Influence of Heat Treatments on Microstructure and Hardness of a High-Strength Al-Zn-Mg-Cu-Zr Alloy Processed by Laser Powder Bed Fusion

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Abstract: Processing 7075 alloy by laser powder bed fusion is complex due to hot cracking. Zr addition is one of the solutions to reduce this susceptibility to cracking and permit the elaboration of crack-free parts. This study explored the microstructural and hardness evolutions of an Al-Zn-Mg-Cu-Zr alloy with respect to different heat treatment routes. In particular, natural and artificial agings are considered from as-built and solution heat-treated tempers. Microstructural characterization was principally carried out by optical, scanning, and transmission electron microscopy. In the as-built state, the melt pools exhibited a bimodal grain structure consisting of very fine grains at their boundaries and coarser elongated grains in the center. The grain boundaries were composed of $\eta$-\(\text{Mg(Al, Zn, Cu)}_2\) eutectic. The associated hardness is quite significant (140 HV\(_{0.1}\)). Natural and artificial aging from this state did not show any significant microstructural and hardness evolutions. In contrast, solution heat treatments modified the microstructure by dissolving eutectics and $\text{Al}_3\text{Zr}$ precipitation without significant grain growth. Natural and artificial aging produced interesting hardening: a maximum of 220 HV\(_{0.1}\) was achieved for the T6 temper. The resulting value completely exceeded the hardness of the AW-7075-T6 alloy. This excellent value was attributed to $\eta'$ and $\text{Al}_3\text{Zr}$ precipitation without significant grain growth.

Keywords: laser powder-bed-fusion (L-PBF); 7075; heat treatments; microstructure; hardness

1. Introduction

Additive manufacturing (AM) processes gather all processes that allow the fabrication of 3D parts to be built layer-by-layer from a CAD model. Laser powder-bed fusion (L-PBF) is one of the most widely used processes due to its geometric freedom and ability to produce thin-walled complex structures. This process has been used for various alloys, such as stainless steel, titanium, nickel, and aluminum alloys. The latter are widely employed in the industry due to their high strength-to-weight ratio. They are important candidates to be developed by L-PBF, particularly for structural applications. However, they are not the easiest alloys to process due to their high reflectivity, high oxidation, low melting point, and susceptibility to hot cracking of some nuances [1–6].

Studies have focused mainly on Al-Si alloys, such as AlSi10Mg, AlSi7Mg0.6, and AlSi12, due to their excellent weldability. The achieved properties of L-PBF Al-Si alloys (UTS = 200–450 MPa) are better than those of cast alloys [2,7–13]. However, they are still inferior to conventional high-performance aluminum alloys (UTS = 100–600 MPa), used in structural applications [2,14–16]. For such applications (aeronautics, aerospace), Al-Cu,
Al-Mg, Al-Si-Mg, and Al-Zn-Mg(-Cu) are more commonly used but are more challenging to elaborate due to hot cracking \cite{17-19}. Developments are currently underway and focus on two main approaches: reducing the thermal gradient and modifying the chemical composition of the base material by adding additive elements \cite{6,20,21}.

The first approach is based on preheating the fabrication plate. Preheating at 200 and 400 °C was tested but did not allow the production of crack-free parts \cite{19,22}.

The second approach aims to modify the solidification process or control the solidification through the addition of a nucleant agent to Al7075 powder.

To modify the solidification process by reducing the solidification range, 7075 alloy was modified by Si addition \cite{23-26}. Elimination of cracking was observed at 4 wt% Si addition. This is accompanied by the formation of fine grains. However, mechanical properties (yield strength, ultimate tensile strength, elongation at break) depend on the Si content up to 5 wt%, the threshold at which brittleness increases \cite{26}. An increase in hardness is achieved by artificial aging at 150 °C and precipitation of MgZn2 and Mg2Si \cite{23}.

