Selective laser melting of rare earth element Sc modified aluminum alloy: Thermodynamics of precipitation behavior and its influence on mechanical properties

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ABSTRACT

The interest of selective laser melting (SLM) Al-based alloys for lightweight applications, especially the rare earth element Sc modified Al-Mg alloy, is increasing. In this work, high-performance Al-Mg-Sc-Zr alloy was successfully fabricated by SLM. The phase identification, densification behavior, precipitate distribution and mechanical properties of the as-fabricated parts at a wide range of processing parameters were carefully characterized. Meanwhile, the evolution of nanoprecipitation behavior under various scan speeds is revealed and TEM analysis of precipitates shows that a small amount of spherical nanoprecipitates \(\text{Al}_3(\text{Sc},\text{Zr})\) were embedded at the bottom of the molten pool using a low scan speed. While no precipitates were found in the matrix using a relatively high scan speed due to the combined effects of the variation of Marangoni convection vector, ultra-short lifetime of liquid and the rapid cooling rate. An increased hardness and a reduced wear rate of 94 HV\(_{0.2}\) and \(1.74 \times 10^{-4}\) mm\(^2\)N\(^{-1}\)m\(^{-1}\) were resultantly obtained respectively as a much lower scan speed was applied. A relationship between the processing parameters, the surface tension, the convection flow, the precipitation distribution and the resultant mechanical properties has been well established, demonstrating that the high-performance of SLM-processed Al-Mg-Sc-Zr alloy could be tailored by controlling the distribution of nanoprecipitates.

1. Introduction

Selective laser melting (SLM) is a rapidly developed additive manufacturing (AM) technique emerged in the late 1980s. Compared to the conventional manufacturing techniques, such as casting, deformation forming and powder metallurgy, SLM provides numerous possibilities of the short time-to-market, near-net-shape-production as well as the high flexibility [1–5]. As a remarkable feature of additive and layer-wise production, SLM processing can allow the fabrication of components with complex geometrical geometries, which cannot be manufactured directly by conventional routes. It is not surprising that SLM has attracted increasing interests in recent years [6]. Aluminum alloys as the most abundant metal in the crust of the earth and the most widely used nonferrous metal, have been extensively used in the aerospace, military, communication and transportation industries. However, Al alloys processed by SLM still suffers from challenges for a long period due to its high laser reflectance, high-thermal conductivity and high tendency of oxidation, which dramatically restrict the SLM of Al alloys [7,8]. The major researches have been focus on AlSi10Mg and AlSi12 due to their readily weldability, which exhibits cellular-denritic grains and eutectic microstructure in the SLM-AlSi10Mg [9] and AlSi12 [10], respectively. However, owing to the limited strength, ductility and heat stability, the Al-Si based alloys fabricated by SLM cannot meet the needs of high strength used for the aircraft and the high-temperature resistance for satellite and rocket applications. Therefore, the development of a novel and high-strength aluminum alloy is essential to further extend their applications.

Aluminum-scandium alloys, put forward by former Soviet Union during The Cold War in 1970s, have excellent mechanical properties due to the high-density existence of elastically hard, coherent and...
nanometer size $\text{Al}_3\text{Sc}$ precipitates [11]. Later, Al-Sc alloy received much attention in the late 1990s. The solidification behavior and the morphology of primary $\text{Al}_3\text{Sc}$ particles of binary Al-Sc alloy were systematically investigated by P. Prangnell at the end of last century [12], which demonstrated that the addition of Sc in a certain composition range could induce remarkable grain refinement of Al with a grain size of 20 $\mu$m, much smaller than that of the conventional grain-refining systems. Meanwhile the yield and creep behavior as well as the corresponding dislocation mechanisms at the ambient and elevated temperatures were systematically studied by D.N. Seidman [13], which revealed that the strengthening mechanism transformed from precipitate shearing to Orowan dislocation looping mechanisms with an increasing radius of precipitates. A completely basic theoretical system for Al-Sc alloy processed by traditional processing method was established at the beginning of the 21st century. As reported by Kendig et al. [14], addition of magnesium can provide solution strengthening and enhance the lattice parameter of aluminum matrix (0.405 nm), which contributes to a good match with $\text{Al}_3\text{Sc}$ (0.410 nm). It was found that zirconium substituted for Sc in the $\text{Al}_3\text{Sc}$ particles reaching nearly 1/3 of the Sc lattice sites and the zirconium can thus contribute to additional stability of these $\text{Al}_3(\text{Sc,Zr})$ particles due to the slow diffusion in aluminum [14]. It is expected that Al-Mg-Sc-Zr alloy was very interesting and would have excellent potentials for aerospace lightweight applications in terms of its high specific strength, creep and fatigue resistances at an elevated temperature. Only very limited work has been focused on SLM processing of Al-Mg-Sc-Zr alloy. The first attempt to fabricate Al-Mg-Sc-Zr alloy using SLM was carried out by Schmidtke et al. [15] of Airbus Group innovation and they demonstrated a processability of Al-Mg-Sc-Zr alloy by SLM. Recently, Spierings et al. [16] reported that the microstructure of ultrafine equiaxed grains and large columnar grains growing along the temperature gradient, was obtained in the SLM processed Al-Mg-Sc-Zr alloy. Wu et al. [17] showed a correlation between densification, hardness and electrical conductivity as well as considerably refined microstructure of the SLM processed Al-Mg-Sc-Zr alloy. Li et al. [18] also investigated the microstructure, phase constituents and mechanical properties of SLM-processed Al-6.2Mg-0.36Sc-0.09Zr parts. It should be pointed out that there are still great challenges to fabricate fully dense parts due to the limited flowability of Al-Mg-Sc-Zr alloy [12]. Moreover, the results showed that the flow behavior of melt and the distribution of element greatly affected the microstructure and precipitation distribution mechanism [19]. But it seemed that no study has been paid attention to a quantitative study of inner mechanism, which plays a key role in the ultimate mechanical properties. An inhomogeneous precipitate distribution of SLM processed Al-Mg-Sc-Zr alloy, is expected by the combined effects of layer-by-layer characteristics, complex heat-mass transfer behavior and super cooling rate during SLM processing. Nevertheless, the precipitation distribution could be dramatically changed at various processing parameters, thus leading to a variation of metallurgical behavior within the molten pool. Therefore, an investigation of precipitation distribution mechanism during SLM and corresponding mechanical properties of SLM-processed Al-Mg-Sc-Zr alloy is essential.

