Microstructural and mechanical properties of maraging steel parts produced by selective laser melting

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ABSTRACT

18Ni-300 maraging steel parts were produced through selective laser melting (SLM) technique, using manufacturer processing parameters. The samples were microstructurally and mechanically characterized in the as build (AB) condition and after a solution treatment (SOL). AB and SOL samples mechanical properties were compared using ageing and tensile tests, while the ageing sequence was studied from a kinetic point of view. The solution treatment resulted to have a detrimental effects on mechanical performances because it changed the microstructure of AB samples. Ageing behavior of AB samples was extensively studied, also considering the influence of austenite volume fraction on mechanical properties. The austenite content seemed to play a little role in modifying the material strength than other mechanisms. Tensile tests showed that mechanical properties depends on layer orientation with respect to loading direction and that porosity affects badly fracture elongation. Defects analysis allowed to assess the influence of SLM system configuration on splats distribution and to identify the mechanisms of porosity generation.

ESTRATTO

Campioni di acciaio maraging 18Ni-300 sono stati prodotti tramite la tecnica selective laser melting (SLM). La microstruttura e le proprietà meccaniche dei campioni sono state studiate nelle condizioni as build (AB) e dopo un trattamento di solubilizzazione (SOL). I campioni sono stati confrontati in queste due condizioni tenendo conto delle curve di invecchiamento isotermico e delle prove di trazione. La sequenza delle reazioni di invecchiamento è stata analizzata con test cinetici. Non sono state rilevate differenze nel comportamento di invecchiamento, anzi il trattamento di solubilizzazione ha causato un abbassamento delle proprietà meccaniche. La ragione di questo fenomeno è la diversa microstruttura dei campioni SOL rispetto a quelli AB. L’invecchiamento dei campioni AB è stato ulteriormente indagato a differenti temperature al fine di comprendere il grado di influenza dell’austenite residua sulle proprietà meccaniche. È stato valutato l’effetto dell’austenite sull’allungamento a frattura e sullo sforzo di snervamento. L’austenite ha un ruolo non significativo sull’allungamento e influenza
poco la resistenza del materiale. Le prove di trazione hanno mostrato che le proprietà meccaniche dipendono anche dall’orientamento dei layer rispetto alla direzione di carico. Questo comportamento e il basso allungamento a frattura di tutti i campioni sono causati dalla porosità tipica di questa tecnica produttiva. Un’analisi della porosità, delle polveri raccolte fuori dal substrato e delle superfici non modificate dei campioni ha permesso di valutare l’influenza della configurazione del sistema SLM sulla distribuzione degli splats e allo stesso tempo di identificare i meccanismi che originano la porosità.
1 INTRODUCTION

1.1 SELECTIVE LASER MELTING

Additive manufacturing (AM) techniques, i.e. techniques that allow direct production by means of material addition, have been developed in order to exploit advantages that traditional processes based on material removal do not have. Additive processes usually generate parts in a layered way. These techniques are well suited for rapid prototyping, rapid manufacturing and rapid tooling, mainly for the production of small series of components. All additive manufacturing techniques have in common some exclusive advantages with respect to other processes. They allow the direct production of parts, this means that components are generated at least in a near net shape quality. This procedure allows AM to require less post-production processes. The major advantage is the geometrical freedom, they have the capability to fabricate parts of very complex shapes and geometries with the smallest feature size of about 100 µm [31]. This geometrical flexibility and the direct production allow the production of customized components. However some restrictions on geometry are given by the requirements of unsolidified material removal from internal cavities and the need of supports to sustain overhangs [13].

There are many different AM techniques; selective laser melting (SLM), electron beam melting (EBM), direct metal deposition (DMD), inkjet printing are the most important. Laser based techniques can process a high variety of materials such as polymers, ceramics, composites, cermets metals and mixtures of them [1]. As regards metal additive manufacturing, there can be different feed systems (powder-bed, powder feed and wire feed systems) and different energy sources (laser, electron beam, arc) [44]. The most used techniques to process metal are SLS and SLM. They are both powder-bed systems and differ in the binding mechanism of the feed metal, i.e. sintering and melting respectively. Selective laser melting process is an evolution of selecting laser sintering. The difference is mainly in the energy provided to the metal powder, SLM is based on the full melting of the handled material.
For metals, SLM process is considered the best between all AM techniques [13]. The construction process is known as powder-bed process, because the fabrications proceed with selective melting of metallic or composite micrometric powders by a high-power laser beam (100-400 W). With SLM, tridimensional parts are produced starting from a CAD model, this model is divided in layers that are perpendicular to the growing direction. So, parts are fabricated layer by layer.

The starting material in form of powder is deposited on a substrate plate, the deposited layer is some tens of micrometres thick (30-50 µm). A laser beam selectively melts powders under inert atmosphere according to the CAD model. Then the substrate lowers down of a layer thickness and another layer of powder is deposited. The process is repeated, the molten powder metallurgically binds with the preceding layer. The final piece will be composed by the superposition of each layer.

![Figure 1. Schematic description of a SLM printer [2].](image)

SLM technique is very important because of the flexibility in practicable materials and the capability to produce functional and structural components with properties comparable to those of materials produced by conventional methods. A big advantage with respect to SLS technique is the possibility to obtain fully dense parts without a post-process densification [1].

Properties of SLMed components depend on accurate control of environmental conditions and process parameters. The most important parameters are the laser power and the beam scanning speed, they strongly influence density and superficial morphology. Other parameters are layer thickness, scanning lines overlapping, scanning
strategy and powder properties (shape, size distribution, composition); all of them must be optimized in order to obtain fully dense parts [2, 3]. The increase in scanning speed and high layer thickness and the decrease of laser power are related to a reduction of density, owing to a lower energy density input [10].

These process parameters modify the layer morphology which is very important because linked to porosity creation. Defects can propagate because a layer with defects does not allow a homogeneous deposition of the powder, moreover wrong parameters lead to a lack of overlapping between scan tracks and therefore pores appear. Some works show the relation between defects in a building layer and defects in preceding layers [17]. In order to obtain a higher density and a better layer morphology, laser remelting can be applied. If applied after scanning each layer, this remelting decreases surface roughness and thus porosity. It is also used to process the surface layer to enhance surface finishing. Also scanning strategies can be optimised to avoid these phenomena; it is common to change scanning direction for each layer. Scanning strategy is very important for the influence on residual stresses too. They arise from high thermal gradients in the melt pool and high solidification velocity [6].

Regarding environmental conditions, the selective laser melting of metals must be conducted in inert atmosphere to avoid surface oxidation. There would be a two-fold problem: unwanted oxide inclusions can form between scan tracks and surface wetting decreases giving the balling phenomenon. Balling is the effect given by the liquid metal that does not wet oxidised surface and tends to form droplets, leaving a rough surface. Roughness hinders a smooth layer deposition during the following layers and it lowers density [5].

Many types of metals can be processed through SLM, both pure or as alloys. Titanium and cobalt chromium alloys are used to produce customised biocompatible implants and prosthesis. Most common metals for SLM production are aluminium alloys, nickel alloys and different kind of steels such as stainless steels, tool steels, precipitation hardening (PH) steels [2] [3] [14]. This thesis is focused on the study of a maraging steel.
1.2 **Maraging Steel**

Maraging steels are a group of martensitic steels with low-carbon and high-nickel content. Their name comes from the contraction of “martensitic” and “aging”, because these steels are subjected to aging heat treatments to highly improve hardness and strength. Maraging steels are characterized by a high number of alloying elements, mainly Ni, Co, Mo, Ti and Al, which are added to promote and produce intermetallic precipitates. These steels exhibit excellent mechanical properties, combining high strength with good toughness. Besides, they are suitable for SLM process because they have a good weldability. Owing to the small size of the melt pool in the SLM process (relative to the size of the substrate), cooling rates are typically very high. Their properties make them well-matched for heavy duty applications in aerospace industry, in engines or for the fabrication of dies and moulds for injection moulding, die casting, extrusion and punching. This class of steels cannot be used for high temperature applications. When temperature becomes higher than 500 °C there will be a strong interference with the previous aging, leading to an excessive drop of strength [20].

The most common grades of maraging are 18% Ni ones, they are usually described with a number (200, 250, 300, 350) that designates the approximate yield stress in ksi (kilopound per square inch), so nominal yield stress for maraging goes from 1400 to 2400 MPa. Maraging steels with low nickel and cobalt content have been developed to decrease costs, but their performances are lower than the results obtained with 18-Ni grades.

High resistance is not obtained by solid solution and martensite strengthening because of low carbon content; it is rather achieved through precipitation of intermetallic compounds in the soft martensitic matrix. The common treatment steps are solubilisation and aging. The material is solubilised in fully austenitic zone between 800°C and 900°C, then it is cooled down in order to achieve a supersaturated solid solution. The resulting microstructure is lath martensite arranged in prior-austenite grains [35]. After this heat treatment, some austenite may be retained due to nickel presence, which is an austenite stabilizer [12]. A subsequent heat treatment (aging) induces diffusive nucleation and growth of intermetallics based on Ni₃Ti phase (or more
generally, Ni$_3$X where X = Ti, Mo, V, W), followed by Fe$_2$Mo or Fe$_2$Mo$_6$ precipitation [16, 19, 36]. In addition to precipitation, also the possibility to have austenite reversion must be taken into account. Reversion, that is the martensite-to-austenite transformation, occurs at temperature above 500 °C because of the dissolution of nickel-rich precipitates. Then, the reverted austenite is retained in a room temperature leading to mechanical properties change.

Ageing treatment can be conducted at different temperatures that range from 450 °C up to 650 °C [7, 8, 22]. Strengthening is function of aging temperature and time, because these two parameters influence precipitation kinetics. During ageing precipitation strengthening and softening due to precipitates coarsening and to austenite reversion occur. Owing to the high solid state diffusion enhanced by temperatures, the softening and strengthening mechanisms may occur simultaneously. Therefore the strength peak decreases as temperature increases because strengthening is readily overwhelmed by softening. Since strengthening reaches a peak at different times for each temperature and, as temperature increases, peaks occur before and have a lower value, a compromise should be done by selecting temperature to have an appropriate strength for a reasonable time.

Maraging steel strength relies on three contributions which are: strength of martensitic matrix, solids solution strengthening and precipitation hardening. These contributions as function of ageing time are depicted in figure 2 [18]. Martensite strength is controlled by the carbon content, by the decrease in grains dimensions and by dislocation density, while solution strengthening depends on solute atom species and concentrations. Co gives the higher contribution to solution strengthening, followed by Ti and Mo. Ni and Al have a lower effect that the other alloying elements [18]. As precipitation starts, solutes depletion induces a drop in solid solution hardening. However, precipitation strengthening gives the most important contribution to hardness.
1.2.1 Precipitation strengthening

In order to exhibit precipitation hardening, a material must undergo a solid-state phase transformation induced by a change in alloying elements solubility due to a decrease in temperature. In age hardenable alloys, precipitation can occur by homogeneous nucleation, followed by particle growth and coarsening, and by spinodal decomposition [16]. In case of maraging steels, only precipitation by nucleation happens. The nucleation of second phases is a thermally activated process because supersaturated solid solution decomposition requires atoms diffusion, and because provided thermal energy helps to overcome the energy barrier to form a nucleus with a critical radius that can grow further. The reason of that energy barrier is the Gibbs free energy for particles nucleation. It is given by two terms, a positive one related to surface energy rise, when radius and therefore interface area increases, and a negative one related to volume increase. Before the critical radius all nuclei are metastable, they can grow or can disappear. When the critical radius, corresponding to a critical Gibbs energy, is reached, nuclei are stable and the growth is assured.

After nucleation, growth and coarsening of precipitates follow, both ruled by diffusion. The main difference between growth and coarsening is the origin of diffusive atoms. For growing particles, the diffusive atoms come from the surrounding saturated matrix; for
coarsening particles, they come from matrix and from smaller dissolving particles. Coarsening is due to chemical gradients and interfacial energy reduction (figure 3) [15].