Solidification control is based on the grain refinement process and was employed for Al-Zn alloys, and Al-Mg and Al-Cu alloys \cite{27-38}. The addition of transition elements (mainly Sc and Zr) with limited solid solubility and a slow diffusion rate seems to be the most effective solution. This addition is achieved by powder functionalization, powder mixing \cite{27,36,39,40}, or pre-alloying \cite{28,37}. During solidification, the heterogeneous formation of coherent L12 nucleant particles (Al3Sc and Al3Zr) takes place, allowing the formation of fine equiaxed microstructures \cite{27,41}. The latter supports the deformation more readily in the semi-liquid state than in oriented granular structures. The addition of 1 wt% of Zr has been shown to be sufficient to reduce the susceptibility to cracking \cite{28,30,31,33-35,41,42}. This chemical modification provided a high hardness, which was enhanced by conventional T6 heat treatment \cite{27,28,37,43}. The 7xxx-modified aluminum has only been characterized in two conditions: the as-built state and after T6 heat treatment \cite{27,28,37,43}.

The present study focuses on the microstructure and hardness evolution of an Al-Zn-Mg-Cu-Zr alloy for different heat treatment routes. In particular, natural and artificial aging from as-built and solution heat-treated tempers are considered. The main objective is to correlate the hardness evolution to microstructural modifications and to compare the achieved hardness with the reference 7075-T6.

2. Materials and Methods
2.1. Material and Manufacturing Conditions

This work focuses on the microstructural evolutions of an Al-Zn-Mg-Cu-Zr alloy. The base material consists of AA7075 atomized powder functionalized with hydrogen-stabilized nano-Zr particles (HRL Laboratories, Malibu, CA, USA). The composition of the powder is 8.4 wt% Zn, 3.8 wt% Mg, 1.7 wt% Cu, and 1.1 wt% Zr. The hydrogen concentration is 420 ppm wt (ICP-OES measurement method). Additionally, the particle size distribution (PSD) of the atomized powder was analyzed by laser particle size measurement (Filab SAS, Dijon, France). D10, D50, and D90 are 24, 41, and 70 µm, respectively. The morphology of the powder particles is shown in Figure 1a.

The material was processed by laser powder bed fusion (L-PBF). The processing was performed on a Renishaw AM400 machine composed of a 400W Yb: YAG pulsed laser (70 µm spot size) (Renishaw plc, Wotton-under-Edge, UK). The building platform was an aluminum plate with an effective surface area of 230 × 230 mm². The platform was not preheated during fabrication. The building parameters represent a volumetric energy density of 73 J/mm³ (power = 200 W, hatching distance = 80 µm, exposure time = 70 µs, spot spacing = 60 µm). Laser scanning is performed by rotating 67° between two successive layers. The dimensions of the raw samples were 16 × 16 × 30 mm³. The coordinate system and cross-sections associated with each sample are presented in Figure 1b.

The composition of the produced material is 6.6 wt% Zn, 3.1 wt% Mg, 1.86 wt% Cu, and 1.9 wt% Zr. The hydrogen concentration is 45 ppm wt in the as-built condition.
The composition of the produced material is 6.6 wt% Zn, 3.1 wt% Mg, 1.86 wt% Cu, and 1.9 wt% Zr. The hydroge... of cross-sections. Building direction is represented by a vertical black arrow or by a dotted circle.

### 2.2. Microstructural and Thermal Characterizations

Various heat treatments were carried out in Nabertherm furnaces (Nabertherm, Lilienthal, Germany): T5 heat treatments at 120 °C with air cooling, solution heat treatments (SHT) (1–8 h at 475 °C, followed by water quenching), and T6 heat treatments (a 2 h solution heat treatment at 475 °C followed by water quenching and a 1–30 h aging at 120 °C and air cooling). The heat treatment campaign is summarized in Table 1.

