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Abstract

In Selective Laser Melting (SLM) layers of atomized powder are spread sequentially on a building platform and melted locally by a laser beam. The melt pool is quenched by the underlying material. SLM of AlSi10Mg alloys results in the development of microstructures consisting of supersaturated primary Al-rich phase surrounded by varied amounts of Al-Si eutectic. The origin of such microstructure is not fully understood. For insight into this issue, this work compares the results of processing AlS10Mgi alloys by SLM and by single-step rapid solidification techniques: Melt Spinning (MS) and Copper Mould Casting (CMC) achieving a range of cooling rates and microstructures which are analysed by means of microscopy, XRD and DSC.

The results obtained in these experiments together with the literature available on rapidly solidified Al-Si alloys suggest a correlation among microstructures of the products made with the three techniques. Data on lattice parameter and enthalpy of Si precipitation from primary Al concur in indicating that Si supersaturation scales in the order SLM > CMC > MS. The type and size of microstructural features, i.e. cells, columns, fibrous and lamellar eutectic, reveal the role of solidification conditions (undercooling, recalescence) and precipitation in the solid state for all techniques. Dendrite growth modelling validates the solidification results.

Keywords: Selective Laser Melting (SLM), rapid solidification, aluminium alloys, solid solubility extension, Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD)

1. Introduction

Additive Manufacturing (AM) is the term used to indicate all 3D manufacturing processes employed to build components by adding material step by step, in contrast with established subtractive manufacturing processes [1]. Among them, laser powder bed fusion process (L-PBF), commonly defined Selective Laser Melting (SLM), is the most widespread for processing metals [2,3]. In SLM layers of atomized powder are spread on a preheated building platform and melted locally by a laser beam according to a CAD model of the designed object. Once the pattern of the first layer is complete, the building platform drops one step down, the build is recoated with new powder, and the process is repeated until an entire object is made additively. The interaction of the moving laser beam with the metal powder produces a melt pool which is rapidly quenched by the pre-solidified layers. This processing route has been extensively studied in the past years for Al-Si alloys [4].

Eutectic and hypoeutectic Al-Si alloys (e.g. AlSi12, AlSi10Mg and A357) have good castability, low shrinkage and low melting temperature, ideal for conventional casting, and were selected by several authors as material to test powder bed AM in which the morphology and amount of refined eutectic Si are acknowledged to be significant factors influencing the mechanical properties of Al-Si alloys [5–10].

Although the production and characterization of AM samples has provided substantial information on processing parameters for these materials [6,11–15], detailed knowledge of the mechanism of formation of microstructure during cooling has not been fully described yet. After fast melting the crystal growth front moves rapidly across the melt pool producing a microstructure made of cells (or columns) and fine eutectic. The primary phase is apparently supersaturated and the eutectic

coupled growth is confined in thin volumes around the cells [12,16,17]: the amounts of trapped solute and of retained eutectic are crucial parameters to be clarified.

Al-Si alloys have been studied since the early development of rapid quenching techniques: the main objectives being the extension of Si solubility in Al and surface hardening. Microstructural features of alloys, change in lattice parameter of Al, the thermodynamics of metastable phases and the kinetics of precipitation were reported for splat quenched, melt spun and atomized samples [18–26]. Moreover, dendritic growth under rapid solidification conditions employing laser melting was studied both with *ad hoc* experiments and through modelling [25,27–30].

This work aims at advancing in the interpretation of the microstructure of SLM Al-Si alloys on the basis of the available information on rapid solidification and new experiments performed by using current alloys. A correlation is sought for microstructures produced by mean of three rapid solidification techniques (Copper Mould Casting (CMC), Melt Spinning (MS), and SLM) to span a large range of cooling rates. The experimental results on supersaturation, calorimetric responses, and dimension of the microstructural features, and the consolidated literature allow proposing mechanisms for processes occurring in different ranges of cooling rates. Dendrite growth modelling validates the results on the microstructure found in AM.

2. Experimental

All samples were produced using gas atomized powders provided by EOS GmbH whose chemical composition is reported in Table 1.