![Diagram](image)

*Figure 3. Comparison of a) growth and b) coarsening mechanisms [15].*

Precipitation strengthening is achieved by producing a dispersion of obstacles to dislocation motion. These obstacles increase the stress required to move dislocations, making an alloy harder and stronger. Precipitates hinder dislocation movements because of their interaction with dislocations. In general hardening depends on structure, size which is the most influential parameter, and distribution of the second phases. Also the volume fraction is important: if there are few particles, dislocation pinning occurs in a smaller amount. At first a fine dispersion of numerous small coherent precipitates forms. Increasing ageing time at elevated temperature, the dispersion coarsens; the number of precipitates decreases and their size and spacing increases, going from coherent to semi coherent precipitates. As ageing proceeds, coarsening and spacing continue increasing, leading to incoherent and dispersed precipitates formation. Dislocation hindering is less effective. After long ageing times, the equilibrium structure is established and the coherency of second phases is completely lost [43].

Different strengthening mechanism are associated to precipitation hardening. Chemical, coherency and dispersion strengthening are involved [16]. These mechanisms can be operative simultaneously. Nevertheless, each mechanism tends to dominate the dislocation-particle interactions at different ageing times. The typical strength-ageing time curve (figure 4) shows two regions in which the different mechanisms act and a peak strength that corresponds to a critical distribution of coherent or semi coherent particles.
In the first region, at early ageing times, the particles are small and coherent or semi coherent. The dislocations are predisposed to cut through them in order to move and the stress required moving those increases with precipitate radius. Here the dominant mechanisms are coherency and chemical strengthening. Coherent precipitates show crystal structure continuity with the matrix. If a misfit between reticular constants is present, lattice strains arise at the interface. To move dislocations, they should be subjected to an equal or higher stress than the one that particle exerts. Since particles relax at interface when radius grows, this mechanism is important only in early stage of ageing.

Chemical strengthening (figure 5) results from the energy consumed by dislocation motion through the particles. The consumption comes from the energy requested to create the additional matrix-precipitate interfaces, to form an antiphase boundary into the precipitates [9] and to increase the dislocation line length.

In the second region precipitates become large and incoherent and it is difficult for a dislocation to overcome the phase boundary between the host lattice and the incoherent precipitation. This results in dislocation bowing around second phases. The
strengthening is due to increase of dislocation length because of bowing. Dislocation lines close around particles forming loops; as deformation proceeds, more loops are formed at each particle and bowing requires more energy, i.e. stress. Here hardness decreases with time and the phenomenon is called *overageing*, indeed strengthening effect of incoherent phases decreases with radius increase. In this case the increment of yield strength follow the Orowan relationship [22]:

\[
\Delta \sigma_{OR} = (0.538 \, G \, b \sqrt{f_v / x}) \cdot \ln(x/2b)
\]

where \( G \) is the shear modulus, \( b \) is Burgers vector, \( f_v \) is volume fraction of precipitates, and \( x \) is diameter of precipitates. The strengthening mechanisms in maraging steels are generally thought to be as said before [9]: in the early stages of aging, strengthening is associated with the stress required for dislocations to cut through coherent precipitates. As the precipitates coarsen and become semi-coherent, the stress required for dislocations to cut the precipitates increases. Consequently, an increase in strength is obtained. Further increase in particle size and spacing at long aging times leads to a decrease in strength; the strength is governed by the Orowan equation.

The most important factors controlling strengthening behaviour in maraging steels are nanometric precipitates formation and austenite reversion. These two central aspects will be separately described in the following sections.

### 1.2.2 Precipitation in maraging steels

Maraging steel hardening is based on a nanometric intermetallic precipitates dispersion due to ageing. Since precipitates are not stable phases, the time governs the composition of all present phases and long ageing times would lead to an equilibrium composition of austenite and ferrite [21]. At different temperatures, dissimilar second phases are found, moreover the composition of precipitate phases depends on the alloy composition. Nickel is the main alloying element because it is a basic constituent for strengthening intermetallic compounds that it forms with Ti, Mo and Al. Addition of Co reduces the solubility of Mo increasing the fraction of nickel intermetallics and promoting the precipitation of Fe-Mo phase [18].
According to Ref. [8] and Ref. [11], phases in maraging steels are:

Table 1. Phases in maraging steels.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Martensite ($\alpha$-Fe)</td>
<td></td>
<td>BCC</td>
</tr>
<tr>
<td>Austenite ($\gamma$-Fe)</td>
<td></td>
<td>FCC</td>
</tr>
<tr>
<td>$\omega$</td>
<td>$A_2B$</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>$S$</td>
<td>$A_8B$</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>$X$</td>
<td>$A_3B$</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Fe$_2$Mo$_6$</td>
<td>Rhombohedral</td>
</tr>
<tr>
<td>$H$</td>
<td>Ni$_3$(Ti,Mo)</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Laves phase</td>
<td>Fe$_2$Mo</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Ni$_3$Mo</td>
<td>Ni$_3$Mo</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>

For ageing at low temperatures, from 400°C to 450°C, ordered and coherent phases such as $\omega$, $S$, $X$ and $\mu$ in the martensitic matrix appear [7, 19, 22]. These precipitates are not investigated because they have not a high influence on strength at common ageing temperatures.

For aging at temperatures higher than 450°C, rapid hardening occurs. Nor the order of precipitation, neither which precipitates are responsible for strengthening, are fully understood and the composition Mo-rich phase appearing in late stages of ageing is still discussed. A reason of this uncertainties is that precipitates are nanometric, thus problematic to be characterized. However, hardening is attributed to precipitation of Ni$_3$(Ti,Mo) and Fe-Mo phase preferentially in dislocations in the martensitic matrix and at lath boundaries [7, 19, 35].

The first precipitate is Ni$_3$Ti and it is believed to provide the higher contribution to strength. Fe and Co can substitute Ni in a small amount, while Ti atoms can be substituted by Mo and Al so this phase is usually identified as Ni$_3$(Ti,Mo). These precipitates can be rod-shaped, or ellipsoidal [11, 18] with approximate width and length of 5 nm and 10-20 nm respectively [22] and can effectively resist to coarsening.
Along with the η phase, also Ni$_3$Mo precipitates in form of needle-like clusters [11]. It is a metastable phase that dissolves as ageing proceeds.

These two phases appear at early stage of aging because Fe-Mo precipitates are not coherent with the matrix. Then the tendency to reach system equilibrium promotes Ni$_3$Mo dissolution. Through this the matrix enriches in Mo, producing spherical Mo-rich phase. The phase composition has not been clearly identified; in some works it is recognized as a Laves phase (Fe$_2$Mo) [8, 22], in other works as a μ phase (Fe$_7$Mo$_6$) [11, 23]. Whatever it is, it has a lower effect on strength respect to η and Ni$_3$Mo and it appears especially in the overaged conditions.

Ageing at temperatures between 500°C and $A_s$ induces a very fast precipitation for which overageing is rapidly reached. In this temperature range another reaction accompanies the precipitation and follows the dissolution of Ni$_3$Mo, it is the austenite reversion. Summarizing, the peak aged condition of maraging steels is reached when a critical dispersion of nanometric features appears; it is mainly composed of Ni$_3$(Ti,Mo) and Ni$_3$Mo particles with a low fraction of Fe-Mo phase.

1.2.3 Austenite reversion

Loss of strength in maraging steels is associated more decisively with reversion of martensite to austenite rather than coarsening of precipitates [9, 26]. The reason of this behavior is that reversion of austenite, beyond the softness of γ-Fe respect to martensite, is linked to dissolution of precipitates.

Austenite reversion occurs essentially in every maraging steel, but the extent of this transformation relies on temperature. At temperatures higher than 500°C, the formation of reverted austenite which has been retained at room temperature, occurs together with hardening, hampering the achievement of high strength. Austenite formation occurs at the same time of Fe$_2$Mo as consequence of the dissolution of Ni$_3$Mo precipitates. The decomposition enriches the martensitic matrix in Mo and Ni, the last being an austenite stabilizer [7, 19]. Thus, high ageing temperatures promote austenite by a diffusion controlled reaction:

$$\alpha' \rightarrow \alpha + \gamma$$
where $\alpha'$ is the martensitic matrix, $\alpha$ is a low Ni BCC phase and $\gamma$ is the Ni-enriched austenite.

The sequence of austenite formation as function of temperature and time has been extensively investigated. About time dependence, $\gamma$-Fe fraction is negligible in solubilized and not aged parts. As ageing begins, austenite appears mainly at the lath martensite boundaries but also at prior austenite grain boundaries; moreover, it can grow around retained austenite regions [23]. After that austenite pockets grow along boundaries and nucleate within the martensite lath [21, 22, 24]. At long ageing times the volume fraction reaches an almost constant value [21, 25, 26].

The content of retained austenite also depends on temperature, it increases with the ageing temperature until a peak value and then decreases. This phenomenon relies on the composition of austenite and thus on the martensite start temperature $M_s$. Since $M_s$ decreases with the increasing content of nickel in austenite and since ageing temperature reduces this content [24, 25], at higher temperatures correspond lower fractions of reverted austenite. This is likely to occurs at temperatures about 600°C.

Austenite is related to softening of the material, its presence modifies mechanical properties. It can have detrimental or beneficial effects depending on its volume fraction. The retention of small quantities at lath grain boundaries in slightly overaged samples is found to increase toughness and ductility with a little drop of yield strength [12]. The material can exhibit a good combination of strength and toughness and the mechanism involved in toughness increase is the increment in crack path length due to the presence of small austenite packets at lath boundaries as shown by Yang et al. [22]. However, for prolonged ageing austenite retention affects badly all mechanical properties. Yield strength and toughness decrease; brittleness is related to the presence of overaged particle which act as nucleation points for cracks, yield drop to the extensive presence of $\gamma$-Fe at grain boundaries [21].

Considering the afore-mentioned phenomena, the achievement of desired mechanical properties in maraging steel relies on a careful optimization of ageing times and temperatures.
2 MATERIALS AND METHODS

2.1 MATERIAL

The material used for the experiments is a 18-Ni 300 maraging steel (1.2709) in form of gas-atomized powder. Chemical composition of the alloy is given in Table 2. Figure 6 shows the typical morphology of powders. Most of powder particles are spherical or quasi-spherical, this shape allows particle to flow without impediments during deposition. Thus a homogeneous layer with less defects is obtained [10]. Particle size distribution, measured by image analysis, shows a mean dimension of 24 µm and a maximum dimension of 60 µm. An example of image analysis is shown in figure 7. There a comparison between the as received powder and a batch of powder collected around the base plate is also proposed. This topic will be discussed in a following section.

<table>
<thead>
<tr>
<th>Ni</th>
<th>Mo</th>
<th>Co</th>
<th>Ti</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>17,6</td>
<td>5,3</td>
<td>9,6</td>
<td>0,7</td>
<td>0,009</td>
<td>0,2</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition (wt%) of studied steel.

Figure 6. 18-Ni 300 powder morphology.
2.2 PROCESSING METHODS

2.2.1 Selective laser melting

The samples have been produced by SLM process, using a Renishaw AM250 SLM system. The set of samples is composed of square section prisms of dimensions 10 mm × 10 mm × 70 mm, horizontally and vertically oriented as shown in figure 8. The terms horizontal and vertical refer to the direction of the longitudinal axis with respect to the base plate.

Bars are printed under argon atmosphere by a single mode fiber laser with a power of 200 W and an estimated beam diameter at a focal point of 75 µm. Scan lines are composed by discrete and partially overlapped melted points. The spots are exposed to the radiation for a fixed time (t) and their distance is called point distance (dp). The laser moves from the end of each scan line to an adjacent one and overlaps it partially. The distance between adjacent scan lines is defined as the hatch distance (dh). The
parameters $d_h$, $d_p$, and $t$ were set to 80 µm, 65 µm, and 80 µs, respectively according to their optimization and manufacturer data. The thickness of each powder layer was set to 40 µm. A meander scanning strategy and the scanning direction rotation of 67° after each layer is used to produce samples.

### 2.2.2 Heat treatment

Aging response of the SLM samples was evaluated starting from samples both in the as built condition and after a standard solution treatment, carried out at 815 °C for 1 hour, followed by water quenching. Ageing was performed at 460°C, 490°C, 540°C and 600°C for times varying from 5 minutes to 14 days. All samples were quenched in water at room temperature after each heat treatment. From now the acronym AB will refer to as build specimens, while SOL to solution treated ones.