#### Table 1. Heat treatment campaign summary.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Temperature (°C)</th>
<th>Holding Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-built natural ageing</td>
<td>25</td>
<td>5 months</td>
</tr>
<tr>
<td>As-built artificial ageing (T5)</td>
<td>120</td>
<td>1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 24, 30 h</td>
</tr>
<tr>
<td>SHT water quenched</td>
<td>475</td>
<td>1, 2, 3, 4, 6, 8 h</td>
</tr>
<tr>
<td>T4 (SHT naturally aged (475 °C–2 h, water quenching))</td>
<td>25</td>
<td>1 h; 1, 7, 14, 28, 56 days</td>
</tr>
<tr>
<td>T6 (SHT at 475 °C for 2 h, water quenching)</td>
<td>120</td>
<td>1, 2, 4, 6, 8, 10, 14, 16, 18, 20, 22, 24, 30 h</td>
</tr>
</tbody>
</table>

The thermal behavior was investigated using differential scanning calorimetry (DSC) and differential thermal analysis (DTA) to detect thermal peaks associated with phase transformation/precipitation phenomena. They were carried out on fresh powder and as-built and heat-treated specimens. Samples were prepared to meet the size and mass requirements: approximately 10 and 50 mg for DSC and DTA, respectively. DSC tests were performed under nitrogen flow on a METTLER TOLEDO instrument (Mettler-Toledo SAS, Viroflay, France). The test consists only of heating to 450 °C at a heating rate of 20 °C/min. DTA tests were realized under argon flow on a SETARAM Instrument apparatus (SETARAM Instrument SAS, Caluire, France) according to the thermal cycle computed in Calisto SETSYS software (version 1.12, SETARAM Instrument SAS, Caluire, France) (5 °C/min heating rate to 700 °C, 5 min holding time, and 5 °C/min cooling rate). The number and position of exothermic peaks were considered on the recorded and normalized signal.

Microstructural characterization of the printed material was carried out by optical microscopy (OM), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and transmission electron microscopy (TEM). The preparation of the metallographic specimens consisted of the selection of cross-sections (XY or XZ), mechanical characterization using optical microscopy (OM), and transmission electron microscopy (TEM).
polishing with SiC grit papers, and a final polishing with colloidal alumina (3 µm) and
colloidal silica (0.25 µm). Finally, the samples were etched using a Keller reagent for 5 to 15 s.
The prepared surfaces were observed using an Olympus PMG3 (OM; Olympus France SAS,
Rungis, France), a ZEISS EVO HD15LS (SEM; ZEISS, Paris, France), and a JEOL JSM-7000F
(FEG-SEM; JEOL, Paris, France) to characterize the microstructure. The ZEISS SEM was
equipped with an Oxford X-Max EDS detector coupled to an Aztec acquisition system
(Oxford Instruments, Tubney Woods, Abingdon, UK).

The microstructure was further characterized by EBSD maps (Oxford Symmetry 2
camera coupled with a Zeiss Supra VP55 FEG-SEM (ZEISS, Paris, France)) and TEM
(JEM-2100F; JEOL, Paris, France). TEM characterization was considered in three modes:
conventional (TEM/HRTEM/diffraction using a CMOS Gatan RIO16IS 4K × 4K acquisition
system; Gatan, Inc., Pleasanton, CA, USA) and scanning (STEM) transmission imaging
(HAADF). EDS mapping (Ultim Max TEM 80 mm² Windowless, Oxford Instruments, UK)
was also performed to analyze compositional distributions. Sample preparation consisted of
mechanical polishing to 30 µm, concave polishing with diamond suspension (0.25 µm), and
ionic polishing (PIPS; Gatan, Inc., Pleasanton, CA, USA) to achieve electron transparency.

2.3. Mechanical Characterization

The evolution of mechanical properties of the material during heat treatments was
followed by Vickers hardness (HV₀.1). It was estimated using a Zwick/Roell EMCO-TEST
instrument (Zwick/Roell, Paris, France). All tests were performed in accordance with
the EN ISO 6507-1 standard. Hardness profiles and associated standard deviations were
obtained from a minimum of 80 hardness indentations in XZ cross-sections.

3. Results

3.1. As-Built State

3.1.1. Hardness

Hardness is evaluated according to XY and XZ cross-sections. The result is indepen-
dent of the cross-section considered (XY = 140 ± 8 HV₀.1 and XZ = 143 ± 8 HV₀.1). The
hardness behavior, therefore, appears to be isotropic. After 5 months of natural aging, there
is a slight increase in hardness (+15 HV₀.1; +11%) and its dispersion (XZ = 157 ± 10 HV₀.1).

