% In addition, it is noted that the amount of impurities in the printed parts, obtained using different processing parameters, are similar to each other and they do not show dependency on the processing parameters.

The amounts of Ni and Ti in the printed samples are also roughly the same with those existing in the used powder (about 63 wt.% Ni and 37 wt.% Ti). Samples obtained using sets 6–8 contain Ni amounts less than 63 wt. % Ni; however, those fabricated using set 9 have Ni contents slightly above 63 wt.%. Evaporation might be the reason for the slight decrease observed in the amount of Ni in the printed samples (using sets 6–8) as compared to that in the used powder. It is known that Ni shows a more tendency to evaporation than Ti and it might be that some evaporation has occurred during the processing of parts and melt pool formation [19, 40]. This has caused in a slight decrease in Ni/Ti ratio as compared to that of the used powder. However, the reason for the slight Ni/Ti ratio increase observed in the samples processed using set 9, fabricated by the lowest laser energy input as compared to sets 6 to 8, is not understood.

Samples processed using set 9 are chosen hereafter to conduct further required studies and 10 more samples were printed using this set of processing parameter (Figure 3). This is because, amongst all the used processing sets, the used powder showed the best printability using this specific set of printing process.

### Table 4. Amounts of different elements and impurities in the as-printed samples.

| Processing sets | Ni (wt.%) | Ti (wt.%) | O (wt.%) | N (wt.%) | S (wt.%) | C (wt.%) | H (wt.%) |
|----------------|-----------|-----------|----------|----------|----------|----------|----------|
| Set 6          | 62.45     | 37.42     | 0.099    | 0.007    | 0 < 0.01 | 0.006    | 0.009    |
| Set 7          | 62.04     | 37.83     | 0.105    | 0.008    | 0 < 0.01 | 0.008    | 0.009    |
| Set 8          | 62.33     | 37.54     | 0.101    | 0.007    | 0 < 0.01 | 0.006    | 0.009    |
| Set 9          | 63.34     | 36.53     | 0.100    | 0.007    | 0 < 0.01 | 0.006    | 0.011    |

As seen in Table 4, the amount of impurities in the printed samples did not change significantly as compared to those existing in the powder (Table 2). Specifically, the amount of O in the printed samples is just about 0.01 wt.% higher than that of the used powder. This is because the amount of O in the fabrication chamber was kept less than 0.01 wt.% In addition, it is noted that the amount of impurities in the printed parts, obtained using different processing parameters, are similar to each other and they do not show dependency on the processing parameters.

The amounts of Ni and Ti in the printed samples are also roughly the same with those existing in the used powder (about 63 wt.% Ni and 37 wt.% Ti). Samples obtained using sets 6–8 contain Ni amounts less than 63 wt. % Ni; however, those fabricated using set 9 have Ni contents slightly above 63 wt.% Evaporation might be the reason for the slight decrease observed in the amount of Ni in the printed samples (using sets 6–8) as compared to that in the used powder. It is known that Ni shows a more tendency to evaporation than Ti and it might be that some evaporation has occurred during the processing of parts and melt pool formation [19, 40]. This has caused in a slight decrease in Ni/Ti ratio as compared to that of the used powder. However, the reason for the slight Ni/Ti ratio increase observed in the samples processed using set 9, fabricated by the lowest laser energy input as compared to sets 6 to 8, is not understood.

Samples processed using set 9 are chosen hereafter to conduct further required studies and 10 more samples were printed using this set of processing parameter (Figure 3). This is because, amongst all the used processing sets, the used powder showed the best printability using this specific set of printing process.

### 3.4. Microstructural homogenization

To eliminate the cracks existing in the as-printed parts and also to obtain a homogeneous microstructure containing phase structure complying with the Ni-Ti binary phase diagram (Ni$_3$Ti and NiTi) for the specific composition of studied samples (about 63 wt.% Ni and 36 wt.% Ti), a HIP process was applied on the samples. To achieve the mentioned goals, the HIP procedure (Elementary-table 5) was done at a high temperature of 1050 °C and for a long time of 4 h under an applied pressure of 180 MPa (the maximum pressure the machine can apply is 200 MPa). Note that a heating rate of 20 °C min$^{-1}$ was used in this procedure to heat the samples from the ambient temperature to 1050 °C. The applied pressure also increased gradually to 180 MPa as the machine was heating the samples (Table 5).