Heat treatments were performed in environment atmosphere in electrical resistance furnaces Carbolite HRF 722D ($T_{\text{max}}=750$ °C) and Carbolite GPC 12/36-3216 ($T_{\text{max}}=1200$ °C), shown in figure 9.

*Figure 9. Electrical resistance furnaces: Carbolite HRF 722D (left), Carbolite GPC 12/36-3216 (right).*
2.3 CHARACTERIZATION METHODS

2.3.1 Optical microscopy

Optical microscopy analyses were performed to examine the microstructure of as built, solution treated and aged samples. A Leitz Aristomet microscope (figure 10) was used at different magnifications from 25x to a maximum of 500x. Samples preparation required grinding and polishing down to 1 µm grit size and etching. Modified Fry’s reagent (1 g CuCl₂, 50 mL HCl, 150 mL H₂O, 50 mL HNO₃) was used on AB and SOL specimens, while Picral etch (4% picric acid in ethanol) was used on aged samples to distinguish between austenite and martensite constituents.

![Figure 10. Leitz Aristomet microscope.](image)

2.3.2 Scanning electron microscopy

Microstructural observations, powder morphology evaluation, fractography analyses and the analysis of top surfaces of as build samples were carried out by Zeiss EVO 50 scanning electron microscope (SEM). This instrument can detect secondary and backscattered electrons, moreover it can perform electron back-scattered diffraction (EBSD) and dispersive x-ray spectroscopy (EDX). This permits to detect texture and to assess phases composition.

SEM scans the investigated material by means of a high energy collimated electron beam. Having electrons a lower wavelength than light, SEM allows to obtain higher...
resolution and higher depth of focus. The material responses to the electron beam are backscattered electrons, secondary electrons and x-rays emissions. Backscattered electrons consist in the beam electrons that are subjected to elastic scattering and are reflected out of the specimen. They can be used to discriminate between areas with different chemical composition. On the base that heavy elements backscatter electrons better than light elements, brighter zones will correspond to heavier elements. Another advantage of backscattered electrons is the capability to be diffracted according to Bragg’s law. The EBSD technique uses diffracted backscattered electrons to characterize the crystalline lattice geometry of the material. Structure, crystal orientation and phase of materials can be detected by using crystallographic data only.

Secondary electrons are emitted from the valence band of atoms excited by the electron beam. Since they are generated by inelastic collisions, which occurs in few nanometers of depth, this response is the best to study material morphology.

The X-ray emission is exploited in electron dispersive x-ray spectroscopy (EDX). It is an analytical technique that allows to obtain elemental characterization of the material. It relies on the fact that each element has a unique emission spectrum. Measuring the spectrum peak intensities after an appropriate calibration, a quantitative evaluation of the chemical composition can be attained.

Samples were prepared in the same way as for optical analysis, i.e. grinding, polishing and etching. In case of EBSD analysis, the preparation consisted in grinding and polishing down to 1 µm grit size followed by a prolonged polishing with colloidal silica. This polishing was necessary to reach the very low roughness surface required by EBSD.

2.3.3 Stereoscope

The analysis of the as build top surfaces was performed with a Zeiss Axiocam ERc 5s stereoscope. Images were taken at 20x magnification to investigate the presence of splats and particles. The ImageJ software was used to process pictures and collect quantitative information by image analysis technique.
2.3.4 Differential scanning calorimetry

Differential scanning calorimetry analyses were performed using a Setaram Labsys TG-DSC-DTA equipment (figure 11) in argon inert atmosphere at three different heating rates (20, 30, 40°C/min) between 20°C and 1540°C. AB and SOL specimens were prepared by cutting small samples having a weight of about 100 mg.

The aim of DSC tests is to assess reactions and phase changes sequence. The DSC testing instrument consists in an empty reference crucible, and another one containing the studied sample. They are simultaneously heated and kept at the same temperature. The amount of energy provided to the sample during endothermic processes or removed during exothermic ones, is recorded as a function of furnace temperature. A DSC curve shows the heat flow, that is the amount of energy exchanged by the sample, versus temperature. If the heat flow direction is outward the sample, it is considered as positive. Using this convention, the curve will show maxima for exothermic processes and minima for endothermic processes.

As DSC makes possible to follow phase transformation sequence under precise non-isothermal heating, it has been used to describe solid state transformation kinetics. Kinetic parameters for each process, such as activation energy, can be evaluated studying the peaks of DSC curves through different models. In order to simplify the problem, all these models describe the transformation rate as the product of two independent functions, one depending on the reaction extent, the other one depending on the temperature:
\[
dY/dt = f(Y)k(T)
\]  
(1)

where \( Y \) is the degree of transformation, \( f(Y) \) is the reaction model and \( k(T) \) is the reaction constant. The reaction constant is described by an Arrhenius-type function [27]:

\[
k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right)
\]  
(2)

where \( E_a \) is the activation energy of the process, \( k_0 \) is a constant and \( R \) is the gas constant. The reaction extent of the transformation at any given time is taken equal to the fraction of heat released or absorbed [27], so:

\[
Y(t) = \frac{\int_{t_S}^{t_E} H \, dt}{\int_{t_S}^{t_E} H \, dt}
\]

where \( H \) is the heat flow, \( Y(t) \) is the reaction extent at any given time \( t \), \( t_S \) and \( t_E \) are the start and end times of the considered transformation. The equation denominator is the total enthalpy for the transformation corresponding to a selected peak. Isoconversional methods are used to determine the activation energy from constant heating rate experiments. These methods rely on the measurement of temperatures at which the same process, at different heating rates, reach the same transformation degree. Methods can be classified in two groups, namely type A and type B [28].

Type A methods, also known as Friedman’s or rate-isoconversion methods, do not use any mathematical approximation. They determine the transformation rate at a fixed extent of reaction for various heating rates. Possible errors come from the inaccuracy of the baseline and the determination of the temperature at constant transformation degree.

This method is obtained by inserting equation (1) in equation (2):

\[
\frac{dY}{dt} = f(Y)k_0 \exp\left(-\frac{E_a}{RT}\right)
\]

Taking the logarithm and considering a fixed transformed fraction \( Y_i \) at temperature \( T_j \):

\[
\ln \left[ \left( \frac{dY}{dt} \right)_{Y_i} \right] = \ln[f(Y_i)k_0] - \left( \frac{E_a}{R} \right) \frac{1}{T_j}
\]
A straight line is obtained by linear regression of the plot $\ln \left( \left( \frac{dY}{dt} \right) \gamma_i \right)$ versus $\frac{1}{T_j}$ for each heating rate, and its slope is $-\left( \frac{E_a}{R} \right)$. In this way the activation energy is obtained.

Type B methods, which includes also Kissinger’s method, use approximations and are based on the temperature integral [28]. The method is derived starting from equation (1) and (2); the final result is:

$$\ln \left( \frac{T_p^2}{\Phi} \right) = -\frac{E_a}{RT_p} + C$$

where $T_p$ is the peak temperature of the studied transformation and $\Phi$ the heating rate.

By plotting $\ln \left( \frac{T_p^2}{\Phi} \right)$ versus $1/T_p$ the activation energy can be evaluated.

2.3.5 Vickers micro-hardness

In order to follow strength evolution during aging, hardness as a function of time at constant temperature was measured. Isothermal aging curves were acquired using Vicker’s micro-hardness test. This test is performed by applying a constant load on a pyramid-shaped diamond indenter with square base and angle between opposite faces of 136°. The indenter penetrates the material leaving a depression in the material. The hardness number is determined by the load over the surface area of the indentation and can be expressed in kilograms-force per square millimeter or in Pascal. The hardness of the material calculated in kgf/mm² is proportional to the applied load $F$ and to the diagonals mean length $d$ according to $HV = 1,8544 \frac{F}{d^2}$.

Before testing, all the samples were polished by abrasive papers with grit sizes from 320 up to 2500 to avoid measurement errors. Tests were performed with a Leica VMHT30A durometer (figure 12), using a load of 2 kg for 15 seconds.
2.3.6 Tensile testing

Tensile tests were performed on cylindrical samples machined out from the SLM processed bars, with dimensions d=4 mm, Lc= 14 mm, LTOT=70 mm, R=3 mm and $S_0=12.57 \text{ mm}^2$, as depicted in figure 13. A first series of tests was performed on vertically and horizontally oriented specimens to evaluate the effect of layer orientation on mechanical properties. Printed bars were machined in order to obtain tensile specimens that were subjected to different heat treatments before testing. Three specimens per condition were tested. Tests were carried out at room temperature with a crosshead speed of 1 mm/min, using a MTS Alliance RT/100 testing machine (figure 14).

![Figure 12. Leica VMHT30A durometer.](image1)

![Figure 13. Tensile specimen scheme.](image2)

![Figure 14. MTS Alliance RT/100 testing machine.](image3)
2.3.7 XRD analysis

A PANanalitica X-Pert PRO diffractometer, equipped with a TMS X’Celerator sensor, was used to collect diffraction patterns. A X ray radiation peak Cu Kα with wavelength 1,5418 Å was used. Patterns were collected from 30° to 83° with a step size of 0,02°.

Pattern peaks were identified using literature references and Maud software. Rietveld refinement method, performed with Maud, allowed to make a quantitative phase analysis. Table 3 gives the structural parameters used for the refinement.

Table 3. Structural parameters of maraging phases.

<table>
<thead>
<tr>
<th></th>
<th>Symmetry</th>
<th>Spatial group</th>
<th>Lattice constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Martensite</td>
<td>Tetragonal</td>
<td>I4/mmm</td>
<td>a=2.8747 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>c=2.8866 Å</td>
</tr>
<tr>
<td>Austenite</td>
<td>Cubic</td>
<td>Fm-3m</td>
<td>a = 3.6136 Å</td>
</tr>
</tbody>
</table>

Number and position of peaks in XRD patterns follow the Bragg’s diffraction law $2d \sin \theta = n\lambda$. The peaks are a function of the angular position and of the crystal structure variables. Height and width of each peak are given by a combination of incident intensity, sample characteristics and instrumental deviations such as beam divergence, non-monochromatic radiation and alignment issues. If there is more than one phase in the sample, the intensity of the peaks corresponding to one phase is proportional to its volume fraction. This phenomenon is that on which is based the quantitative phase analysis. Rietveld refinement consists in the generation of a fitting of a generic experimental pattern; it uses a least square method to match a theoretical pattern with the real one. The theoretical computed intensity of i-th reflection of phase k will be [30]:

$$I_i^k \propto I \frac{f_k}{V_k} \cdot C_{i,k}$$

where $I$ is the incident intensity, $f_k$ is the k-th phase volume fraction, $V_k$ is the k-th phase cell volume and $C_{i,k}$ contains absorption, structure, texture, Lorentz polarization factors and profile peak shape function. The total intensity of calculated i-th reflection $I_{i,calc}^k$ will be the sum of all $I_i^k$ and the background factor $bkg_i$. The refinement purpose is to minimize the residual function WSS:
\[ WSS = \sum_i w_i (I_i^{exp} - I_i^{calc})^2 \]

where \( w_i = 1/I_i^{exp} \) is the statistical weight, \( I_i^{exp} \) is the experimental reflection intensity, \( I_i^{comp} \) is the computed fitting intensity. The reliability of the fit is recognized by comparing two factors, \( R_{wp} \) (weighted profile R-factor) and \( R_{exp} \) (expected R-factor), the goodness of the fitting \( GofF = R_{wp}/R_{exp} \) [29]. Having \( N \) data points and \( P \) parameters, R-factors are:

\[ R_{wp} = \sqrt{\frac{\sum_i w_i (I_i^{exp} - I_i^{calc})^2}{\sum_i w_i (I_i^{exp})^2}} \]

\[ R_{exp} = \sqrt{(N - P)\sum_i w_i (I_i^{exp})^2} \]

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3 RESULTS AND DISCUSSION

3.1 AS BUILD AND SOLUTION TREATED SAMPLES COMPARISON

First, an investigation between solution treated and as build samples was conducted. The aim was to assess the microstructural differences and the changes in the achievable strength between AB and SOL samples. In order to analyse microstructures optical microscopy, SEM and EBDS examinations were carried out. Regarding the strength, ageing treatments, hardness tests and tensile tests were performed. Kinetic analysis was done to evaluate the ageing sequence and the activation energies.

