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1 **Effect of Laser Welding Parameters on the Austenite and**
2 **Martensite Phase Fractions of NiTi**

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11 **Abstract**

12 Although laser welding is probably the most used joining technique for NiTi shape memory
13 alloys there is still a lack of understanding about the effects of laser welding parameters on the
14 microstructural induced changes: in both the heat affected and fusion zones martensite may
15 be present, while the base material is fully austenitic. Synchrotron X-ray diffraction was used
16 for fine probing laser welded NiTi joints. Through Rietveld refinement the martensite and
17 austenite phase fractions were determined and it was observed that the martensite content
18 increases towards the weld centreline. This is related to a change of the local transformation
19 temperatures on these regions, which occurs due to compositional variation in those regions.
20 The martensite phase fraction in the thermally affected regions may have significantly
21 implications on functional properties on these joints.

22 **Keywords:** Shape memory alloys (SMA); Laser welding; Synchrotron radiation; phase fraction;
23 phase transformations.

24 **Introduction**

25 In order to obtain complex shaped structures using NiTi shape memory alloys joining methods
26 are required owing to the poor machinability of these materials [1]. Among the different
27 joining techniques available, fusion-based ones, such as tungsten inert gas (TIG) [2] and laser
28 welding [3–6], have presented the best results in terms of the mechanical properties of the
29 joints. Laser welding is by far the most used process for welding NiTi due to the reduced
30 extension of the thermally affected regions, which is especially important for NiTi due to the
31 deterioration of its functional properties (shape memory effect and superelasticity) at high
32 temperatures.

33 It was observed that laser welding is responsible for a change of the local chemical
34 composition, thus changing the transformation temperatures of those thermally affected
35 regions. Namely, an originally fully austenitic base material can present either martensite or a
36 mixture of both martensite and austenite in those regions after welding.

37 Conventional analytical techniques for determining the phase transformation characteristics of
38 NiTi shape memory alloys are differential scanning calorimetry (DSC) [7,8] and X-ray diffraction
39 [9,10] using conventional lab sources. However, these techniques are not suited to provide the
40 spatial resolution required for an in-depth understanding of the microstructural changes
41 occurring along both the heat affected and fusion zones due to the laser welding procedure.

42 While for DSC it is not possible to ensure that only the heat affected or fusion zone are being
43 analysed [6], these regions tend also to present a microstructural gradient thus preventing a
44 reliable analysis of the phase transformation characteristics. Additionally, for X-ray diffraction
45 analysis using conventional lab sources, it is known that in the Bragg-Brentano geometry, often
46 used for such analysis, does not ensure the required spatial resolution for detailed analysis of
47 the thermally affected regions.

48 A possible way to surpass this setback is with the use of high energy synchrotron-based X-ray
49 diffraction operating in transmission mode. Owing to the high photon flux of these sources,
50 the beam spot size can be very narrow, while still providing good statistics [11]. Additionally, it
51 is possible to obtain precise control of the beam position, ensuring that the analysed region
52 corresponds entirely to a given region. If necessary, it is still possible to probe the material
53 within these thermally affected regions, in order to determine the existence of any
54 microstructural gradient.

55 In this work, synchrotron X-ray diffraction was used for fine probing the different regions of
56 laser welded NiTi joints. This is the first investigation addressing the effect of laser welding
57 parameters on the phase content in the thermally affected regions of NiTi welds.

58 Experimental Procedure

59 Ni-rich NiTi shape memory alloys, 50.8 at. % Ni, superelastic at room temperature, purchased
60 from Memry in the flat annealed condition, were used in this investigation in the form of 1 mm
61 thick plate. Differential scanning calorimetry (DSC) of the base material was performed in a
62 temperature range between -160 °C and 70 °C, at a heating/cooling rate of 10 °C/min, to
63 determine its transformation temperatures. It was confirmed that, at room temperature, the
64 material was fully austenitic.