SLM cubic samples with side of 15 mm were fabricated with an EOSINT M270 Dual Mode version employing the process parameters reported in [8] and repeated for clarity in Table 1 of Supplementary Information.

Samples were analysed both in the as built condition (AM_AB) and after annealing for stress relieving at 300°C for 2 hours (AM_SR). Pellets of powder were produced by gentle pressing and used for MS and CMC. Induction melting was performed with the help of a susceptor, i.e. a Ta foil surrounding the respective silica and boron nitride crucibles. AlSi10Mg melt spun ribbons were obtained by ejecting the melt onto a copper wheel rotating at either 10 m/s or 15 m/s (MS_N10 and MS_N15 respectively). CMC samples were obtained by ejecting the molten alloy into a conical mould of diameter varying from 5 mm to 1 mm.

For microscopy samples were embedded in conductive resin, mechanically polished, and etched for 10 s using Keller's solution. Secondary electron imaging was carried out both in SEM and FESEM mode using a LEICA STEREO SCAN 420 and a ZEISS SUPRA TM 40.

X-ray diffraction (XRD) was performed in Bragg-Brentano geometry with a PANalytical X'Pert PRO diffractometer by Philips, using the K_α emission line of a Cu filament (λ_{Cu}=1.5418 Å). Patterns were acquired in the 2θ range from 20° to 140° at steps of 0.0167°. The SLM build was analysed on the top (AM_AB top and AM_SR top), side (AM_AB side and AM_SR side), and inner surface after cutting (AM_AB in and AM_SR in). For all samples, including an alloy portion cooled from 660°C to room temperature at 3°C/min representing the solidification in near equilibrium condition, the face centred cubic (fcc) Al lattice parameter was computed with the cosθcotθ method.

Thermal analyses were made with a TA Q100 Differential Scanning Calorimeter (DSC) in the temperature range from 50 to 450°C at the heating rate of 5 and 20°C/min equilibrating the heat flux at both temperatures.

3. Results

3.1 Rapid solidification microstructures

Fig. 1 reports images of the microstructures obtained in AlSi10Mg samples produced by means of different rapid solidification techniques. CMC samples were analysed after sectioning the cone along its vertical axis. A thin zone (< 1 μm) near the outer surface is almost featureless due to faster solidification occurring in contact with the mould. Then, cells and columns are seen, surrounded by fibrous eutectic (Fig. 1-a). Their size increases from 1 to > 5 μm from the tip to the base and from the outer surface to the core of the cone (Fig. 1-b).

It is well established [31] that the microstructure of ribbons changes from the wheel side to the outer side (Fig. 1-c). Here it starts almost featureless, becoming than primary plus eutectic with subdivided fine Si particles and ending with primary cells surrounded by fibrous eutectic. The length scale of the cells is finer with respect to CMC samples (cell size of 1-2 μm) (Fig. 1-d).

As already reported in literature [11,13,32–34] the microstructure of the SLM as built AlSi10Mg part has a transition from very fine cellular-dendritic to a coarser dendritic structure going from the centre to the border of the melt pools. This is clearly visible in Fig. 1-e, where the primary Al cells are surrounded by fibrous Si eutectic and change in size because of heat flux generated during subsequent laser scans. Looking across a melt pool, three zones appear: a finer microstructure in the centre (mpc), a coarser cellular microstructure in the transition zone from the centre to the border (mpb), and coarser Si particles in the heat affected zone around the melt pool in the layers deposited previously (haz). The cellular-dendritic structure is to some extent columnar along the building direction following the path of heat extraction via the substrate [5,16,32,35]. As evident in Fig. 1-f, the cells contain occasional Si

particles (white contrast) and voids of the same size (dark grey contrast) at points where Si particles were removed by etching.

From the set of images it is apparent that the amount of Al-Si eutectic differs among various samples. Its percentage was determined by careful image analysis and averaging the results obtained for more than 10 micrographs taken at different magnification. It is compared with the expected equilibrium value calculated using the lever rule in Table 2. It is underlined that the microstructure changes when process parameters are changed, since the final result depends on the parameters defining the strategy for the SLM process which results in varied temperature gradient, solidification and cooling rate. Therefore, the results reported here on the amount of eutectic are quantitatively valid for the processing parameters and instrumentation employed for the production of the present samples. However, the methodology applied in this work appears well applicable to other sets of parameters.