The reason for choosing 1050 °C as the temperature to do the HIP process is that a eutectic liquid is estimated to be generated at above 942 °C at a composition of 29.5 wt.% Ni amongst β-Ti and Ti$_2$Ni intermetallic phases (Figure 1) [32, 41–43]. As discussed before, Ti$_2$Ni is formed around β-Ti in as-printed samples and the generation of a eutectic liquid between them is expected to result in an increased reaction rate enhancing homogeneity and crystallinity in samples [32]. However, note that the DSC tests done on the as-printed samples, heated from ambient temperature to 1350 °C by the heating rate of 20 °C min$^{-1}$, did not show any sign of an exothermic reaction, related to the eutectic reaction occurring between Ti$_2$Ni and β-Ti, at temperatures around 942 °C (for the sake of brevity the results of these DSC tests are not shown here). This might be because all the phase transformations determined in Figure 1 are for equilibrium conditions close to thermodynamic state. This might not be the case for the LPBF printed samples.

As seen in Figure 8, cracks are still prevalently observed in the microstructure of the treated samples and the applied HIP procedure was not successful to eliminate the cracks existing in the microstructure of the as-printed samples.

However, as seen in Figure 9, the microstructure of these HIP treated samples appear to be homogenized and as a result different than their as-printed ones having heterogeneous microstructures (Figures 6 and 7). Note that, as mentioned in Section 2, all the samples, regardless of their processing conditions, were etched after being prepared for microstructural studies.

As seen in Figure 10(a) and based on the results obtained from elemental dot mapping, Ni-rich precipitates are formed in the matrix. Further conducted EDS studies show that these Ni-rich precipitates are mostly Ni$_3$Ti.
| HIP treatment | Applied on | Start temperature (°C) | Final temperature (°C) | Heating rate (°C min⁻¹) | Applied pressure at final temperature (MPa) | Holding time at the final temperature (hrs) |
|---------------|------------|-------------------------|-------------------------|-------------------------|-------------------------------------------|-------------------------------------------|
| Elementary    | As-printed samples | Ambient temperature | 1050                     | 20                       | 180                                       | 4                                         |
| Secondary     | Homogenized samples | Ambient temperature | 1124                     | 20                       | 1127                                      | 11129                                     | 1131                                      |
containing about 76 wt.% Ni and 24 wt.% Ti which are formed in a matrix having about 56 wt.% Ni and 44 wt.% Ti, corresponding to NiTi phase (figure 10(b)). It is noted that, other than the majority of EDS test results correlating to NiTi and Ni$_3$Ti, the results of few tests can also be correlated to Ni$_3$Ti$_2$. Ni$_3$Ti$_2$ is a metastable phase which as similar to stable Ni$_3$Ti can precipitate in NiTi matrix upon slow cooling from high temperatures that the HIP treatment was applied at [8].

As discussed before, based on the binary Ni-Ti phase diagram, NiTi and Ni$_3$Ti are stable phases for the specific composition (about 63 wt.% Ni and 37 wt.% Ti) of samples studied in this research (figure 1). The obtained results show that the applied HIP procedure was successful to increase the reaction rate between the existing phases in the as-printed samples and result in the elimination of the undesirable phases including elemental Ni and Ti in the printed parts. In essence, it appears that a homogeneous microstructure complying with that expected from the Ni-Ti binary phase diagram was formed in the printed samples being HIP treated at 1050 °C for 4 h under an applied pressure of 180 MPa.

Table 6 shows the size of the square cross-section in the top part of the samples (fabricated by processing set 9) and the density of the samples before and after applying the HIP treatment.

As seen, applying the HIP treatment did not affect the dimensional integrity of the samples and the treated parts, other than experiencing a slight shrinkage in size and consequently an increase in the density, exhibited an identical geometry to the as-printed samples.
3.5. Crack elimination

To eliminate the cracks existing in the microstructure of homogenized samples obtained by applying the discussed HIP treatment, secondary HIP procedures were designed and conducted on the samples (Table 5).

As seen in the equilibrium binary Ni-Ti phase diagram, the stoichiometric NiTi alloy can dissolve an increasing amount of Ni in NiTi phase with increasing temperature above about 625 °C (Figure 1) [8]. As the temperature is increased further and it approaches the solidus line, melting of NiTi phase starts to occur. Figure 11 shows the result of DSC tests done on the homogenized samples printed by processing set 9 and HIP treated at 1050 °C for 4 h under an applied pressure of 180 MPa. As seen, an endothermic peak having the start temperature of about 1126.7 °C is observed in the DSC graph of these processed samples. Since no exothermic peak is observed in the DSC graph of samples at temperatures around 1118 °C (or any other temperature in the range of the conducted DSC test), it might be concluded that the Ni3Ti phase existing in the samples is almost fully dissolved inside the NiTi phase at high temperatures and the Ni-rich NiTi starts to get melted at about 1126.7 °C as it passes the solidus line. Note that, under equilibrium conditions, a eutectic liquid (resulting in the emergence of an exothermic peak in the DSC graph) could be generated at a composition of about 67 wt.% Ni amongst Ni3Ti and NiTi intermetallic phases, in case Ni3Ti phase existed in the microstructure of samples at 1118 °C (Figure 1). As mentioned before, all the phase transformations determined in Figure 1 are for equilibrium conditions close to thermodynamic state. This might not be the case for the samples studied in this research.