65 Laser butt welding of 30 x 30 mm NiTi plates was performed using a Nd:YAG laser from Rofin
66 Sinar, operating in continuous wave mode. The base material was cleaned using alcohol and
67 acetone, prior to welding, to remove impurities. Two distinct welding conditions (varying
68 power, P, and welding speed, v) were selected in order to ensure that full penetration was
69 achieved, with no microstructural defects, such as porosity or lack of penetration. The selected
70 welding parameters were: a) P = 990 W and v = 25 mm/s, for sample A; b) P = 1485 W and v =
71 20 mm/s, for sample B. So, it was ensured that significantly different heat inputs (HI), which is
72 defined as the power (P) to welding speed (v) ratio (P/v), allowed to obtain defect-free joints.
73 Shielding gases were used to prevent oxidation: argon on the face and helium on the root.

74 Microstructural characterization by means of X-ray diffraction analysis using synchrotron
75 radiation was performed at beamline P07 High Energy Materials Science of Petra III/DESY. A
76 high energy beam of 87 keV (corresponding to a wavelength of 0.1426 Å) was used and the
77 sample to the 2D detector Mar345 was set at 1.35 m. The beam spot was a 200 x 200 µm². The
78 samples were analysed perpendicularly to the weld bead, starting in the base material, going
79 through the heat affected and fusion zones and finishing on the other side on the base
80 material. A length of nearly 6 mm was probed with a distance of 200 µm between two
81 adjacent analysed spots. All X-ray diffraction analysis were performed at room temperature.

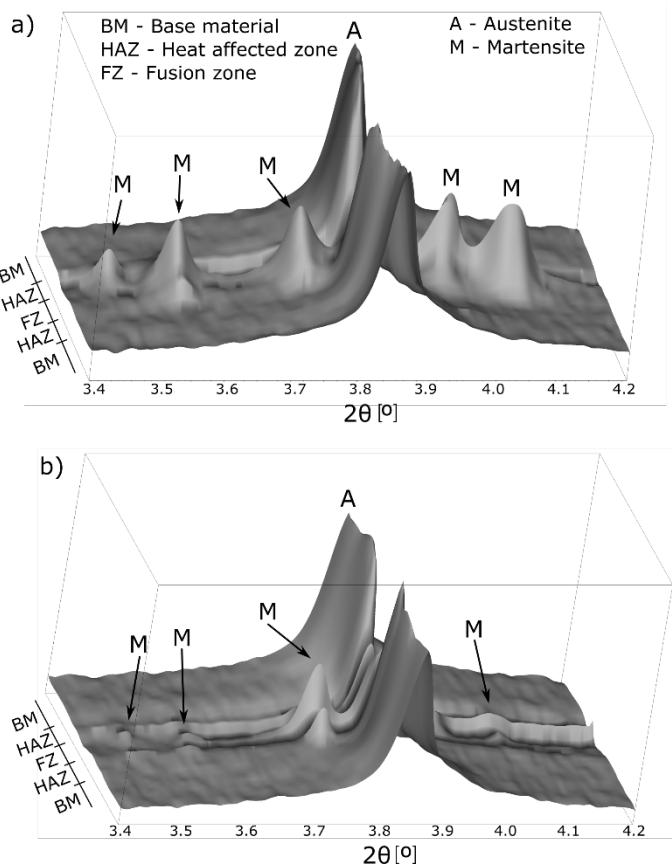
82 The raw 2D images were treated using Fit2D [12] as described in [13]. Determination of the
83 phase fraction of the existing phases at each analysed spot was performed using Rietveld code
84 available in Material Analysis Using Diffraction (MAUD) program [14].

85 **Results and Discussion**

86 The X-ray diffractograms of samples A and B at room temperature exhibit similar information:
 87 while the base material is fully austenitic, the thermally affected regions present a mixture of
 88 both austenite and martensite (Figure 1). The formation of this thermally stable martensite
 89 occurs by two distinct reasons:

- 90 (i) in the heat affected zone, Ni₄Ti₃ precipitation increases the transformation
 91 temperatures allowing for martensite to be stable at room temperature [15,16],
 92 (ii) in the fusion zone, preferential Ni volatilization has the same effect of increasing
 93 the transformation temperature in this region [15,17].

94 As a consequence of this increase of the transformation temperatures, different amounts of
 95 martensite, which will vary on each analysed region, will be stable at room temperature in
 96 coexistence with austenite. It can also be observed the effect of the heat input on the
 97 extension of the thermally affected regions: the higher heat input, gives a larger extension of
 98 those regions.