3.1.1 Microstructural characterization

Optical and SEM micrographs were taken to assess macro and microstructure of as build and heat treated bars. Bars were sectioned and top (perpendicular to building direction) and lateral (parallel to building direction) surfaces were inspected. Analyses were performed on samples AB and SOL without ageing.

As build microstructure

As regards AB sample, the images taken with the optical microscope show how the SLM process occurs, that is the interconnection among molten lines. In the top view (figure 15a) we can see that scanning direction of different layers is rotated, moreover also some distinct pools of the same track resulting from the pulsed laser beam are visible. The lateral view (figure 15b) clearly shows the overlapping among different scan lines in order to avoid porosity. This is the typical appearance of as build printed metals as shown for instance in [10], [23], [32] and [33].

In SEM micrographs the solidification structure is clearly recognised as composed by very fine elongated grains that result from cellular solidification. The intercellular spacing is in the sub-micrometer scale (≤1 µm). In figure 16 the top view suggests the presence of epitaxial growth between scan track boundaries. These are common
characteristics of SLM microstructures as shown by Ref. [33] and Ref. [23] for maraging steel and Ref. [31] for stainless steel.

This kind of solidification structure is expected because of the high cooling rates of the melt pool. The laser spot diameter is around 75 µm, considering the power level applied, it can be confirmed that the melt pool is small. The high dimensional difference between the pool and the surrounding solid part, which extract easily heat from it, makes solidification faster. The columnar growth depends on the thermal gradient in the molten metal. The higher the cooling rate, the finer the microstructure features.
Solution treated microstructure

The microstructure of SOL sample is completely different because of the high temperature treatment and the following rapid quench. In the optical micrograph (figure 17), it is visible that the previous cellular microstructure completely disappears and scan line boundaries are no more visible. The cellular solidification structure is replaced by the characteristic martensitic matrix composed by packets of martensite blocks. These blocks consist in fine parallel laths as shown in literature [35]. By comparing this microstructure with the AB one, we can see that it is coarser with bigger features and a different structure.

![Figure 17. Optical micrograph of top (a) and lateral(b) view of SOL sample.](image)

EBSD was carried in order to evaluate the grain orientation and to phase map. The coarse martensitic structure is evident in the EBSD orientation image (figure 18a) that shows the martensite blocks. As we can see in figure 18b, fractions of retained austenite (pink) were likely to be found at martensite (grey scale) boundaries. This result agrees with literature results that indicate martensite lath boundaries the place where γ-Fe retains and stars to nucleate when reversion occurs [21, 24, 35]. The presence of austenite in the solution treated sample also suggests the possibility to find it in the AB specimens. No precipitates were detected because of their small sizes.
3.1.2 Kinetic analysis of ageing sequence

DSC scans were recorded for the two different kinds of samples AB and SOL, at three different heating rates (20°C/min, 30°C/min, 40°C/min). The ageing sequence analysis was conducted in two steps: identification of peaks and determination of kinetic parameters for each peak.

**Peaks recognition**

The recognition of peaks was performed by considering the curves recorded at 20°C/min because in this condition peaks are more evident. The collection of DSC curves at that heating rate for AB and SOL samples is reported in figure 19. The curves at 30°C/min and 40°C/min for both AB and SOL are shown in figure 20.

![Figure 18. EBSD orientation (a) and phase (b) maps.](image)

![Figure 19. Comparison between DSC curves of AB and SOL samples at 20°C/min.](image)
The attribution of each peak was done by comparing the obtained results with data found in literature for the same alloy. There are four peaks: the first (1) and the second (2) are exothermic and linked to precipitation, while the third (3) and the fourth (4) are endothermic and linked to austenite reversion and precipitate dissolution. According to literature, peak 1 is associated to the first precipitation stage, that is carbide and coherent phases precipitation, and to martensite recovery [27]. Peak 2 corresponds to the formation of the main strengthening precipitates, Ni$_2$(Ti, Mo) and Fe$_7$Mo$_6$ or Fe$_2$Mo [27, 34]. The first endothermic peak, peak 3, is connected to the austenite reversion by diffusion, while the second one, peak 4, to the $\alpha'$ \rightarrow $\gamma$ transformation by shear and to dissolution of precipitates [27, 34, 36].

About the presence of two different peaks corresponding to the austenite reversion, Kapoor and Batra [36] report that the splitting in two step of $\alpha'$ \rightarrow $\gamma$ transformation in dilatometric curves is enhanced by slow heating rates. They report the onset of the splitting at heating rates slower than 120°C/min in a 350 maraging steel. The obtained DSC curves seem to have a good agreement with this report; as we can see in figure 19 and 20 the difference between peak 3 and peak 4 tends to become less pronounced as heating rate increases. At lower heating rates, martensite starts to transform into austenite by a long-range diffusion process; at sufficiently high temperatures (>720°C) the remaining austenite transforms into austenite by a shear mechanism [27, 36]. The reason of this behaviour is that diffusion has no time to take place at fast heating rates. The peak temperatures for all peaks and conditions are listed in table 4, 5, 6 and 7. Even if the exact values of peak temperatures are not very significant, their increase with
increasing heating rate suggests the hypothesis of the diffusional mechanism controlling both precipitation and reversion, as reported in some works [27, 34, 36]. Start and end temperatures of processes have the same increasing behavior. Moreover, the temperature range, at which each process occurs, is similar to the results specified by Sha et al. [27]. As regards the enthalpy associated to precipitation and reversion processes, it is directly correlated to the amount of formed species. Since the enthalpy values do not differ much (table 8, 9, 10 and 11), AB and SOL samples exhibit similar behaviors in precipitation and reversion. The similarity in ageing sequence is shown by DSC curves and by isothermal ageing curves (figure 27). The recorded curves for the different samples are qualitatively parallel except for the curve recorded for AB at 30°C/min, probably because of some errors in experimental setup. Therefore it can be stated that there are no significant differences between them. After this general analysis, the comparison among the different samples was done by analysing the computed kinetic data.

Table 4. Peak temperatures of peak 1.

<table>
<thead>
<tr>
<th>Peak 1</th>
<th>AB</th>
<th>SOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (K/min)</td>
<td>Peak temperature (°C)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>470,01</td>
<td>465,86</td>
</tr>
<tr>
<td>30</td>
<td>480,32</td>
<td>477,3</td>
</tr>
<tr>
<td>40</td>
<td>484,36</td>
<td>478,28</td>
</tr>
</tbody>
</table>

Table 5. Peak temperatures of peak 2.

<table>
<thead>
<tr>
<th>Peak 2</th>
<th>AB</th>
<th>SOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (K/min)</td>
<td>Peak temperature (°C)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>580,72</td>
<td>579,23</td>
</tr>
<tr>
<td>30</td>
<td>597,47</td>
<td>589,19</td>
</tr>
<tr>
<td>40</td>
<td>599,48</td>
<td>596,96</td>
</tr>
</tbody>
</table>

Table 6. Peak temperatures of peak 3.

<table>
<thead>
<tr>
<th>Peak 3</th>
<th>AB</th>
<th>SOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (K/min)</td>
<td>Peak temperature (°C)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>676,75</td>
<td>679,39</td>
</tr>
<tr>
<td>30</td>
<td>689,55</td>
<td>689,19</td>
</tr>
<tr>
<td>40</td>
<td>695,11</td>
<td>695,64</td>
</tr>
</tbody>
</table>
### Table 7. Peak temperatures of peak 4.

<table>
<thead>
<tr>
<th>Peak 4</th>
<th>AB</th>
<th>SOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (K/min)</td>
<td>Peak temperature (°C)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>776,05</td>
<td>771,89</td>
</tr>
<tr>
<td>30</td>
<td>779,47</td>
<td>775,26</td>
</tr>
<tr>
<td>40</td>
<td>780</td>
<td>777,06</td>
</tr>
</tbody>
</table>

### Table 8. Enthalpies of peak 1.

<table>
<thead>
<tr>
<th>Peak 1</th>
<th>AB</th>
<th>SOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (K/min)</td>
<td>Enthalpy (J/g)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2,08</td>
<td>2,03</td>
</tr>
<tr>
<td>30</td>
<td>1,47</td>
<td>3,8</td>
</tr>
<tr>
<td>40</td>
<td>1,53</td>
<td>2,18</td>
</tr>
</tbody>
</table>

### Table 9. Enthalpies of peak 2.

<table>
<thead>
<tr>
<th>Peak 2</th>
<th>AB</th>
<th>SOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (K/min)</td>
<td>Enthalpy (J/g)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>8,74</td>
<td>8,79</td>
</tr>
<tr>
<td>30</td>
<td>9,57</td>
<td>7,89</td>
</tr>
<tr>
<td>40</td>
<td>10,52</td>
<td>7,01</td>
</tr>
</tbody>
</table>

### Table 10. Enthalpies of peak 3.

<table>
<thead>
<tr>
<th>Peak 3</th>
<th>AB</th>
<th>SOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (K/min)</td>
<td>Enthalpy (J/g)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-10,28</td>
<td>-8,78</td>
</tr>
<tr>
<td>30</td>
<td>-13,19</td>
<td>-10,47</td>
</tr>
<tr>
<td>40</td>
<td>-13,99</td>
<td>-7,23</td>
</tr>
</tbody>
</table>

### Table 11. Enthalpies of peak 4.

<table>
<thead>
<tr>
<th>Peak 4</th>
<th>AB</th>
<th>SOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (K/min)</td>
<td>Enthalpy (J/g)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-2,41</td>
<td>-3,1</td>
</tr>
<tr>
<td>30</td>
<td>-1,56</td>
<td>-4,16</td>
</tr>
<tr>
<td>40</td>
<td>-1,9</td>
<td>-2,73</td>
</tr>
</tbody>
</table>
**Determination of activation energy**

DSC scans were performed at three different heating rates for each sample in order to extract kinetic data. The obtained curves for AB and SOL samples are reported in figures 21 and 22.

![DSC curves of SOL samples](image)

*Figure 21. DSC curves of SOL samples.*

![DSC curves of AB samples](image)

*Figure 22. DSC curves of AB samples.*

The reaction extent $Y$ of precipitation and the rate of precipitation $dY/dT$ were computed for each sample, examining all peaks. An example of the results of the analysis of peak 1 in AB sample is depicted in figure 23. The other curves and plots are reported in appendix 5.4-5.7. The transformation degree curves always show a characteristic sigmoid shape and they shift at higher temperatures as heating rate increases. Also $dY/dT$ plots show the same behavior; these features confirm that precipitation and reversion are controlled by diffusion.
By working out the data recorded with DSC tests the activation energies were evaluated. The Friedman method allows to obtain the so-called Arrhenius plots, i.e. $\frac{dY}{dt}$ vs $\frac{1}{T}$. The activation energy was computed through the average slope of the calculated linear fittings. The application of this method on peak 1 of AB samples is shown in figure 24.
Also the Kissinger method was applied and the plots $\ln\left(\frac{T_p^2}{\Phi}\right)$ vs. $\frac{1}{T}$ were obtained. The calculated slope is proportional to the activation energy. The method applied again on peak 1 of AB samples is reported in figure 25. The resulting activation energies for each peak and sample are listed table 12.

Table 12. Activation energies (kJ/mol) for all peaks in AB and SOL samples.