After annealing for 2 hours at 300°C for stress relieving samples produced by means of the AM route, Si particles become coarser and precipitation of new Si particles inside the primary phase occurs, Fig. 1-h. Moreover, the heat treatment has an homogenizing effect on the size of Si particles in the matrix, Fig. 1-g.

3.2 XRD

Fcc Al and diamond cubic Si phases were identified in XRD patterns of all samples. Occasionally, minor reflections of Al_2O_3 were found, i.e. the oxide produced by coalescence into fine particles of the surface skin of the starting powder particles and, possibly, some oxidation occurring in the building chamber in spite of the protective atmosphere. Fcc Al reflections are always sharp, indicating the presence

of large crystallites. Limited evidence of preferred orientation of crystals could be noticed for samples produced by means of CMC and SLM by measuring the X-ray line intensity, indicating that, even if columns can be seen in these samples, they are not predominant in the microstructure. The absence of textures in the SLM samples is related to the scanning strategy adopted [32] since in other works substantial texturing has been reported [12]. On the air side of the samples produced by MS the patterns shows preferential orientation on the (111) plane and to a lesser extent the (220) plane, while the wheel side show textures on the (200) plane and to a lesser extent the (311) plane. Together with the microstructural features reported in the previous paragraph, these findings confirm the long-standing view that structural inhomogeneities occur in melt spun Al-Si alloys [18,22] in relation with local differences in heat subtraction.

The intensity of reflections of diamond cubic Si are low with respect to those of fcc Al in all samples (in Fig. 2(a) are reported the XRD patterns of the AM_AB and AM_SR samples). Moreover, the higher is the cooling rate the broader and lower are the reflections pointing to increased supersaturation and reduced crystallite size. After annealing, Si reflections increase in intensity and become sharper (Fig. 2(b)) [5,31]. Patterns of the SLM samples (AM_AB) taken on various surfaces show enlargement of the (222) and (420) reflections with respect to the (311) and (331) reflections occurring at close angles, respectively (Fig. 2(c)). This result indicates localized strain along those directions possibly caused by solute clusters.

The lattice parameters of the Al-rich phase are reported in Fig. 3. All rapidly solidified samples have smaller lattice parameter with respect to that solidified in equilibrium (dashed line in Fig. 3). The lowest values are for the AM samples, followed by the as received powder and the core of the CMC sample. The lattice constant of the Al

phase in ribbons is lower for the wheel side with respect to the air side. After stress relieving all lattice parameters approach the equilibrium value.

3.3 DSC

DSC signals obtained at the scanning rate of 20°C/min for cast, melt spun and SLM samples are reported in Fig. 4 and the relevant temperatures for all signals in Fig. 5. Exothermic signals are obtained in each case, the first one being more intense. The first peak of the as built SLM sample is centred at approximately 200°C, a second one at 317°C and a third one, seen as a shoulder on the previous signal, at 340°C. The signal at 317°C is present only in the sample produced by means of SLM. For the CMC and MS samples the first peak occurs at higher temperatures while the peak at 340°C is invariant in temperature. The onset and peak temperatures of the first signal rank in the sequence MS > CMC > SLM.

The enthalpy released in the first DSC signal changes with processing route: it decreases from 33 ± 9 J/g in SLM to 26 ± 2 J/g in CMC and 17 ± 2 J/g in MS samples. The total enthalpy released in the other minor signals of the SLM samples is of the order of 8 ± 4 J/g. The high temperature signal for CMC and MS samples provides 1-2 J/g. Since the amount of enthalpy released for the first precipitation signal by the samples produced by CMC and MS has less scatter with respect to that of SLM samples, the reproducibility of the SLM samples was verified by performing several measurements at 20°C/min with samples produced using the same process parameters in different runs and employing different batches of powder. The resulting thermograms, reported in Fig. 2 of the Supplementary Information, show differences both among different jobs and parts of the same sample. However, all of them have three precipitation signals at around 200°C, 317°C and 340°C. The onset

temperatures, maximum temperatures and heats for precipitation signals are reported in Table 2 of the Supplementary Information.