3.1.2. Macrostructure

The melt pool morphology in various cross-sections is shown in Figures 2 and 3.
No cracks were detected, confirming the processability of the modified alloy. This result
is consistent with the theory of alloy development described by J.H. Martin et al. [27].
However, residual porosity due to hydrogen content was observed and estimated to be
4% (image analysis and Archimedes method). The shape of the melt pool is difficult to
determine due to the metallurgical structure of the printed material and the rotations
between layers. However, from Figures 2 and 3, the melt pool size on an XZ section can be
estimated to be: a width of 115 ± 7 µm and a height of 50 ± 5 µm.

Figure 3 shows the EBSD IPF crystallographic orientation map in an XZ cross-section
of the as-built sample. The microstructure of the Al matrix is a bimodal structure, composed
of ultrafine grains, located at the melt pool boundaries, and coarser grains located in their
center. Ultrafine grains are less than a micrometer in size, whereas elongated grains have a
width of 2.6 ± 0.8 µm and a length of 5.4 ± 2 µm. The EBSD mapping gives an average
grain size of 0.82 ± 0.57 µm.
They are rich in Mg, Zn, and Cu (80.6 at% Al, 8.8 at% Mg, 5.6 at% Zn, 4.0 at% Cu, and 0.4 at% Zr). They may be η precipitates. Furthermore, STEM-EDS mapping shows that the grain boundaries are rich in copper precipitates. The precipitate diffraction pattern (Figure 5c) shows a superstructure (yellow boxes) of the matrix diffraction pattern. The superstructure is characteristic of a microstructure oriented similarly to the structure. The chemical analysis (Table 2) and the diffraction images, therefore, confirm that the square section precipitates are Al₃Zr precipitates of the L1₂ structure, coherent with the matrix.

Other more globular precipitates are visible within the grains (yellow circle in Figure 6). They are rich in Mg, Zn, and Cu (80.6 at% Al, 8.8 at% Mg, 5.6 at% Zn, 4.0 at% Cu, and 0.4 at% Zr). They may be η-Mg(Al,Zn,Cu)₂ or T-Mg₃2(Al,Zn)₁₉ enriched with copper precipitates.

3.1.3. Microstructure

The microstructure of the as-built condition is shown in Figures 3–5. Dispersoids are visible in the granular structure (yellow circles, Figure 4a). They can reach a size of several microns and are randomly distributed. STEM-EDS analysis showed that they are rich in Zr (77 at% Zr). In the center of very fine grains (Figures 4b and 5a), precipitates with a square cross-section are observed in the XY and XZ sections. These precipitates have a width of 260 ± 17 nm. STEM-EDS analysis (Figure 6) revealed that they are zirconium-rich particles. The atomic composition is given in Table 2. SAED patterns performed at the matrix and at the precipitate (circles 1 and 2 in Figure 5, respectively) are shown in Figure 5b,c. The precipitate diffraction pattern (Figure 5c) shows a superstructure (yellow boxes) of the matrix diffraction pattern. The superstructure is characteristic of a microstructure oriented similarly to the structure. The chemical analysis (Table 2) and the diffraction images, therefore, confirm that the square section precipitates are Al₃Zr precipitates of the L1₂ structure, coherent with the matrix.

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Figure 2. Optical micrographies showing melt pool morphology in (a) XY; (b) XZ cross-sections. The black arrow indicates the building direction.

Figure 3. EBSD map in the as-built state (XZ cross-section) showing grain orientations within a melt pool (XZ cross-section).

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(a) (b)

Figure 2. Optical micrographies showing melt pool morphology in (a) XY; (b) XZ cross-sections. The black arrow indicates the building direction.