<table>
<thead>
<tr>
<th>$E_a$ (kJ/mol)</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AB</td>
<td>SOL</td>
<td>AB</td>
<td>SOL</td>
</tr>
<tr>
<td><strong>Kissinger</strong></td>
<td>204,97</td>
<td>205,73</td>
<td>174,48</td>
<td>274,41</td>
</tr>
<tr>
<td><strong>Friedman</strong></td>
<td>196,51</td>
<td>179,68</td>
<td>183,61</td>
<td>315,68</td>
</tr>
</tbody>
</table>

First of all, only the result obtained with Kissinger method are considered reliable because they are coherent with literature reports. The high differences between the results achieved by applying Kissinger and Friedman for peaks 2 and 3 should be attributed to the difficulties in evaluating the start and end temperatures. No results were found in literature for the activation energies of peak 1 and peak 4, but a qualitative consideration can be made about peak 1. Since peak 1 is related to short-range diffusion such as clustering, there are no differences in activation energy between AB and SOL specimens. On the contrary the processes related to long-range diffusion, i.e. main strengthening precipitates formation (peak 2) and austenite reversion by diffusion (peak 3), show differences in activation energy.
As regards precipitation Sha et al. [27] reported an activation energy of 205.1 kJ/mol in the case of wrought 250 maraging steel. Kapoor and Batra [36] found a value of 265 kJ/mol in 350 maraging steel. Menapace et al. [34] obtained the values of 150 kJ/mol and 269 kJ/mol corresponding to a 300 maraging steels sintered in two different conditions; the dissimilar energy values are attributed to the difference in grain sizes and defects number. Looking at the Kissinger method results for peak 2, we can see that the energies given by Ref. [34] and Ref. [36] are close to the SOL precipitation energy, while the smaller value in [34] is closer the AB activation energy.

For austenite reversion activation energies of 342 kJ/mol [27] and of 423 kJ/mol [36] were reported. The corresponding result for SOL is similar to the first value. It is notable that SOL activation energies are comparable to those for lattice diffusion of Ni (245 kJ/mol), Ti (272 kJ/mol), Mo (238 kJ/mol) in α-Fe. This confirms that both reversion and precipitation are processes under diffusive control. The activation energy of AB samples is lower than SOL samples owing to the different microstructures. The fine cellular AB microstructure facilitates diffusion: the smaller the crystalline size is, the smaller the activation energy is because of the effects of grain boundaries on diffusion.

3.1.3 Ageing tests

Since maraging is a precipitation hardenable alloy, it can be subjected to hardening during the printing process. During processing the steel is exposed to a complex thermal history depicted in figure 26.

![Figure 26. Scheme of thermal history of SLM processed parts [14].](image)

The powder production and the laser melting involve high cooling rates so that precipitation cannot occur. However the heat provided to melt powders may modify the
hardness in region near the melt pool, i.e. in the heat affected zone. So the chance to have precipitation hardening is localized in the already solidified material. The heat affected zone does not reach the melting temperature but it is subjected to a cyclic heating in the right temperature range to have ageing. This can be considered as an intrinsic ageing treatment.

To investigate the influence of the intrinsic heat treatment, hardness tests were performed on as build and solubilised samples. After that ageing treatments were conducted to estimate how different heat treatments can affect the mechanical response of the material.

Isothermal ageing at 460°C and 490°C were carried out and the corresponding hardness curves are depicted in figure 27. The difference between AB and SOL samples is clear in the non-aged condition; hardness drops from 371 HV in AB to 279 HV in SOL. All the values are listed in appendix 5.2.

As ageing proceeds the gap readily disappears, after 30 min of ageing the hardness values are comparable and remain similar for the rest of the considered ageing times. The higher hardness of AB sample in the non-aged condition can be due to the finer microstructure that leads to the Hall-Petch strengthening, to the formation of small amount of precipitates or to the formation of dislocations due to extremely fast cooling [23].

The hardness slowly and continuously increases until the hardness peak is achieved. In this first zone the hardening is due to precipitation of coherent particles while the peak

Figure 27. Isothermal ageing curves of AB and SOL at 460°C and 490°C.
hardness is related to $\text{Ni}_5(\text{Ti, Mo})$ precipitation. The precipitation of Fe-Mo phases after Ni compounds contributes to maintain the hardness also in overageing [7]. Both kind of samples reach the peak hardness at the same time for the same temperature. After 8 hours of ageing at 460°C, AB and SOL samples arrive at 632 HV and 613 HV, respectively. While after 4 hours of ageing at 490°C, they reach 607 HV and 616 HV peak hardness, respectively. A characteristic of both temperatures is that at long ageing time the loss of hardness is quite moderate. This behaviour can be explained by the low ageing temperature; coarsening, dissolution of precipitates and austenite reversion take place to a lower extent and more slowly.

The activation energy for precipitation can be extracted also from isothermal ageing curves, by plotting the time at which peak hardness is reached versus the reciprocal of the ageing temperature. This plot can be fitted by the following equation:

$$\ln(t) = \frac{E_a}{RT} + C$$

where $t$ is the time at which peak hardness is reached in hours, $E_a$ is the activation energy and $C$ is a constant. The slope of the fit will provide the activation energy: using the results of AB ageing (table 14) the computed $E_a$ is 137 kJ/mol, very close to 132±10kJ/mol reported by Pardal et. al [19] for a solution treated 300 maraging steel.

The isothermal ageing curves and the computed activation energy provide another argument in favour of the small gap of mechanical differences in ageing between as build and solubilised samples.

### 3.1.4 Tensile test

In order to fully investigate the differences of AB and SOL samples their tensile properties were compared. Tensile tests were performed on non-aged samples and on the peak aged condition at 460°C for 8h; all specimens were horizontally oriented. The resulting curves are reported in figure 28. While the mechanical properties are listed in the following table 13.
Table 13. Tensile tests results of AB and SOL samples, non-aged and peak aged at 460°C.

<table>
<thead>
<tr>
<th></th>
<th>( \varepsilon_R ) (%)</th>
<th>UTS (MPa)</th>
<th>YS (MPa)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As build</td>
<td>6.1 ( \pm ) 1.3</td>
<td>1188 ( \pm ) 10</td>
<td>898 ( \pm ) 18</td>
<td>164 ( \pm ) 5</td>
</tr>
<tr>
<td>Sol. treated</td>
<td>6.8 ( \pm ) 0.8</td>
<td>1074 ( \pm ) 11</td>
<td>718 ( \pm ) 5</td>
<td>162 ( \pm ) 3</td>
</tr>
<tr>
<td>AB-460°C 8h</td>
<td>1.5 ( \pm ) 0.2</td>
<td>2017 ( \pm ) 58</td>
<td>1955 ( \pm ) 43</td>
<td>183 ( \pm ) 5</td>
</tr>
<tr>
<td>SOL-460°C 8h</td>
<td>1.3 ( \pm ) 0.1</td>
<td>1995 ( \pm ) 113</td>
<td>-</td>
<td>181 ( \pm ) 7</td>
</tr>
</tbody>
</table>

Figure 28. Stress-strain curves of non-aged (a) and peak aged (b) samples.

As regards non-aged samples, the effect of the solution treatment is an overall reduction in mechanical properties. SOL samples show lower ultimate tensile strength (UTS), namely 1074 MPa instead of 1188 MPa, and a much lower yield strength (YS), 718 MPa instead of 898 MPa. However they have an analogous elastic modulus (E) and an analogous elongation at fracture (\( \varepsilon_R \)%). In both non-aged and peak aged conditions.

Moreover it can be noted that SOL samples exhibit a low work hardening ability. Stress-strain curve show a peak stress after a relatively small plastic deformation, followed by a continued decrease of stress. The low extent of work hardening is a typical characteristic of maraging steels but the understanding of this behaviour is limited [9, 37, 38]. On the contrary AB samples show a quite stable plateau, with higher work hardening, thus higher UTS. The reason of this performance, considering the microstructural analyses, may be the finer microstructure. By looking at the non-aged hardness and at these tensile test results, it appears that the Hall-Petch strengthening causes such a behaviour.
By looking at the peak aged samples, we can see that the behaviour changes from ductile to brittle and that the differences disappear. As the intermetallic precipitates interact with the dislocations, they are the main strengthening mechanism, thus the other strengthening mechanisms are overwhelmed in the peak aged conditions. The mechanical properties of aged samples are similar, even if SOL samples appear slightly less performing.

To summarize, the analyses on as build and solution treated samples show a change in the microstructure whose effects emerge in the hardness in not-aged conditions, in mechanical performances and in the change in activation energies. Looking at the ageing behaviour, no significant differences can be found. The solution treatment seems to have a detrimental effect on the mechanical properties. Therefore, based on isothermal ageing curves, tensile tests and DSC results further analyses were carried on as build samples, only aged at different ageing time, without any solution treatment.

3.2 AS BUILD SAMPLES CHARACTERIZATION

Based on the previous results an extensive characterization of ageing of as build samples was carried out. Isothermal ageing curves were collected at different temperatures; then tensile tests were performed on samples aged at significant times. The microstructural analysis, using optical microscopy, SEM and XRD, allowed to assess the presence of retained austenite and its influence on the mechanical properties.

3.2.1 Ageing test

Further ageing tests were performed on as build samples at different ageing temperatures. The selected ageing temperatures were 460°C, 490°C, 540°C and 600°C and the resulting isothermal ageing curves are represented in figure 29. The complete list of hardness values is in appendix 5.2 and 5.3.

The typical ageing behaviour occurs in all curves. Each curve shows a sharp hardness increase from the AB hardness (371 HV) due to coherent precipitation and to the onset of the main strengthening precipitation. Then hardness continuously increases, following the increase of precipitate volume fraction, until a peak is reached. After the
peak overageing occurs and hardness decreases. The hardness drop due to overageing is moderate at 460°c and 490°C, while it is pronounced at the higher temperatures of 540°C and 600°C. The time at which the same hardness is reached decreases with temperature, i.e. the hardening is more rapid because temperature accelerates diffusion and thus solid state transformations. It can be noted also that peaks occur earlier and have a lower hardness value as temperature grows. The temperatures and times recommended by ASTM for 300 maraging steel ageing vary from 450°C to 510°C for times from 3 hours to 8 hours [33]. As we can see the ageing curves for temperatures in that range does not exhibit a marked overageing and the peak hardness is high.

The dependence of peak hardness with temperature is linked to the processes involved in ageing: as temperature increases precipitation and coarsening proceed faster and can also occur along with austenite reversion [34, 36]. So the full hardness cannot be achieved at high temperatures such as 540°C and 600°C. The pronounced difference in achievable hardness is mainly related to precipitates coarsening and dissolution and to austenite reversion. At ageing temperatures higher than 500°C the fraction of retained austenite increases [7]. The austenite presence affects hardness and influences the tensile properties. Peak hardness and the time at which it is reached are reported table 14.

Figure 29. Vickers hardness evolution in isothermal ageing of AB samples.
Table 14. Peak hardness at different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>460°C</th>
<th>490°C</th>
<th>540°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>8 h</td>
<td>4 h</td>
<td>1 h</td>
<td>10 min</td>
</tr>
<tr>
<td>Hardness (HV)</td>
<td>632</td>
<td>608</td>
<td>567</td>
<td>537</td>
</tr>
</tbody>
</table>

These results are in good agreement with other studies. They show that the peak hardness at similar temperatures occurs in the same range of time for SLM processed maraging steel [10, 33]. The hardness values are similar to wrought aged maraging steels [19, 33].

3.2.2 Microstructural characterization of aged samples

The microstructure of aged samples was investigated through SEM, optical microscopy and X-ray diffraction (XRD) analyses. Using SEM and optical analyses, a qualitative investigation was performed to assess the occurrence of austenite reversion. In order to evaluate the effect of reverted austenite fraction on the mechanical properties, a quantitative phase analysis was carried out with Rietveld refinement on the XRD results. Also an image analysis evaluation was performed to assess the phases balance starting from SEM micrographs using the ImageJ software.

**Optical and SEM analysis**

The microstructure of samples was investigated after surface polishing and etching. The etchant was 4% picral solution that attacks in a different way austenite and martensite. They appear bright and dark, respectively.

Optical and SEM micrographs of peak aged (460°C 8h, 490°C 4h, 540°C 1h, 600°C 10min) and overaged (540°C 8h, 600°C 4h) samples were taken. SEM micrographs are summarized in figure 32. Ageing causes nucleation and growth of austenite at cell boundaries where it is already present, even though in a lower amount, as shown in figures 32a, 32b and 32c. The high temperature (540°C, 600°C) ageing promotes further austenite reversion. γ-Fe is extensively present at cell boundaries of the corresponding samples and it also appears within the cells in overaged samples (figure 32d, 32f). An extreme case is depicted in figure 32f, austenite reversion occurs in such an extent that
the previous microstructure is barely visible. These results are consistent with literature; it is demonstrated that γ-Fe starts to grow at lath martensite and, as ageing proceeds, nucleate within the martensite lath [21, 22, 24]. In the case of SLMed samples the microstructure is not composed by lath martensite but the nucleation sequence is the same. The optical micrographs are consistent with these aspects. At low ageing temperatures austenite is found at cell boundaries only as small pockets (figure 30a). At increasing temperatures it grows extensively at that boundaries (figure 30b). In the end at high temperature and prolonged ageing, the growth within grains occurs and it is difficult to distinguish the microstructure (figure 31).