4. Discussion

4.1 Microstructural features

The progressive refinement of microstructural features with increasing cooling rate is apparent in Fig. 1 both from the reduction of primary Al cells size and the modification of the eutectic from plate-like, characteristic of equilibrium solidification, to fibrous morphology. In CMC even if a consistent refinement in the microstructure occurred from the base to the tip of the cone, the microstructure reported in Figs. 1-a and 1-b is coarser with respect to that obtained with other technologies and part of the eutectic is still lamellar. Full modification of the eutectic occurs both with MS and SLM. The portion of MS samples having eutectic morphology (Fig. 1-d) is similar to that produced by SLM, however, primary Al cells are larger.

The samples produced by MS show a peculiar gradient in microstructure from an apparently homogenous solid solution on the wheel side to a cellular dendritic structure surrounded by fibrous Si eutectic on the air side (Fig. 1-c). The formation of an homogeneous solid solution without solute partitioning indicates that solidification occurred below the T_0 temperature, i.e. the temperature at which the free energies of the liquid and crystalline solutions are equal. The transition from partitionless primary to primary plus eutectic solidification gives clear evidence of the decrease in the solidification front velocity across the ribbon thickness which accompanies the local decrease in cooling rate [26,30]. This is brought about by two events: (i) the formation of a layer of solid solution causes release of latent heat with associated recalescence; (ii) the heat extraction through the quenching medium ceases when

the ribbon is detached from it, therefore, cooling by convection and radiation to the surrounding atmosphere occurs.

In the samples produced by SLM with the present set of processing parameters, the microstructure is made of fine primary Al cells surrounded by fibrous eutectic (Fig. 1-e). The cells are elongated in the zones at the edge of the melt pool which underwent repeated fusion in subsequent laser scans. Since in these samples there is no evidence of formation of an homogeneous solid solution alone, it is inferred that solidification has occurred above the T_0 temperature. The pre-existing Al-rich crystals are heterogeneous nuclei upon which cells grow in condition of constitutional supercooling [5] leaving between them a Si-enriched melt which gives rise to the eutectic. The energy injected by the laser beam and the heat released upon solidification is continuously and effectively dissipated by conduction in the cool support and built object as suggested by the steady distribution of cell size and eutectic amount in the whole sample at variance to the solidification morphology of the melt spun ribbons.

The fraction of Al primary phase with respect to the eutectic changes substantially in samples produced by means of different rapid solidification techniques as quantified in [36] where increasing eutectic fractions from 20 to 60% were measured in atomized powders of size ranging from 10 to 100 μm. The eutectic fraction is always lower than the expected quantity computed by using the equilibrium Al-Si phase diagram. The Al-Si system has a skewed coupled zone for the eutectic with increasing growth rate [27] entailing the increase in supersaturation of Si in the primary Al. This occurs especially in SLM samples due to the high cooling rates achieved in solidification [2,9,10,13,15].

The primary cells as well as the featureless zone of the melt spun ribbon contain clear evidence of the presence of precipitated Si (Figs. 1-d and 1-f). It is deduced that it was produced in the solid state because of self-annealing cause by dissipation of the latent heat of solidification. Coarsening of Si particles and precipitation of new ones inside the primary phase occur by heat treatment along with homogenization of the microstructure (Figs. 1-g and 1-h) in agreement with the literature [5,6,11].

Overall, the microstructure produced in AM is unique, differing from those obtained with established rapid solidification techniques. This results from the distinctive action of adding material track after track and layer after layer together with the fast and directional cooling rates obtained in this process also in the solid state.

4.2 XRD and lattice parameter

The reflections of fcc Al and diamond cubic Si in XRD patterns (Fig. 2-a) are now employed as a tool for the interpretation of the events occurring during solidification.

The intensity of Si reflections decreases on increasing the cooling rate because of Si supersaturation in the primary phase (Fig. 2-b). Within the scatter of results due to the limited number of reflections detectable, the lattice constant corresponds to that of elemental Si. The broadening, much evident in the SLM and MS samples, relates to the fine scattering domains present in the Si particles after rapid solidification.