Figure 3. EBSD map in the as-built state (XZ cross-section) showing grain orientations within a melt pool (XZ cross-section).
Furthermore, STEM-EDS mapping shows that the grain boundaries are rich in Zn, Mg, and Cu. The estimated chemical composition at these grain boundaries is 73.8 at% Al, 12.3 at% Mg, 7 at% Zn, and 4.9 at% Cu. These boundaries are therefore composed of an \( \eta \)-Mg(Al,Zn,Cu)\(_2\) eutectic structure.

Finally, the composition of the solid solution is given in Table 2. The contents of Zn, Mg, Cu, and Zr are above the maximum solubility of each element in aluminum at room temperature (1, 1.7, and 0.05 wt% for Zn, Mg, and Cu, respectively) [44–47]. The solid solution is, therefore, slightly saturated with the alloying elements.

Table 2. Chemical composition of the as-built condition naturally aged, obtained by STEM-EDS from yellow circles of Figure 4a.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Zn</th>
<th>Mg</th>
<th>Cu</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1 (at%)—matrix</td>
<td>Bal.</td>
<td>1.3</td>
<td>1.7</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Point 2 (at%)—precipitate</td>
<td>Bal.</td>
<td>1.1</td>
<td>0.6</td>
<td>1.8</td>
<td>12.5</td>
</tr>
</tbody>
</table>

![Figure 4](image)

Figure 4. Microstructure in the as-built state at different scales (backscattered electron micrography; XZ cross-section). (a) General overview (×1000), (b) fine-grained zone (×20,000).

![Figure 5](image)

Figure 5. (a) TEM examination of the as-built microstructure. (b,c) Diffraction patterns corresponding to yellow circles of image (a).
3.2. Influence of Solution Heat Treatment and Natural Aging

Hardness Evolution

The effect of solution heat treatment on hardness is evaluated from the following perspectives. The first considers the effect of the solution time on as-quenched properties, and the second considers the effect of the natural aging time.

In the as-quenched condition (Figure 7), the hardness mean value is $126 \pm 4$ HV$_{0.1}$. A slight difference appears between solution times: the longer the holding time, the lower the hardness appears to be, despite the relative standard deviations of the individual means. After 24 h at 25 °C, the hardness increases ($+30$ HV$_{0.1}$; $+24\%$) with respect to the as-quenched values for all conditions. The hardnesses continue to increase with aging, reaching their maximum values after two weeks. They are then constant. The hardness difference between the solution heat treatment holding times observed after quenching is maintained for long natural aging times.

Figure 7. Hardness HV$_{0.1}$ evolution in function of SHT time and natural ageing (XZ cross-section).
After a 2 h solution time, the traces of the melt contours are still distinguishable with their bimodal structure (fresh quenching and aging, Figure 8a,c). The number of Zr-rich dispersoids does not appear to be greater than in the as-built state. The grain boundaries no longer consist of a continuous network of particles (eutectic structure) but of a set of spaced particles (Figure 8b,d). The network structure has been dissolved during the solution heat treatment. The square precipitates in the raw state are still visible in the finer grains and have the same geometry after this treatment.

A wide variety of precipitates were formed during solution heat treatment (Figure 8b,d). They are heterogeneously distributed as there are areas rich and others poor in precipitates. They are mainly formed at the grain boundaries and within the finest grains. The geometries observed are very different. For the alloy in the T4 state, almost all the precipitates observed are rich in zirconium, and some in Mg-Zn-Cu (Figure 9). The Zr-rich precipitates are located in quite different forms at the grain boundaries and within the grains. Around these precipitates, there is a zone depleted in zirconium atoms. The Mg-Zn-Cu-rich precipitates appear at the grain boundaries. They are rather elongated and thin. Their formation probably occurred during natural aging. Finally, Al-Cu-Fe intermetallic particles appear during holding.

The chemical composition of the matrix is shown in Table 3 and represents a state of supersaturation of the aluminum-rich solid solution [44,45].

![Image of microstructures](image-url)

**Figure 8.** Microstructures obtained after (a,b) water quenching of SHT sample and (c,d) naturally aged for 45 days (backscattered electron micrographies; XZ cross-section).