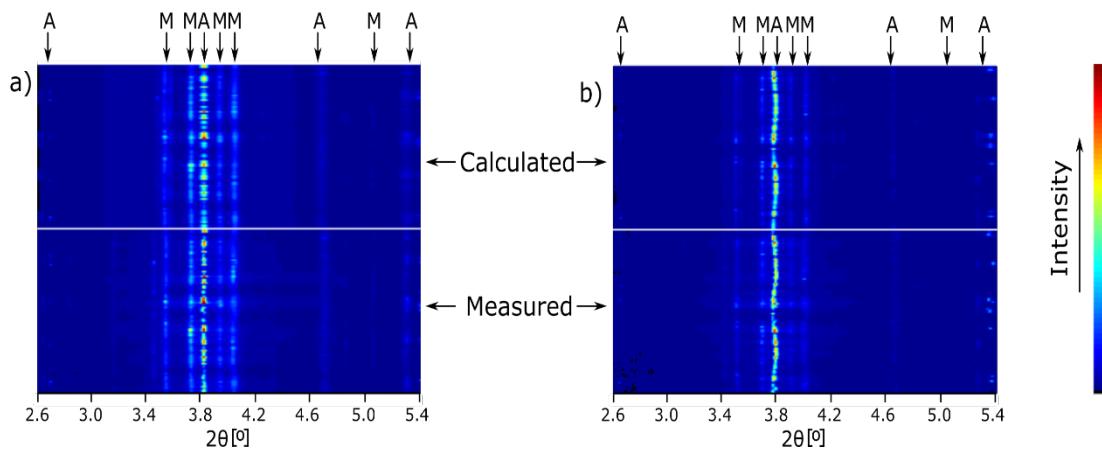
99
 100 *Figure 1 – X-ray diffraction patterns of samples A (a) and B (b).*

101 The precipitation of Ni₄Ti₃ in the heat affected zone will not be homogenous throughout this
 102 region. The reason for this is related to the permanence times at temperatures which enable
 103 for this phenomenon to occur: near the fusion zone, the permanence times will be higher, thus
 104 more Ni₄Ti₃ precipitation will occur, promoting a more significant change in the chemical
 105 composition of the surrounding matrix and thus allowing for more martensite to be stable at
 106 room temperature; on the other hand, closer to the base material, the permanence times at
 107 the interval range required for precipitation is shorter, thus resulting in less martensite formed

108 at room temperature, due to a lower compositional change. As such, the martensite content
109 increases from the base material/heat affected zone interface towards the heat affected
110 zone/fusion zone interface. In the fusion zone similar compositional changes occur allowing for
111 martensite formation: at the weld centreline the Ni volatilization will be significantly higher
112 than near the heat affected zone, as a result of the increased temperatures reached in the first
113 region. As such, more martensite is stable near the weld centreline. It is known that for Ni-rich
114 NiTi shape memory alloys any decrease in Ni content promotes a significant raise of the
115 transformation temperature [18].

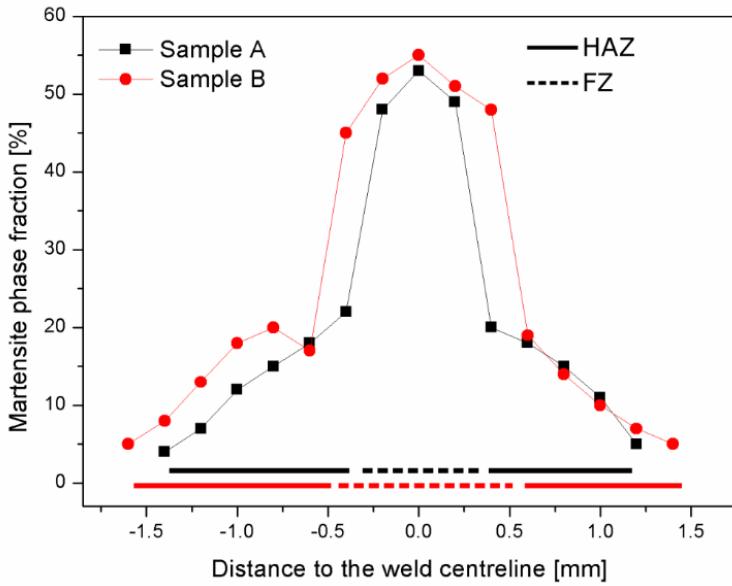
116 Rietveld refinement was used to determine the phase fraction of martensite and austenite in
117 both the heat affected and fusion zone of these laser welded NiTi joints. Good agreement
118 between the calculated and experimental patterns in terms of width, position and intensity
119 was observed after Rietveld refinement (Figure 2), thus indicating a good fit [19].