Figure 31. Optical micrographs of samples: (a) aged at 460°C 8h, the pockets of austenite are indicated by arrows; (b) aged at 540°C 8h, the white constituent indicated by arrows is the austenite at cell boundaries.

Figure 30. Optical micrograph of sample aged at 600°C 4h.
Figure 32. SEM micrographs of samples aged at temperature and time: 460°C 8h (a), 490°C 4h (b), 540°C 1h (d), 540°C 8h (d), 600°C 10min (e) and 600°C 4h (f).
Austenite starts to nucleate at cell boundaries. This phenomenon can be attributed to three factors. The first factor involves diffusional processes that are accelerated by defects, namely grain boundaries. The second factor rely on the similarity between SLM processed metal microstructure and weld metal microstructure. Because of the fast cooling of the melted weld metal, elemental segregation at the cellular grain boundary occurs. Such segregation lowers austenite transformation start temperature ($A_s$) [22]. Since there is higher content of Ni at cell boundaries, $A_s$ in that region is lower, thus γ-Fe appears earlier. The third factor is the presence of retained austenite at cellular boundaries in AB samples; the energy needed to have heterogeneous nucleation on it is lower than that needed to nucleate a new pocket [23].

The SEM micrographs were analysed to obtain the phase balance and to provide a comparison with the quantitative phase analysis performed with Rietveld method. The results are listed in table 15.

*Table 15. Phases balance from chromatic analysis.*

<table>
<thead>
<tr>
<th></th>
<th>Martensite (%)</th>
<th>Austenite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As build</td>
<td>90,7</td>
<td>9,3</td>
</tr>
<tr>
<td>460°C 8h</td>
<td>81,2</td>
<td>18,8</td>
</tr>
<tr>
<td>490°C 4h</td>
<td>82,8</td>
<td>17,2</td>
</tr>
<tr>
<td>540°C 1h</td>
<td>79,6</td>
<td>20,4</td>
</tr>
<tr>
<td>540°C 8h</td>
<td>80,8</td>
<td>28,7</td>
</tr>
<tr>
<td>600°C 10 min</td>
<td>71,3</td>
<td>19,2</td>
</tr>
</tbody>
</table>
Rietveld refinement

The quantitative phase analysis was performed on diffraction patterns obtained from AB, peak aged (460°C 8h, 490°C 4h, 540°C 1h, 600°C 10min) and overaged (540°C 8h) samples using Maud software with Rietveld method. According to literature XRD analysis of maraging steel should show the presence of martensitic ($\alpha'$) and austenitic ($\gamma$) phases reflections, while the peaks related to precipitates presence have a very low intensity because of their small size and small volume fraction [39]. The peaks identification allowed to associate each peak to a plane reflection for each phase, namely $(111)_\gamma$, $(110)_{\alpha'}$, $(200)_{\gamma}$, $(200)_{\alpha'}$, and $(211)_{\alpha'}$ [12, 25, 33]. The XRD patterns are reported in figure 33.

As we can see ageing heat treatment increases the intensity of the peaks that correspond to austenite; the reflex $(111)_\gamma$ appears, while martensite peaks intensity decreases. This is related to the increase of austenite fraction, because the intensity of each peak is proportional to the volume fraction of the matching phase. To evaluate the reliability of the refinement, the ratio $GOF = R_{wp}/R_{exp}$ was computed (table 16). The accuracy of the fitting procedure should be lower than 2 to have a statistical consistency, therefore improvements in the fitting can be done. The results of the quantitative phase

*Figure 33. XRD patterns of AB, peak aged and overaged samples.*
analysis and a comparison with the result of chromatic analysis are listed in table 16 and figure 34.

Table 16. Rietveld refinement results.

<table>
<thead>
<tr>
<th></th>
<th>Martensite (%)</th>
<th>Austenite (%)</th>
<th>GohF</th>
</tr>
</thead>
<tbody>
<tr>
<td>As build</td>
<td>88,7</td>
<td>11,3</td>
<td>2,33</td>
</tr>
<tr>
<td>460°C 8h</td>
<td>84,5</td>
<td>15,5</td>
<td>2,06</td>
</tr>
<tr>
<td>490°C 4h</td>
<td>83,9</td>
<td>16,1</td>
<td>1,81</td>
</tr>
<tr>
<td>540°C 1h</td>
<td>82,8</td>
<td>17,2</td>
<td>2,25</td>
</tr>
<tr>
<td>540°C 8h</td>
<td>78,7</td>
<td>21,3</td>
<td>1,90</td>
</tr>
<tr>
<td>600°C 10 min</td>
<td>82,9</td>
<td>17,1</td>
<td>1,65</td>
</tr>
</tbody>
</table>

These data show a high increase of austenite volume fraction resulting from the ageing. As expected the γ-Fe fraction grows with temperature and time. Literature reports similar fractions of austenite at similar temperatures [25]. It is notable that also the AB sample contains a fraction of γ-Fe. The presence of austenite in as build samples was also reported by Kempen et al. [33]. On the contrary in solubilized steels the γ-Fe content is so low to be considered as negligible.

Figure 34. Rietveld refinement and chromatic analysis results comparison.
3.2.3 Tensile test

In order to have a deeper understanding of the influence of ageing temperature on mechanical properties, tensile tests were performed on AB and aged specimens at room temperature. The influence of porosity and defects on the achievable strength and elongation is also considered. The correlation between reverted austenite fraction and the mechanical properties is investigated.

At first vertically (V) and horizontally (H) oriented specimens were compared. Tests on AB and 460°C-8h samples, that is the peak aged condition at 460°C, provide the following results (figure 35). As we can see V samples show worse performances than H samples in both conditions. Only a stress-strain curve corresponding to V samples is shown in figure 35b because of the premature failure of the other tested specimens. Lower elongation and lower tensile strength are attributed to the orientation of the layer with respect to the loading direction [32].

![Stress-strain curves of as build (a) and aged (b) samples, horizontally and vertically aligned.](image)

The production technique causes a preferential position of defects. Porosity and melting defects are more likely found at the interface among different layers hence aligned on the horizontal plane. In vertical samples the loading direction is orthogonal to the layer surfaces, while in horizontal ones it is parallel to them. Since defects are placed orthogonal to the loading direction in V samples, they can lead to cross section reduction. However it should be noted that porosity causes earlier failure and scattering of results in all tested conditions.
Further tensile tests were performed on all peak aged conditions. A test on 540°C-8h sample was added in order to evaluate the mechanical behaviour in overaged conditions, and to investigate the effects of austenite reversion. The stress-strain curves for all tested conditions are depicted in figure 36 and the average elongation at fracture, UTS and 0.2% yield strength (YS) are reported in table 17.

Table 17. Results of tensile tests on AB, peak aged and 540°C-8h samples.

<table>
<thead>
<tr>
<th>Condition</th>
<th>εR (%)</th>
<th>UTS (MPa)</th>
<th>YS (MPa)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As build</td>
<td>6.1 ±1.3</td>
<td>1188 ±10</td>
<td>915 ±13</td>
<td>160 ±9</td>
</tr>
<tr>
<td>460°C 8h</td>
<td>1.5 ±0.2</td>
<td>2017 ±58</td>
<td>1955 ±43</td>
<td>183 ±5</td>
</tr>
<tr>
<td>490°C 4h</td>
<td>1.2 ±0.1</td>
<td>1815 ±95</td>
<td>1793 ±97</td>
<td>189 ±7</td>
</tr>
<tr>
<td>540°C 1h</td>
<td>2.1 ±0.3</td>
<td>1957 ±54</td>
<td>1870 ±54</td>
<td>190 ±6</td>
</tr>
<tr>
<td>540°C 8h</td>
<td>1.8 ±0.1</td>
<td>1656 ±88</td>
<td>1546 ±103</td>
<td>193 ±15</td>
</tr>
<tr>
<td>600°C 10 min</td>
<td>1.6 ±0.1</td>
<td>1659 ±119</td>
<td>1557 ±140</td>
<td>181 ±6</td>
</tr>
</tbody>
</table>

The differences between aged and AB specimens involves all the collected data. AB samples show a higher ductility with a moderately low yield strength and a lower elastic modulus. Low temperature ageing leads to a very large increase in yield strength, from 915 MPa of as build samples to 1955 MPa and 1793 MPa for 460°C and 490°C peak aged samples, that is an increase of 113% for AB-460-8h and of 96% for AB-490-4h. The ageing also promotes an increase in Young’s modulus and a very large reduction in the achievable elongation, from 6.1% to 1.5% and 1.2% for the same samples. For all specimens the tensile tests show an increase in elastic modulus from 160 GPa to around 189 GPa. This result is almost the same of that reported by Yasa et al. [10]. This behaviour is ascribed to the precipitation of Ni₃(Ti,Mo); the reduction of Ni content in
the martensitic matrix may lead to such an increase. The mechanical properties of samples, aged in the right interval of temperature (460°C 8h, 490°C 4h, 540°C 1h), are similar to wrought maraging 300 apart from ductility which is reduced in all conditions.

The presence of an increasing austenite fraction may lead to a growth of ductility and toughness together with a decrease in yield strength and UTS, as reported in literature [21, 22, 37]. Specifically, Viswanthan et al. [21] studied a wrought 350 maraging steel and reported that austenite reversion causes a decrease strength and an increment in elongation and impact toughness. However the increase occurs only in the first stages of overageing, because coarsening and extensive austenite reversion reduce all mechanical properties as time proceeds. In order to evaluate the effect on studied specimens, yield strength and elongation at fracture of each tested specimen were plotted versus the austenite fraction, as depicted in figure 37.

![Figure 37. Elongation (a) and yield strength (b) plotted against austenite fraction.]

The ductility reduction is a characteristic of aged maraging steels [9, 38], and it is related to the strengthening of the matrix because of the presence of precipitates. However the fracture elongation of selective laser melted components is quite lower than the elongation of wrought maraging steels both in as build and aged samples [41]. The low ductility of aged specimens is consistent with literature and datasheet that reports fracture elongation between 1.5% and 2% [10, 32, 42]. The austenite effect on elongation seems negligible, all aged specimen elongations are in a small range of values irrespectively to austenite content (figure 37a). The presence of porosity and melting faults, that are typical defects in SLM processed parts, along with the intrinsically brittle full-strength aged matrix are considered to explain such a reduction. Indeed big voids
and unmolten particles are distributed in the tested specimens as we can see in fracture surfaces. They cause early failure of specimens so that the austenite effect be barely seen: the overaged specimen (540°C 8h, 21,3% γ-Fe) shows a mean elongation of 1,8%, close to the value 1,5% of the low temperature peak aged sample (460°C 8h, 15,5% γ-Fe). The effect on yield strength is less clear because the reduction in strength is ruled not only by the austenite content. The total effect of ageing is a combination of softening and hardening mechanisms which cannot be fully separated. The precipitation of strengthening intermetallic compounds, the austenite reversion and the coarsening and embrittlement of the alloy in overageing contribute to the final performance.

γ-Fe effect was not the expected from what is reported in literature. It is one of the causes of strength loss in the studied samples, but its influence on the ductility is limited with respect to strengthening mechanisms and to precipitate coarsening. Therefore SLM processed components show a strength ruled mainly by precipitation hardening and a ductility governed mainly by defects and precipitates coarsening.

3.2.4 Fracture analysis

The failure mode is examined by means of SEM and optical analysis on fracture surfaces and sectioned broken samples, respectively. The lack of ductility caused by the ageing treatment shown in tensile tests was confirmed by the fractographies. On the contrary specimens without ageing show ductile fracture with extensive plastic deformations. The difference is well visible in figure 38. It is also clear from figure 38(b) that the fracture of this specific specimen orginated from a rather large defect, highlighted by the arrow.