**Table 3.** Chemical composition of the SHT condition naturally aged (T4 state), obtained by STEM-EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Zn</th>
<th>Mg</th>
<th>Cu</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>T4 condition (at%)</td>
<td>Bal.</td>
<td>2.2</td>
<td>3.2</td>
<td>1.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>
3.3. Influence of Artificial Aging T5

When artificially aged at 120 °C from the as-built condition, the hardness increases, starting from 12 h, and reaches 160 ± 13 HV$_{0.1}$ after 30 h (Figure 10). It is possible that longer times would have allowed for a more significant increase.

At peak hardness in the T5 condition, the microstructure is still duplex with some very fine grains and others slightly less fine (Figure 11). The Al$_3$Zr precipitates in the center of the grains are still visible, and the phases at the grain boundary phases are preserved. Microscopically, the structure is identical to that of the as-built condition.
3.4. Influence of T6 Heat Treatment

For the T6 heat treatment, a 475 °C–2 h solution heat treatment is selected, and artificial aging is initiated immediately after quenching. The hardness evolution from the quenched condition is shown in Figure 10. After one hour of aging, an increase in hardness of +55 HV_{0.1} (+44%) is observed. The hardness continues to increase with the holding time, reaching a peak at 218 ± 11 HV_{0.1} after 20 h. The increase in hardness is significant for this T6 heat treatment. The hardness was also evaluated on the XY cross-section for the peak aged condition. The value is independent of the cross-section considered.

In the peak-aged condition, the microscopic characteristics are identical to those described after the solution heat treatment (Figures 7 and 12). Different types of precipitates can be seen. They have different shapes and contrasts. A SEM-EDS analysis shows some trends (Figure 12b). The different circles symbolize the areas where chemical analysis points have been made. The central black precipitate (blue circle) is rich in Mg and Si. The green circles are located in areas where few precipitates are present; the chemical composition that emerges is that of the base alloy. The analyses carried out in the yellow circles show an atomic concentration of Mg of between 25 and 44% of the sum (Mg+Zn+Cu). Zr and Mg-Zn-Cu rich precipitates are at the grain boundaries (Figure 13).

![Figure 11](image1.png)

**Figure 11.** Microstructures obtained after 24 h aging at 120 °C (XZ cross-section). (a) General overview (×1000), (b) fine-grained zone (×6000).

![Figure 12](image2.png)

**Figure 12.** (a) SEM and (b) SEM-EDS examinations of the alloy after following a T6 heat treatment (475 °C–2 h + water quenching + 120 °C–20 h) (XZ cross-section).
An EBSD map (Figure 14) shows that the bimodal structure remains visible after the T6 heat treatment. The size of the coarser grains is 5.4 ± 2 μm high and 2.6 ± 0.8 μm wide. The EBSD mapping gives an average grain size of 0.89 ± 0.73 μm.

4. Discussion

The bimodal structure obtained in the as-built state is a characteristic of aluminum alloys whose chemistry has been modified by adding Sc or Zr elements [27,30–32,34,36,37,41,42,48–50]. The formation of this structure for modified materials has been associated with the heterogeneous formation of Al₃Zr or Al₃Sc seed particles within the melt pool. The concentration of these particles depends on the temperature and the solidification rate. In the case of Al-Mg-(Sc-)Zr alloys, it has been shown that the seeds can only exist at temperatures below 800 °C [32,41,42,49]. At the boundaries of the melt pool, where the
temperature is considered to be lower than 800 °C, Al$_3$Zr particles are present and can play their role as seeds for solidification of the α-Al phase (peritectic reaction). The grains formed are then very fine and randomly oriented. In the center of the melt pool, where the temperature is higher, the Al$_3$Zr particles are dissolved. During cooling, the Zr atoms are found in a solid solution as the solidification rate increases. The low concentration of nuclei within the melt pool favors columnar grain growth along the thermal gradient and perpendicular to the melt [28,30,51].