The lattice parameters of the Al primary phase (Fig. 3) testifies the varied quantity of solute Si. The reference lattice parameter is that of the equilibrium AlSi10Mg alloy, 0.40515 ± 0.0003 nm, consistently larger with respect to that of pure Al, 0.40494 nm [37]. Considering that solute Si and Fe decrease [37,38] while Mg increases the lattice parameter of Al [37,39], the increment of the equilibrium lattice parameter must be due to the presence of solute Mg in the Al phase. Si and Fe are contained in

the eutectic and minority compounds (see below). For all samples produced by means of rapid solidification the decrease in the lattice parameters indicates that excess Si is trapped inside the primary Al [11]. The lattice parameter of AM_AB is the lowest, confirming the high supersaturation of Si already suggested by the results on the percentage of eutectic. It is worth noticing that the lattice parameter corresponding to the top surface of the sample is the lowest of all. This is understood by considering that the last layer is not affected by further scans, while the layers underneath which are accessed when analysing the other surfaces are re-solidified more times. The lattice parameters calculated for the samples produced by SLM and subjected to stress relieving are in accordance with that obtained for the sample solidified in equilibrium condition, indicating complete precipitation of Si from the Al primary phase. It is interesting to notice that the lattice parameters of melt spun ribbons are slightly lower for the wheel side with respect to the air side but higher with respect to that of the CMC sample, opposite to what expected considering the cooling rates typically reached with the two techniques. This trend clearly differs from that of the eutectic fraction in the microstructure. The two sets of data can be reconciled by considering that the microstructures seen in Fig. 1 are the outcome of the solidification process whereas the XRD patterns refer to the crystal in samples cooled to room temperature. The as solidified CMC and SLM samples remain in contact either with the quenching medium or a cool portion of the same alloy down to low temperature: i.e. with a heat sink of high thermal conductivity which extracts heat continuously. On the other hand, in MS an initial fast heat exchange occurs when the molten alloy impinges onto the rotating Cu wheel, then the ribbon detaches from the wheel and the release of latent heat gives rise to recalescence resulting in the precipitation of Si which decrease the level of supersaturation. The occurrence of

sharp XRD reflections of Si in patterns taken on the wheel side of ribbons support this reasoning.

The lattice parameter of the starting atomized powder which contains a mixture of primary cells and fibrous eutectic, is also low. Although the occurrence of recalescence phenomena was reported in powders as well [36], the average size of the powder particles is 3-4 μm, about one order of magnitude less than the thickness of ribbons, therefore, the average cooling rate of small particles in gas atomization cab be faster than the average cooling rate during MS.

Vergard's law was employed to evaluate the amount of Si dissolved in fcc Al, x_{Si}, ($a = -0.0174 \cdot x_{Si} + 0.40515$) [21]. The average concentration of solute Si resulted 1 at% in MS samples, 2 at% in CMC samples and 4 at% in SLM samples.

4.3 Calorimetry

The first DSC peak given by all samples is attributed to the precipitation of supersaturated Si from the primary phase, also in view of the numerous literature findings [15,24,40]. To enforce this, it is noted that a melt spun ribbon produced from an AlSi10 master alloy not containing Mg gave the same peak. For quantitative discussion of the heat effect, the thermodynamics of Al-Si system is considered as recently assessed [41]. Fig. 6 reports the enthalpy of mixing Si to Al in the fcc structure and the enthalpy of the equilibrium phase mixture (fcc Al and diamond cubic Si). It turns out that the maximum amount of heat that can be released by precipitation of Si from a fully supersaturated alloy containing 10 wt% Si is -85 J/g. This value is larger than those of the precipitation enthalpy obtained for the first signal of the present samples confirming that only a portion of Si was retained in solution. The heat release data concur with lattice parameter results in indicating that

the average concentration of solute Si in Al amounts to 1 at% in MS ribbons, 2 at% in the CMC sample and 4 at% in the SLM built. This values are indicative of the general outcome from the diverse solidification processes although in the samples there might be differences in Si content in neighbouring zones. Remembering that the solubility of Si is 1.8 at% at the eutectic temperature [41], it is confirmed that precipitation in the solid state soon after solidification takes place in the ribbon, but not in the CMC sample, whereas the SLM built is more supersaturated.