In addition, the amount of absorbed energy, absorbed due to the melting of the samples, increases as the temperature is increased. Considering these, it is thought that applying HIP treatments, on the homogenized samples, at selected temperatures around that of the start of the melting start temperature, where the samples are

| Samples Conditions | Size of square cross-section in the top part of the samples (mm) | Density of the samples (gr cm⁻³) |
|--------------------|---------------------------------------------------------------|---------------------------------|
| As-printed         | 6.19 × 6.28                                                   | 6.68                            |
| HIP treated        | 6.19 × 6.23                                                   | 6.73                            |

Table 6. The size of square cross-section in the top part of the samples and the density of the samples before and after applying the HIP treatment (at 1050 °C for 4 h under an applied pressure of 180 MPa). Note that the original dimensions in the CAD file consisted of cubic samples having 12 mm height and 6 × 6 mm square cross-section.
not fully melted, can result in the closure of existing cracks in the microstructure of homogenized samples. In essence, it is thought that the effect of pressure applied by the HIP process combined with the malleability and softness of the samples caused by the generation of an optimum amount of liquid (which can also fill the gaps) can result in the elimination of cracks existing in the microstructure of samples.

Considering these and to understand the specific temperature resulting in the generation of the optimum amount of liquid, needed to increase the softness of the samples but not melting them fully or affecting their dimensional integrity, the secondary HIP treatments were designed at different temperatures of 1124 °C, 1127 °C, 1129 °C and 1131 °C. Note that for each separate designed temperature, the HIP procedure was done for 1 h and under an applied pressure of 180 MPa. The heating rate of 20 °C min⁻¹ was used in these procedures to heat the samples from ambient temperature to the mentioned selected temperatures (table 5).

Figure 12 shows the SEM image of the homogenized samples treated by the secondary HIP treatment done at 1124 °C for 1 h and under an applied pressure of 180 MPa. As observed, no noticeable difference is observed in the morphology of cracks in the microstructure of these samples as compared to their homogenized conditions (figures 8(b) and 10). This might be because at this temperature, being below the onset of melting start temperature, there was no or just a minor amount of liquid generated in the samples and as a result, the treatment was still practically done under a solid-state.

On the other hand, as seen in figure 13, increasing the secondary HIP treatment temperature to 1127 °C resulted in a partial closure of the cracks. It is noticeable that the large cracks replaced themselves to smaller cracks or pores, as the gap between the cracks got eliminated (figure 13(b)). This crack elimination effect might
be due to the localized generation of small amount of liquid inside the samples filling the crack gaps. It also might be that the samples are in a soft condition at this temperature and crack gaps got partially closed by the applied pressure of the HIP process.

Increasing the temperature of the secondary HIP procedure to 1129 °C led to the full elimination of cracks existing in the microstructure of the homogenized samples. As seen in figure 14, no evidence of initial or residual cracks are observed and just some pores (mostly spherical) are seen in the microstructure of these samples. These pores might have no relation with the position of the initial cracks and might have been formed due to the effect of localized liquid generated at this temperature moving around in the samples. Alternatively, these pores might be the residues of the initial cracks which got eliminated under this specific secondary HIP treatment by the generated liquid filling the crack gaps.

On the other hand, samples lost their dimensional integrity and large irregular pores are observed in the microstructure of samples HIP treated at 1131 °C (figure 15). This means that too much liquid was generated in the samples at this temperature damaging the dimensional integrity of the parts. As a result, this temperature is not suitable for treating the homogenized samples to eliminate their cracks. It needs to be noted that applying secondary HIP treatments on the samples at temperatures 1124 °C, 1127 °C and 1129 °C did not have any noticeable effect on the dimensions of the treated samples.

Considering these results, it is concluded that the narrow range of temperature lying between 1127 °C to 1129 °C results in the generation of an optimum amount of liquid and consequently desirable softness in the studied homogenized samples. Treating the samples at temperatures below this range has no significant effect in the elimination of the cracks and applying HIP treatments at temperatures above this range damage the dimensional integrity of the samples as they result in the generation of too much liquid.
Based on the results obtained from the EDS studies, it was concluded that, regardless of the applied temperature used in the secondary HIP treatments, the samples contained the same phase structure as the homogenized ones. Note that for the sake of brevity the results of EDS tests are not shown here. XRD tests were done to obtain more information about the effect of HIP treatments on the crystallinity of the samples. These tests were done on the homogenized samples (HIP treated at 1050 °C for 4 h under an applied pressure of 180 MPa) and homogenized ones treated by the secondary HIP treatment at 1124 °C (below the onset of liquid formation in the samples) and 1129 °C (above the onset of the liquid formation in the samples) for 1 h and under an applied pressure of 180 MPa. As seen in figure 16, these results again confirm the success of the elementary HIP treatment in homogenizing the as-printed samples. This is because no peaks related to elemental Ni or Ti is observed in the XRD pattern of the homogenized samples. In addition, all the samples contain identical phases.