The hardness values obtained for an Al-Zn-Mg-Cu alloy produced by L-PBF in the as-built condition are in agreement with the results from the literature (around 130 HV) [17,18]. Some authors also obtain lower bulk hardnesses than those obtained here, whether the alloys are modified with Zr or not [37,43,52]. Other authors give a higher value (159 ± 2 HV$_{0.5}$) than that obtained in our study [28]. As the combined building parameters are close, the difference can be explained by a different porosity rate (4% vs. 1% for A. Martin et al. [28]).

The increase in hardness due to natural aging is not surprising, as 7xxx series alloys are known to ‘age’ at room temperature after solution treatment [53,54]. However, we have seen in the previous section that solutes are present in the supersaturated solid solution of the matrix (Table 2) and are located at the grain boundaries. Short-range diffusion should therefore allow the formation of GP zones that participate in the hardening of the alloy.

After a 2 h solution heat treatment, the microstructure partly differs from the as-built condition. The grain structure is still duplex, but the eutectic network is dissolved. Grain boundaries are only decorated with particles of different sizes and shapes. These particles are mainly Zr and Mg-Zn-rich particles. After T6 heat treatment, the grain size did not really increase compared to the as-built condition (Figures 3 and 14). This means that the grain size after solution heat treatment (SHT) is the same as in the original condition.

In the as-quenched state, the hardness is lower than in the as-built condition (126 vs. 143 HV$_{0.1}$). However, the SHT as-quenched state is susceptible to being naturally aged (Figure 7) and surpasses the as-built condition after 1 day.

To understand in more detail the possible phase transformations of this Al-Zn-Mg-Cu-Zr alloy from the as-built and SHT conditions, a DSC study was conducted (Figure 15a). It should be remembered that the solid solutions are supersaturated (Tables 2 and 3), which may allow precipitation by decomposition of the solid solution. The three peaks A, B, and C correspond, respectively, to the dissolution of the GP zones (A, 130–140 °C), the precipitation of η′ (B, 210–220 °C), and η (C, 230–240 °C) [55–58]. Thus, the increase in hardness during natural aging is due to the decomposition of the solid solution and the formation of GP zones. The dissolution of eutectics at grain boundaries and the higher supersaturation in the SHT state lead to a higher material response during natural aging. Furthermore, the observed precipitation sequence means that the alloy is likely to be further hardened by the formation of fine precipitation during artificial aging.

The microstructure of the as-built artificially aged condition is similar to that of the as-built state (Figures 4 and 11). However, the hardness of the 24 h treatment is higher than that of the initial state. Thus, η′-MgZn$_2$ precipitates have formed during aging. They are not detectable at the scales studied and can form within the grains and at the grain boundaries. In both cases, this leads to a modification of the solid solution and of the grain boundaries. The increase in hardness for as-built and as-built naturally aged conditions is significant after a holding time of more than 12 h.

In the case of the T6 condition (peak-aged), the microstructure is not significantly different from the SHT state. However, the DSC curve shows that the endothermic peak is shifted to high temperatures (A′, 195 ± 1 °C). It corresponds to the dissolution of the GP zones and η′ precipitates formed during artificial aging. Peak C corresponds to the precipitation of η (235 ± 1 °C) [55,56,58]. A third exothermic peak can be observed (258 ± 1 °C), which may be the formation of the T' or T phase since the Mg concentration is high. Finally, a second inflection point is noticed at 389 °C (peak E); it may correspond to the dissolution of the η phase since the dissolution temperature of the T and T' phases is
higher [59]. Therefore, the precipitation of $\eta'$ takes place and allows the significant increase in hardness observed during artificial aging.

![DSC and DTA curves](image)

**Figure 15.** (a) DSC and (b) DTA curves of different tempers.

The DTA curves (Figure 15b) show the end-of-phase transitions likely to occur at high temperatures. For the powder sample, two endothermic peaks are observed at 478 and 625 °C. The first is associated with the dissolution of eutectic phases, and the second with the alloy’s melting [60-62]. In the as-built condition, two endothermic peaks and a plateau appear. This plateau extends from 470 to 520 °C. It is probably due to the presence of Zr and corresponds to the baseline. In this case, the inflection just before it corresponds to a dissolution, probably of the T phases. Including zirconium leads to a shifting of the melting temperature towards higher temperatures (633 ± 1 °C). Finally, the peak observed at 520 ± 1 °C would be related to the dissolution of Al$_3$Zr particles. The latter observations are valid for the other thermal states. This confirms the presence of Zr-rich precipitates up to high temperatures, ensuring structures’ stability and confirming the low enlargement of the grains after solution heat treatment.