Since it has been demonstrated that the Si precipitated already in all samples, at least partially, it is deduced that nucleation of crystals must have occurred and the heat release is mostly due to growth by diffusion. The temperature shift can be attributed to two phenomena which can favour Si diffusion: (i) excess Si solute [20] and (ii) excess vacancies inside the Al matrix [40,42], both due to the rapid solidification processing.

The variations in temperature and heat, detectable although limited (Fig. 1 in Supplementary Information), for different parts of the SLM samples and different jobs depend on inhomogeneity in the microstructure of as built samples. This is because of inherent fluctuations in powder layer deposition and scanning mode for the skin, the contour and the core. Also, different batches of powder can have different impurity levels. Therefore, although within the general framework just outlined, a certain variability in the results is unavoidable. These results, however, show that DSC can be considered a very sensitive tool for understanding the local level of supersaturation present in the samples and could help in evaluating the reproducibility of the AM process of Al-Si.

Turning now to discuss the origin of the second DSC signal occurring at 317°C in the samples produced by SLM, it is noted that Mg_2Si is a likely precipitate in AlSi10Mg.

Considering the enthalpy of formation of Mg_2Si [43], the maximum amount of heat releasable by one gram of an alloy containing 0.35 wt% Mg is -8 J/g, i.e. a quantity of the same order of magnitude as the heats measured for the precipitation signal. This suggests to assign the second signal to the precipitation of Mg_2Si from the primary phase still supersaturated in Mg. This signal is absent in the DSC traces provided by samples produced by CMC and MS, in spite of the evidence of the presence of Mg deduced from the values of lattice parameters after annealing. It is likely that the solute Mg in these samples corresponds to the equilibrium amount expected in the ternary Al-Mg-Si phase diagram [44,45]. The second DSC peak of the SLM samples cannot be separated from the minor one which is found in all the other samples as well. Its enthalpy contribution is limited, probably related to the formation of another precipitate containing impurity elements, e.g. Fe, present in the alloy.

4.4 Application of a model for dendritic growth

From the discussion in the previous sections, it is apparent that the increment in solidification rate results in the reduction of the volume fraction of eutectic and in increased supersaturation of Si inside the primary Al cells. To interpret the set of experimental findings, the model for dendritic growth under rapid solidification conditions described in [30] is applied to the Al-Si system.

The model assumes linear *liquidus* and *solidus* lines in the Al-Si phase diagram and is valid for dilute solutions. According to it the *liquidus* temperature is expressed as:

$$T_L = T_M + m\,(1 + (k - k_v + k_v \ln(k_v/k)) / (1 - k))\, C_L - (2\Gamma / R) - (V/\mu_k) \qquad (1)$$

where T_M is the melting temperature of solvent element, m the *liquidus* slope (dT_L/dC), k the equilibrium distribution coefficient (dC_S/dC_L), with C_S and C_L the solid and liquid composition, respectively, Γ the Gibbs-Thomson coefficient, R the dendrite

tip (or column, cell) radius, V the rate of interface movement, μ_k the interface kinetic coefficient ($\mu_k = V_0 (1-k)/m$ *with* V_0 the limiting crystallization velocity of the order of the velocity of sound) and k_v the non-equilibrium distribution coefficient, defined by Aziz [29,46] as:

$$k_v = (k + P_i)/(1 + P_i) \quad (2)$$

where P_i, the interface Pèclet number for solute redistribution, is defined as $P_i = a_0 V/D_i$ with a_0 interface diffusion length and D_i interface diffusion coefficient. k_v expresses the deviation from equilibrium on fast solidification and approaches unity when the *liquidus* approaches the T_0 line. The physical constants reported in Table 3 were employed to perform the calculation.

In the present study, the microstructure length scale, R, of the primary phase varies about one order of magnitude in the samples produced with different techniques. The growth velocities, however, are not known. Therefore, an inverse approach was used to calculate both *liquidus* and *solidus* curves for the Al-rich and Si-rich sides of the phase diagram starting from the known parameters. The aim is to draw a metastable phase diagram with approximate tie lines for the Al-Si system to match the eutectic percentage determined in each microstructure.