In addition, it is noted that both XRD patterns related to the homogenized parts treated by the secondary HIP treatment show significantly larger peak length/background ratios than the homogenized samples treated by just the elementary HIP treatment. It can be concluded that the secondary HIP treatments, regardless of the applied temperature and whether the liquid was generated in the samples or not, noticeably increased the crystallinity of the formed phases in the samples as compared to those treated by the elementary HIP treatment. These might be due to the effect of higher temperatures applied to treat the samples during the secondary HIP
treatments, causing a higher diffusivity between the atoms, than that for the samples treated by the elementary HIP treatment.

It is estimated that the same results and outcome can be obtained by merging these two elementary and secondary HIP treatments to one process for treating the as-printed samples. In addition, HIP itself is considered as a near-net shape powder technology so perhaps this technology, in combination to or without printing processes and by developing the idea used in the current work, has the potential to fabricate Ni-rich Ni-Ti parts from elementally blended powders using other creative methods [44–46].

4. Conclusion

The purpose of this research was to investigate the possibility to eliminate the cracks and inhomogeneity which commonly exist in the parts LPBF printed using mixtures of elemental Ni-Ti powder. In this study, different sets of processing parameters were used to print samples from a mixture of elemental Ni-Ti powder, consisting of about 63 wt.% Ni and 37 wt.% Ti, using a LPBF method. At the first stage, effects of printing processing parameters on the printability of the powder, microstructure, phase structure, composition and dimensional integrity of the samples were investigated. In the next stage, different HIP treatments and procedures were used to enhance the microstructural properties of the samples.

Detailed results obtained in this investigation show that:

1. The used powder did not show printability with the employed processing sets having laser powers above 50 watts. In addition, for the sets of processing parameters having a laser power of 50 watts, the powder showed the best printability with the set of processing parameters (set 9) having the lowest laser energy input (39.68 J mm⁻³). All the 20 samples (asked from the printing machine) were successfully fabricated using this set of processing parameters (laser power = 50 W, scanning velocity 350 mm s⁻¹, hatch spacing = 0.12 mm, layer thickness = 0.03 mm). It was noted that the printed samples showed good dimensional integrity having the geometry very similar to that designed in the CAD file (cubic samples of 12 mm height with a 6 × 6 mm square cross-section). However, due to the warping effect, having roots in the high residual stresses that are formed in the first layers of the printing process, the bottom sides of the printed samples were curvy.

2. As expected, the printed samples contained a significant amount of cracks parallel to the building direction and the microstructure of the samples consisted undesirable phases including elemental Ni and Ti phases. It was noted that the region between these two phases were filled with other phases in a gradient way. Areas attributed to elemental Ti were next to Ti-rich Ti₂Ni and elemental Ni areas were surrounded by Ni-rich Ni₃Ti with a grey NiT and Ni₃Ti₂ phases in the middle of these areas.

3. Applying a HIP treatment on the printed samples at 1050 °C for 4 h under an applied pressure of 180 MPa could successfully homogenize the samples and remove elemental Ni and Ti from the microstructure. The matrix of these homogenized samples consisted of phases mainly attributed to NiTi and Ni₃Ti, complying with the equilibrium Ni-Ti phase diagram for Ni-Ti binary alloys having about 63 wt.% Ni and 37 wt.% Ti in their composition (figure 1). However, cracks were still prevalent in the microstructure of these homogenized samples.

4. Secondary HIP treatments were conducted on these homogenized samples with the aim of removing the cracks from the microstructure. These treatments were done at different temperatures of 1124 °C, 1127 °C, 1129 °C and 1131 °C for 1 h and under an applied pressure of 180 MPa. These temperatures were selected based on the endothermic peak (belonging to the melting process) observed in the DSC trace of the homogenized samples and to understand the temperature resulting in an optimum amount of liquid generation and softness in samples. It was concluded that applying a HIP treatment at 1124 °C did not have any obvious effect on the existing cracks, however, it was noted that the gaps between the cracks were partially removed once the treatment was done at 1127 °C. Applying the secondary HIP treatment at 1129 °C could successfully replace the cracks to some small pores. However, once the samples were treated at 1131 °C, probably due to the generation of too much liquid, samples lost their dimensional integrity and large pores were generated in their microstructure.

5. It was understood that applying the secondary HIP treatments increased the crystallinity of the phases existing in the parts as compared to the homogenized ones.

Results and experience obtained in this research will be useful in future researches to process other grades of Ni-rich Ni-Ti parts having practical applications, e.g. 60NiTi, using LPBF technique and by employing mixed Ni-Ti elemental powder mixture.
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