As the grain size is constant, the modification of the eutectic structure and the alloy’s precipitation state determine the differences in hardness obtained between the different heat treatments. When comparing the hardness values obtained with the reference value, 7075-T6 alloy (170 HV [16]) (Figures 7 and 10), only the T4 and T6 conditions allow it to be
This is possible through the formation of GP zones and the precipitation of $\eta'$. Direct artificial aging after production does not sufficiently increase in hardness for similar times. Solution heat treatment, i.e., dissolution of grain boundary phases, is necessary to achieve maximum hardness.

5. Conclusions

This work aimed to characterize and correlate microstructural and hardness evolutions according to different heat treatments of a novel Al-Zn-Mg-Cu-Zr alloy. The heat treatments considered were natural aging, direct artificial aging, and solution heat treatment followed by natural or artificial aging. The main conclusions are summarized below:

- In the as-built state, melt pools present a bimodal grain structure composed of very fine grains at their borders and coarser elongated grains at their center. This dual structure results from the heterogeneous formation of Al$_3$Zr precipitates during solidification. These precipitates are preferentially located in the center of very fine grains and act as solidification seeds for the supersaturated aluminum solution. Moreover, grain boundaries are composed of $\eta$-Mg(Al,Zn,Cu)$_2$ eutectic.
- Hardness in the as-built state is relatively high at 140 HV$_{0.1}$ and does not depend on the direction of observation but is lower than 7075-T6 hardness. A slight increase is noticed during natural aging due to solid solution decomposition.
- Artificial aging at 120 °C does not significantly increase hardness (+20 HV$_{0.1}$ for a 30 h holding time; +15%). No major changes in microstructure were observed.
- During solution heat treatment, the grain boundaries’ eutectic is broken. Many particles nucleate in fine grains zones (at grain boundaries and inside grains). In particular, Al-Zr and Mg-Zn precipitates are observed. An abrupt drop in hardness is observed after quenching, whatever the holding time. An increase in hardness is noticed with natural aging; after 14 days, hardness exceeds the hardness of 7075 alloy in T6 temper (170 HV) thanks to solid solution decomposition and GP zone formation.
- Aging at 120 °C after SHT provides an outstanding increase in hardness (+80 HV$_{0.1}$ compared to the as-built state; +57%), completely exceeding the value of the reference alloy, thanks to $\eta'$ precipitation and without significant grain growth.
- Solution treatment is required to increase the hardness of the modified Al-Zn-Mg-Cu-Zr significantly.

Author Contributions: Conceptualization, N.C., O.D., and J.A.; methodology, N.C., O.D., and J.A.; validation, N.C., O.D., A.D.-M., J.-M.C., O.B., and J.A.; formal analysis, N.C.; investigation, N.C.; writing—original draft preparation, N.C.; writing—review and editing, N.C., O.D., A.D.-M., J.-M.C., O.B., and J.A.; supervision, O.D., O.B., and J.A.; project administration, O.B. and J.A.; funding acquisition, J.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by ANRT (Association Nationale de la Recherche et de la Technologie), grant number "CIFRE N°2019/0751".

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank Morgane Mokhtari, Nathalie Aubazac, Guillaume Morel, and Jade Pécue (ENIT/LGP) for their technical support and Antoine Vezirian from the CEF3D platform (ENIT) for the sample production. The authors would also like to thank Laurent Weingarten (Centre de Microcaractérisation Castaing) for TEM sample preparation and Jean-Michel Desmarres (CNES) and Nicolas Maillard (ELEMCA laboratory) for sample preparation and EBSD mapping.

Conflicts of Interest: The authors declare no conflict of interest.

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