Figure 38. AB (a) and 460°C 8h aged (b) fracture surfaces.
The ductile failure mechanism consists in nucleation, growth and coalescence of microvoids that arise where there are precipitates or defects, and the fracture surface is characterised by the presence of many dimples. These characteristics are visible in SEM fractographies of AB samples. Cavities between scan tracks, unmelted powder particles and splats are the defects that can be found (arrows in figure 39a). As regards the brittle failure, nucleation sites are the same of ductile failure. The fracture mode is different, the brittle mechanism of fracture growth in the aged samples which has a very low extent of plastic deformation, mainly developed by cleavage decohesion (figure 39b).

![Figure 39. High magnification micrographs of fracture surface of AB (left) and aged(right) samples.](image)

The AB and aged sample were also longitudinally sectioned in order to examine the profile intersecting the fracture surface. Figure 40a shows that close to the fracture profile of AB samples, delamination of scan tracks can be identified; it is supposed that during the loading the crack develops easily along these track boundaries because they are regions of preferential defect accumulation. Figure 40b shows the aged sample section. It displays that the amount of plastic deformation is small, and that the fracture occurs by limited modification of the original cellular shape.
Figure 40. SEM micrographs depicting fracture line of AB (a) and aged (b) samples.
3.3 DEFECTS ANALYSIS

The presence of defects is an important issue because it prevents the achievement of full density and affects the mechanical properties, lowering the performance of SLM processed specimens. Parallel- and perpendicular-to-layer sections were analysed to evaluate the causes of defect generation. An investigation on the amount of geometrical irregularities found on as build top surfaces that could possibly affect the deposition and consolidation of the subsequent layers, their dimensions and has been performed. Particularly it was investigated the role of the argon flow direction and powder dispenser direction on the defects distribution. In addition, a dimensional analysis was performed on as received powder and on powder collected around the base plate. This powder was affected by the laser beam because it came from the melt pool but was not embedded in the consolidated layers. This study was carried out to assess the origin of particles that generate defects.

3.3.1 Section analysis

Stereoscope imaging show a widespread presence of porosity (bright) in both parallel and perpendicular sections. It is notable that the statement made before about the preferential disposition of defects among layer boundaries is true as depicted in figure 41. In the parallel-to-layer sections the pores have larger sizes than those in the perpendicular-to-layer section. The optical analysis and the fractography allowed to obtain a complete description of the different kinds of defects created during SLM process.

![Figure 41. Stereoscope picture of sections parallel (a) and perpendicular (b) to layers.](image)
There are two main type of defects that appears in the studied SLM processed samples (figure 43b):

- Unmelted powder particles.
- Splats, that are melted particles coming out from the melt pool submerged in the subsequent layers (figure 42).

The analysis of porosity in parallel-to-layer sections displays the existence of rather big particles in the middle of pores (figure 43a). It can be stated that the presence of such particles causes an inhomogeneous powder deposition and therefore higher probability of porosity generation. The presence of cavities due to the lack of bonding between layers is caused by occurrence of poor deposition quality. The measurement of particle sizes in the pores shows that dimensions range from 40 µm to 250 µm, with a mean size of 117 µm, these are much bigger than the as received powders dimensions. The microstructure of such elements is dendritic and splats are submerged in the layer as shown in figure 42.

![Figure 42. Optical micrographs of splats engulfed in the layer.](image1)

![Figure 43. Stereoscope picture of porosity in parallel-to-layer sections (a), SEM micrograph of a pore showing splats and unmelted powder (b).](image2)
By looking at fractographs the presence of unmolten powder particles in the pores and splats that have a rather bigger size are depicted in figure 44. Splats and powders are indicated by arrows. It seems that splats are the main cause of porosity in studied samples, they are suggested to be the reason of big pores in which we can see unmolten particle presence.

![Figure 44. SEM fractographs of AB (left) and aged (right) specimen showing splats and unmolten powder.](image)

### 3.3.2 Powder characterization

SEM analyses were performed on powders to evaluate the effect of laser melting process on them and to compare them with the defects found in specimens. Two different kinds of powders were analyzed: as received powders and powders collected out from the base plate after processing. The second type of powders is made up of splats that came from the melt pools and are blown away from it by the argon gas flow. Figure 46 depicts the building camera of the used Renishaw AM250 system, it is specified the area of powder collection and the direction of the argon flux.

SEM images show the shape and solidification structure of both powders groups. As regards the shape, the processed particles are bigger and more spherical than the as received ones. The blown particle are affected by heat in such an extent to cause melting and coarsening. The different morphologies at the same magnification are shown in figure 47.
All powders present dendrites as shown by micrographs of figure 45; the optical micrograph of an unmelted particle in a pore is reported, it has the same microstructure of collected powder. The cause of this microstructure can be ascribed to the cooling rate resulting from the powder production method in case of as received powders and from the blowing in case of collected powders.
In order to evaluate the changes in size distribution, pictures as in figure 48 were analyzed with the software ImageJ for image analysis. Through this program it was possible to estimate the statistics about particle diameters by using two approximations: (i) all particles were reduced to their 2D projection, then projections areas were computed; (ii) diameters were obtained by considering all projections as circular.

The results of this computation are summarized in table 1 and figure 49. They show how the processed-particle size increases: minimum, maximum and mean diameter rise and the distribution peak shifts towards higher dimensions and becomes sharper. It is difficult to find particles smaller than 20 µm in the collected powder. Since the collected powders present a different distribution with bigger particles, it can be stated that they may act as starting points for defect generation, being them larger than the layer thickness. By comparing the defect sizes with the sizes of the particles in the pores, it appears that they are smaller in the average. The cause is that the collected particles are

Figure 48. Scheme of the first approximation: backscattered electron micrograph (left) transformed in 2D image (right).

Figure 49. Cumulative (left) and relative (right) frequency (%) of studied powders.
the smaller ones because the bigger blown particles are supposed not to be able to reach long distances from the molten pool.

Table 18. Diameter changes in as received and collected powders.

<table>
<thead>
<tr>
<th></th>
<th>Mean diameter (µm)</th>
<th>Minimum diameter (µm)</th>
<th>Maximum diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received powder</td>
<td>24,31</td>
<td>5,24</td>
<td>59,70</td>
</tr>
<tr>
<td>Collected powder</td>
<td>35,01</td>
<td>7,17</td>
<td>83,78</td>
</tr>
</tbody>
</table>

3.3.3 As built top surfaces analysis

In order to have a better understanding of the defect generation process the as built top surfaces of samples were analysed, and the same approximations used for powder size measurement was applied. The aim was to extend the analysis performed on collected powders and pores and to validate two hypotheses:

- The particles on layer surfaces are the same that were found in the pores.
- The defect quantity and sizes show a trend ruled by gas flow direction and powder dispenser direction

At first an investigation on a small area was carried out. An example of analysed SEM images is shown in figure 50 and 51. There is a distribution of particles welded on the top surface in addition to the evidence of the scanning lines. Particles consists in small unmolten powders and bigger splats of various dimensions.

![Figure 50. SEM image at high magnification of as built top surface.](image-url)
By comparing the obtained results with the results of the collected powders, it is verified that the bigger particles fall near to the melt pool. The relative frequency graph in figure 52b shows the possibility to find rather big particles (>90 µm) on scan tracks; such a dimension is not found in collected powders. The measurements carried on the parallel to layer section showed the presence of big particles that are in the same size range of those found on top surfaces. The difference is that the pores contain more large particles than the number found on unmodified layer surfaces Because the smaller are likely melted during the scanning of the above layer.
Trends in defect distribution

Analysis of the porosity revealed a dependency on the position of samples over the building plate. The amount of defects was found to increase diagonally with respect to the base plate according to the direction of gas flow and powder dispenser direction. To evaluate the effect of the single transport contribution two series of samples, consisting in three 20mm×60mm surfaces, aligned as depicted in figure 53, were analysed. Samples were designated with an increasing number from the “origin” to the plate border. Each surface was divided into smaller areas of 5 mm × 4 mm, obtaining 4 rows and 15 columns (figure 54). These areas were alternatively chosen and processed using Photoshop to isolate splats and particles and then analysed to measure their diameters. Then the number and the diameter of particles in each area was computed and the total particle number and mean particle diameter for each column was plotted against the respective investigated direction. Therefore the following graphs were obtained, as depicted in figure 55.

Figure 53. Scheme of the base plate with studied samples.

Figure 54. Scheme of samples surface partition and of analysed areas.
The result of the analysis shows that even if a trend within all the samples does not clearly appears, the overall behaviour is evident when considering the trend line. In both directions the number of particle increases as the distance from the origin increases (figure 55a, 55c). This result was expected because, as seen before the particles are blown away from the melt pool by the argon flow. So it is likely to found an increasing number of blown particles as we move toward the border of the base plate. The effect of the powder delivery position is less evident. In order to deposit the powder it moves over the baseplate and it probably drags large particles along its path. This is confirmed by the particle diameters which grows with increasing distance (figure 55b). As regards the blown particle dimensions, the data confirm the results reported before. The size is found to decrease along the direction of gas flow (figure 55d). This means that only small particles can reach long distances from the melt pool as we can see also in the size distributions of collected powders and on top surfaces.

Figure 55. Particle number along powder supplier direction (a), toward gas flow (c) and particle diameter along supplier direction (b), gas flow direction (d).
However this analysis does not provide a complete description of defect generation mechanisms. The analysed surfaces appearance, the scattering of the values and the absence of a clear trend suggest that there are also other mechanisms which generate defects. A view of as built top surfaces in different regions is depicted in figure 56. We can see a smooth surface with small round particles corresponding to the splats in figure 56b and very rough surface in figure 56a.

The cause of such roughness cannot be attributed only to the inhomogeneous deposition caused by particles. According to the literature it also involves instabilities of the melt pool and substrate denudation. The melting process and the melt pool flow description is very complex. It is ruled by the laser beam parameters (speed, power), by the preceding layer morphology and by the distribution of the new powder layer. Moreover the fluid-dynamics of the melt pool depends on evaporation, wetting issues related to surface tensions and capillary forces, recoil forces and convection in the melt pool (Marangoni effect) [46, 47, 48]. The convection in the melt bath is considered to play an important role in melt pool stability. The Marangoni effect drives the melt flow from the hot laser spot toward the cold surrounding solid, generating liquid motion and splattering, i.e. the ejection of liquid metal from the melt pool as demonstrated by Khairallah et al. [47].

In addition to convection, the stability of the melt bath depends strongly on its own dimensions and on surface tension. The description of a liquid in contact with a surface can be given by the Young’s equation, which relates the surface free energy with the contact angle (figure 57). By approximating the melt pool with a half cylinder, the melt
pool becomes instable and balling effect occurs when the total surface of the pool becomes larger than that of a sphere with the same volume. Thus the melt bath should have a length-to-diameter ratio as small as possible [5]. Because of this phenomenon, balling can occur also when the environmental conditions are controlled and the substrate is not oxidized.

Substrate denudation refers to coalescence of powders that do not reach the melt pool. The laser beam interacts with the powder and with the substrate that can be the base plate or the previously processed layer. The energy provided by the laser heats the powder and the underlying surface. The heat leads to the formation of the track but it is also conducted through the substrate causing sintering and melting of near the scan line. The denudation zone is the zone around the track where the powders have a lower density [46, 47]. The subsequent scan tracks will find a lower amount of powders and inhomogeneous distribution, so they may generate defects. Another issue is the formation of satellites, remelted particles partially linked to the track that could cause porosity. They are produced by melt splattering and partial powder melting near the scan track [31]. The extensive presence of satellites was found during the surface analysis of lattices created by SLM on the same maraging steel, as reported in appendix 5.1 (figure 58), so it can be considered a possible cause of porosity also during bulky parts production.

Figure 5.7. Young’s equation (a) and balling effect (b) scheme [5].
To summarize the origin of such defects is attributed to the SLM system configuration (gas flow direction and powder dispenser direction) by the analysis of blown powder and unmodified top surfaces. Moreover it can be stated that the roughness arises also from the used process parameters, mainly laser beam power and speed. They are additional sources of porosity because they strongly influence the tracks morphology and the fluid-dynamics of the melt pool. The final porosity will be an overall contribution of all these defect-generating mechanisms.