In Fig. 7 the results of calculation are reported together with the equilibrium phase diagram and T_0 curves determined according to the assessed Al-Si system (TCBIN Thermo-Calc®). The metastable eutectic shifts to higher Si content when the growth velocity and the corresponding cooling rate are increased from the quasi-equilibrium condition to those occurring in CMC and SLM. For each technique, a range of growth rates was assumed in order to reproduce the findings on the respective percentage of eutectic. The results of the calculations show that the rate of interface movement for the CMC samples should be comprised between 0.45 and 0.7 m/s, while for SLM

samples should be comprised between 0.66 and 1.025 m/s. Despite the approximations outlined above, it is remarkable that these growth rates reproduce those found experimentally by recording the interface displacement in Al-Si thin films imaged in TEM during solidification after laser melting [51]. The band for the highest growth rates in Fig. 7 intersects the T_0 line of the Al-rich solid solution representing the initial stage of solidification found in MS and CMC samples. For the SLM process, the presence of fcc Al crystals as substrate causes fast growth of the primary phase, in epitaxial fashion [12]. Si rejection brings the local composition of the melt to the eutectic which is incorporated into the primary phase. Re-nucleation may then occur at heterogeneous sites.

5. Conclusions

In this work the correlation between the microstructure, the phase constitution and the thermal behaviour of AlSi10Mg samples produced by means of different rapid solidification techniques was established. The cooling rate, i.e. velocity of the solidification front, determines the morphology and size of microstructural features. In CMC and MS samples a thin featureless zone indicates that the initiation of solidification occurred below the T_0 line. With the subsequent increase in temperature due to recalescence, the microstructure became mixed, primary plus eutectic. Actually, there is progressive change of the morphology of eutectic Si from dispersed particles to fibrous and lamellar network.

The microstructure is more refined in MS with respect to CMC samples and even more in SLM parts which are entirely made of cells or columns of primary Al and fibrous eutectic. Together with the change of eutectic morphology, a clear increase in eutectic fraction is found in the order SLM ~ MS (air side) < CMC < master alloy.

The decrement of the Al lattice parameter when changing processing technique gives a measure of the extension of the solid solubility of Si in the primary phase. The lattice parameter decreases in the sequence: master alloy or annealed samples > MS (all sides) > CMC > SLM. The surprising amount of solute Si in CMC samples, corresponding approximately to the solubility at the eutectic temperature, is understood by considering the fast cooling in the solid state after solidification provided by the continuous contact of the sample with the heat sink. This is also the reason for the extension of solubility in SLM parts where the melt pool is in direct contact with the already solidified material. Accordingly, the low solute content in MS samples must be due to decrease in cooling rate and the consequent self-heating of the ribbon because of recalescence after leaving the quenching wheel.

DSC analyses provided evidence of precipitation of excess solutes in the temperature range from ~ 150 to 350 °C (heating rate of 20°C/min). The first and main DSC peaks is due to Si precipitation for which a correlation between the level of extended solid solubility and the onset temperature of the signal was evidenced: the lower is the temperature the higher is the amount of released enthalpy. Thermodynamic analysis of the Al-Si system confirmed that the released enthalpy corresponds to the level of supersaturation reached in the samples produced by means of different processing routes. Further exothermic signals are attributed to the precipitation of Mg_2Si (signal detected only for SLM samples around 317°C, since probably the cooling conditions allow the Mg to reach equilibrium in CMC and MS samples) and possibly Fe-containing intermetallics around 340°C.

The ensemble of results on eutectic fraction and solubility extension are interpreted by applying a current model of cellular/dendritic solidification [30] which implies the progressive narrowing of the distance between *liquidus* and *solidus* lines in the

phase diagram as a function of solidification front velocity. Approximated metastable phase diagrams for front velocities in between 0.5 and 1 m/s reproduce the eutectic fractions found in experiments. Remarkably, these correspond to those directly measured recently [51] by observing the movement of the primary solidification front in Al-Si.

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