A - Austenite
M - Martensite



120
121 *Figure 2 – Measured and calculated diffraction patterns after Rietveld refinement: a) from the heat affected
122 zone; b) from the fusion zone. A – Austenite, M – Martensite.*

123 A clear distinction between the heat affected zone and fusion zone is observed for both
124 samples: while in the former the martensite phase fraction ranges between 4 and 20 %, in the
125 latter a significant increase to roughly 50 % of martensite is observed, as shown in Figure 3.
126 These results are in line with the aforementioned relative importance of the mechanisms that
127 promote Ni depletion: precipitation in the heat affected zone changes less the chemical
128 composition than preferential volatilization occurring in the fusion zone, thus justifying the
129 sharp difference in the martensite content in both regions.



130

131 *Figure 3 – Evolution of the martensite phase fraction in samples A and sample B. HAZ – Heat affected zone; FZ –*
 132 *Fusion zone.*

133 An increase in the martensite phase fraction is observed from the base material/heat affected
 134 zone interface to the weld centreline (Figure 3). However, that variation is more notorious in
 135 the fusion zone. The preferential Ni evaporation occurring during keyhole welding in the fusion
 136 has a greater influence as it promotes a higher Ni depletion than in the heat affected zone,
 137 thus allowing for more martensite to exist in this region, when compared to the heat affected
 138 zone.

139 Considering the heat input of both welded samples, it was also observed that the difference in
 140 austenite or martensite phase fractions is not significant, with those differences ranging
 141 around 5% for equivalent points on both samples. Such minor differences occur by two
 142 reasons: in the fusion zone the temperatures reached are higher for sample A (due to higher
 143 heat input introduced during welding); in the heat affected zone the permanence time for Ni-
 144 rich precipitation is also higher for sample A.

145 Conclusions

146 In conclusion, synchrotron X-ray diffraction was used for fine probing of laser butt welded NiTi
 147 joints. As a consequence of the welding procedure, martensite is formed in the thermally
 148 affected regions, while the base material maintains its fully austenitic original structure.

149 The martensite phase fraction varies from the heat affected zone to the weld metal and within
 150 each zone, that is, the amount of martensite in the fusion zone is higher than in the heat
 151 affected zone. Additionally, the martensite content increases in the heat affected zone
 152 towards the fusion zone, due to higher temperatures experienced during welding. Such
 153 feature is also observed in the fusion zone but with a different underlying mechanism: in the
 154 heat affected zone Ni-rich precipitation promotes a local modification of the matrix
 155 composition, hence raising the transformation temperatures and allowing for martensite to be
 156 stable at room temperature; in the fusion zone, preferential Ni volatilization has the same
 157 effect of raising the transformation temperatures.

158 Using Rietveld refinement, it was possible to observe that the martensite phase fraction
159 increases from the base material/heat affected zone interface towards the weld centreline.
160 Within the heat affected zone, the martensite phase fraction increases towards the fusion
161 zone, as a result of longer periods for precipitation phenomena. This precipitation process is
162 responsible for the increase of the transformation temperatures due to a local compositional
163 change of the surrounding matrix, giving rise to the formation of martensite at room
164 temperature.

165 It can be inferred from these results that the local transformation temperatures should differ
166 from point to point in the thermally affected regions. The determination of these
167 transformation temperatures using in-situ techniques would be of great interest to determine
168 the feasibility of obtaining a gradient of functional properties aiming applications that may
169 require laser welded NiTi joints.

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