4 CONCLUSIONS

Selective laser melting (SLM) technique was used to process a 18Ni-300 maraging steel (1.2907). This processing method is an additive manufacturing technique that consist in melting and consolidating micrometric metal powders into solid layers by means of a laser beam. The produced parts are made of a sequence of metallic layers composed of a series of overlapped scan tracks that bounds metallurgically one over the other. Maraging steels are age-hardenable alloys with a low-carbon and high-nickel martensitic matrix. Their usual heat treatment sequence involves at first a solution treatment in fully austenitic region, followed by quenching and an ageing treatment at lower temperature. The ageing treatment temperatures and times are very important for the achievable strength. Strengthening precipitation of Ni$_3$(Ti,Mo) can occur. Additional softening
mechanisms due to coarsening of precipitates and austenite reversion is recorded on overageing.

Since SLM technique is an atypical processing method which involves high cooling rates of the melt pool and the superposition of many layers, the microstructure of as build (AB) samples is very different with respect to common solution treated wrought maraging steels. Micrographs of AB samples made evident the additive procedure and the high cooling rates influence. Scan track boundaries and melt pools were visible; the microstructure was made of cells with size lower than 1 µm and exhibited epitaxial growth among scan line boundaries. Some SLM parts were subjected to solution treatment (SOL) to assess the microstructural modifications of such a heat treatment. SOL samples microstructure was completely different from the AB one. It was composed by fairly coarse laths of martensite, much coarser than the AB cells. EBSD analysis on SOL showed the presence of retained austenite at grain boundaries.

A comparison between solution treated and as build samples was carried out in order to evaluate the differences in ageing sequence and in mechanical properties given by the different microstructures. Kinetic analysis of precipitation was performed using differential scanning calorimetry tests. The resulting DSC curves showed two exothermic peaks corresponding to precipitation and two endothermic peaks corresponding to austenite reversion. The similarity between DSC curves and computed enthalpies of AB and SOL samples suggested small differences in the ageing sequence. AB samples showed a lower activation energy than SOL samples because of the finer microstructure that enhances diffusion. Ageing tests presented a quite similar behavior, peak hardness was reached in the same time at the same temperatures. The only difference appears in non-aged samples likely because the Hall-Petch strengthening given by the finer microstructure of AB samples (371 HV vs 279 HV) was partially lost after solution treatment. Tensile test results showed that solution treatment has a detrimental effect on mechanical properties both in non-aged, and in peak aged conditions. AB samples presented a higher work hardening ability and higher yield strength in all ageing conditions because of the finer microstructure.
Since the solution treated samples were proved to have lower performance and therefore convenience, only AB samples were subjected to further investigation. Ageing tests were performed at temperatures in the ASTM advised ageing temperature range (450-510°C) and at higher temperatures. Ageing times and high temperatures were extended to study overageing behavior, to stimulate austenite reversion and to evaluate its influence on mechanical properties. Isothermal ageing curves reported a decreasing hardness peak which occurs at shorter times as temperature increases. This phenomenon is due to the enhancement of diffusion by temperature which causes the simultaneous occurrence of strengthening and softening mechanisms. The loss of strength in overageing at high temperature is more pronounced than that found in low temperature ageing, owing to massive precipitates coarsening and austenite reversion. The microstructural characterization was performed on all peak aged and an overaged AB samples to study the austenite reversion. Austenite was present in all conditions; the reversion occurs firstly at cell boundaries and then, for the longest ageing times, within the cells. Image analyses based on SEM micrographs and quantitative phase analysis using Rietveld refinement method on XRD patterns allowed to obtain the austenite volume fraction for the investigated samples. As expected, they exhibited an increasing content of γ-Fe for increasing time and temperature. Tensile tests on peak aged and overaged samples were performed. The obtained yield strength, UTS and elastic modulus are similar to those reported for wrought maraging steels with the exception of fracture elongation. Even if it was reported in literature an increment of elongation with increasing austenite fraction, in the preset investigation the influence of γ-Fe on fracture elongation was found to be almost negligible. Thus the reason of such a reduction of elongation can be attributed to the high sample porosity and to the matrix embrittlemnt due to marked strengthening. As regards the γ-Fe effect on yield strength, there is no clear correlation between the decreasing strength and the increasing amount of austenite content. This is because during ageing the reversion occurs along with other softening mechanisms. It seems that austenite has a lower softening effect than coarsening of precipitates. Fracture analysis showed ductile fracture behavior of AB samples with dimples creation and brittle fracture mode of aged samples with cleavage decohesion.
In the end, an analysis on defects found in SLM processed parts was performed. The reason of this analysis were the results of tensile tests and of the fracture analysis. Tensile tests on samples with different layer orientation with respect to loading direction allowed to find the preferential site of porosity generation, the interlayer boundary. The fractographic analysis show that porosity is the main cause of nucleation of cracks and early failure. Analyses on samples section, on powders and on as built top surfaces showed that splats, particles blown away by gas flow from the melt pool, are one of the main type of defects at the origin of porosity. Other results of the analysis of SLM surfaces were that the splats number increases along the gas flow direction and the powder dispenser motion direction, while their dimension decreases along gas flow direction and increases along dispenser motion direction. Another cause of porosity was identified in the instability of the melt pool, probably caused by wrong process parameters (laser beam power and speed).
5 APPENDIX

5.1 LATTICE MICROSTRUCTURE

SLM process allows to produce both massive parts and complex structures with small features. To evaluate the effect of laser melting on small structures, BCC lattices were produced and analysed through optical and SEM microscopy. Lattices were not solution treated. Small and high magnification view of such lattices is reported in figure 59.

These images show an extensive presence of satellites, i.e. powder particles which sinter and metallurgically join with the scan tracks. This effect is clearer in sections of the lattices; the dendritic structure of satellites confirms that the powders stick to the scan tracks (figure 60). This phenomenon is more visible when the tracks create a new surface and does not lay on the preceding layers.
Lattice sections also provide an example of the influence of cooling rate on grains dimensions (figure 61). The bottom of the piece was in contact only with the powder bed, so its cooling rate was slower with respect to the subsequent layers. It is easy to see that the microstructure becomes finer as the solid part becomes larger, i.e. the solidification is more rapid. However the lattices microstructure is the same of as build microstructure, consisting in fine cellular colonies.

5.2 AGEING OF AB AND SOL SAMPLES AT 460°C AND 490°C

Table 19. Hardness values of AB and SOL samples aged at 460°C.

<table>
<thead>
<tr>
<th>Ageing time</th>
<th>AB-460°C</th>
<th>SOL-460°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hardness (HV)</td>
<td>Std. Dev.</td>
</tr>
<tr>
<td>Non aged</td>
<td>371,05</td>
<td>12,85</td>
</tr>
<tr>
<td>30 min</td>
<td>483,96</td>
<td>15,97</td>
</tr>
<tr>
<td>1 h</td>
<td>539,9</td>
<td>13,16</td>
</tr>
<tr>
<td>2 h</td>
<td>560,02</td>
<td>12,35</td>
</tr>
<tr>
<td>3h</td>
<td>579,56</td>
<td>10,30</td>
</tr>
<tr>
<td>4h</td>
<td>600,48</td>
<td>10,60</td>
</tr>
<tr>
<td>6h</td>
<td>603,64</td>
<td>13,46</td>
</tr>
<tr>
<td>8h</td>
<td>632,41</td>
<td>4,654</td>
</tr>
<tr>
<td>12h</td>
<td>610,74</td>
<td>8,36</td>
</tr>
<tr>
<td>16h</td>
<td>611,78</td>
<td>7,79</td>
</tr>
<tr>
<td>24h</td>
<td>607,53</td>
<td>7,39</td>
</tr>
<tr>
<td>2 day</td>
<td>620,84</td>
<td>4,84</td>
</tr>
<tr>
<td>5 day</td>
<td>595,38</td>
<td>6,24</td>
</tr>
<tr>
<td>10 day</td>
<td>588,18</td>
<td>5,13</td>
</tr>
<tr>
<td>14 day</td>
<td>586,6</td>
<td>4,07</td>
</tr>
</tbody>
</table>
### Table 20. Hardness values of AB and SOL samples aged at 490°C.

<table>
<thead>
<tr>
<th>Ageing time</th>
<th>AB-490°C</th>
<th>SOL-490°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hardness (HV)</td>
<td>Std. Dev.</td>
</tr>
<tr>
<td>Non aged</td>
<td>371,05</td>
<td>12,8</td>
</tr>
<tr>
<td>30 min</td>
<td>562,85</td>
<td>6,53</td>
</tr>
<tr>
<td>1 h</td>
<td>565,94</td>
<td>5,08</td>
</tr>
<tr>
<td>2 h</td>
<td>590,96</td>
<td>4,24</td>
</tr>
<tr>
<td>3h</td>
<td>604,35</td>
<td>5,32</td>
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<tr>
<td>4h</td>
<td>607,75</td>
<td>4,70</td>
</tr>
<tr>
<td>6h</td>
<td>594,68</td>
<td>3,36</td>
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<tr>
<td>8h</td>
<td>599,62</td>
<td>5,67</td>
</tr>
<tr>
<td>12h</td>
<td>600,28</td>
<td>4,51</td>
</tr>
</tbody>
</table>

### 5.3 Ageing of AB samples at 540°C and 600°C

### Table 21. Hardness values of AB samples aged at 540°C and at 600°C.

<table>
<thead>
<tr>
<th>Ageing time</th>
<th>AB-540°C</th>
<th>AB-600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hardness (HV)</td>
<td>Std. Dev.</td>
</tr>
<tr>
<td>Non aged</td>
<td>371,0563</td>
<td>12,854</td>
</tr>
<tr>
<td>5 min</td>
<td>478,1429</td>
<td>5,744811</td>
</tr>
<tr>
<td>10 min</td>
<td>530,8286</td>
<td>7,736001</td>
</tr>
<tr>
<td>15 min</td>
<td>534,2</td>
<td>4,345496</td>
</tr>
<tr>
<td>30 min</td>
<td>568,4571</td>
<td>6,305515</td>
</tr>
<tr>
<td>1 h</td>
<td>582,8429</td>
<td>6,948107</td>
</tr>
<tr>
<td>2h</td>
<td>561,5857</td>
<td>3,700643</td>
</tr>
<tr>
<td>3h</td>
<td>567,1429</td>
<td>6,884973</td>
</tr>
<tr>
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5.4 $Y$ and $dY/dT$ vs. $T$ Curves for Precipitation

Figure 63. $Y$ and $dY/dT$ versus temperature curves for peak 1 in AB samples at different heating rates.

Figure 64. $Y$ and $dY/dT$ versus temperature curves for peak 1 in SOL samples at different heating rates.

Figure 62. $Y$ and $dY/dT$ versus temperature curves for peak 2 in AB samples at different heating rates.
Figure 65. Y and dY/dT versus temperature curves for peak 2 in SOL samples at different heating rates.

5.5 ARRHENIUS AND KISSINGER PLOTS FOR PRECIPITATION

Figure 66. Arrhenius (left) and Kissinger (right) plots for peak 1 in AB samples.

Figure 67. Arrhenius (left) and Kissinger (right) plots for peak 1 in SOL samples.
5.6 $Y$ AND $dY/dT$ VS. $T$ CURVES FOR REVERSION

Figure 68. Arrhenius (left) and Kissinger (right) plots for peak 2 in SOL samples.

Figure 69. Arrhenius (left) and Kissinger (right) plots for peak 2 in AB samples.

Figure 70. $Y$ and $dY/dT$ versus temperature curves for peak 3 in AB samples at different heating rates.
Figure 71. Y and dY/dT versus temperature curves for peak 3 in SOL samples at different heating rates.

Figure 72. Y and dY/dT versus temperature curves for peak 4 in AB samples at different heating rates.

Figure 73. Y and dY/dT versus temperature curves for peak 4 in SOL samples at different heating rates.
5.7 **Arrhenius and Kissinger Plots for Reversion**

**Figure 74.** Arrhenius (left) and Kissinger (right) plots for peak 3 in AB samples.

**Figure 75.** Arrhenius (left) and Kissinger (right) plots for peak 3 in SOL samples.

**Figure 76.** Arrhenius (left) and Kissinger (right) plots for peak 4 in AB samples.
Figure 77. Arrhenius (left) and Kissinger (right) plots for peak 4 in SOL samples.
6 Bibliography


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