In this study, phase analysis and densification behavior at various SLM processing parameters were examined and the mechanisms of precipitation distribution at various scan speeds were revealed and compared. Also, a theory to explain the variation of precipitate distribution was proposed and the mechanical properties in terms of different precipitation distribution, hardness and wear resistance were measured. This work would establish a relationship between processing conditions, precipitate distribution, and resultant mechanical performances of Al-Mg-Sc-Zr alloy processed by SLM.

2. Experimental methods

2.1. Powder materials

Gas-atomized Al-Mg-Sc-Zr powder was applied in this study. The powder shows a spherical shape (Fig. 1a) with a particle size $d_{50} = 22.4$ $\mu$m and $d_{90} = 45.2$ $\mu$m (Fig. 1b). Before SLM processing, the powder was dried under a temperature of 393 K for 10 h in vacuum to improve the flowability. The chemical composition of the initial powder is listed in Table 1.

2.2. SLM process

The SLM system was developed by Nanjing University of Aeronautics and Astronautics (NUAA) and consisted mainly of an YLR-550 Ytterbium fiber laser (with a maximum laser power of 500 W, a spot size of 70 $\mu$m), an automatic powder layering apparatus, an inert argon gas protection system and a computer system for process control. Forty cubic specimens with the dimensions of 10 mm $\times$ 10 mm $\times$ 5 mm were built to find the optimal processing parameters, densification behavior, as well as the mechanical properties. The orthometric laser scan strategy with a stacking fault between continuous two layers was used (Fig. 2a) and the processing parameters were set as follows: laser power $p = 325$ W, scan speeds $v = 1800–3600$ mm/s, hatch spacing $h = 60$ $\mu$m and layer thickness $l = 30$ $\mu$m. In order to assess the effect of laser energy input on the processed powder layer, the volume energy

![Fig. 1. (a) Particle morphology and (b) particle size distribution of the starting Al-Mg-Sc-Zr powder.](image-url)
density $\eta$ was defined by:

$$\eta = \frac{P}{h \cdot v \cdot l}$$  \hspace{1cm} (1)

Four specimens with various scan speeds of 3000 mm/s, 2600 mm/s, 2200 mm/s and 1800 mm/s (correspondingly with laser volume density $\eta$ of 60 J/mm$^3$, 70 J/mm$^3$, 82 J/mm$^3$, 100 J/mm$^3$) were selected for analysis in this study (Fig. 2b).

2.3. Microstructural characterization

The relative density of consolidated part was determined by the Archimedes method, using a theoretical density of 2.67 g/cm$^3$. Phase identification was conducted by a Bruker D8 Advance X-ray diffractometer (XRD) with Cu K$\alpha$ radiation using a continuous scan mode at 40 kV and 40 mA. A quick scan speed of 4° min$^{-1}$ was first applied over a wide range of $2\theta$ = 20-90° to give a general overview of the diffraction peaks. Then a slow scan rate at 1° min$^{-1}$ was performed over $2\theta$ = 37.8–38.5° to obtain a further accurate determination of the diffraction peaks. For microstructural observations, specimens were cut, ground and polished according to the standard procedures, and etched with a solution consisting of HF (1 mL), HCl (1.5 mL), HNO$_3$ (2.5 mL) and distilled water (95 mL) for 20 s. Microstructure was characterized by a PMG3 optical microscope (Olympus Corporation, Japan) and using a Zeiss Sigma 04–95 field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) was performed on a JEOL 2100 F operating at 200 kV, and high-resolution transmission electron microscopy (HRTEM) equipped with selected area electron diffraction (SAED) apparatus.

2.4. Mechanical properties tests

The Vicker hardness of the samples was measured by a Buenhler MicroMet 5010 microhardness tester at a load of 200 g and an indentation time of 20 s. According to the ASTM G99 standard, wear/tribological properties of specimens were characterized by dry sliding wear tests conducted in a HT-500 ball-on-disk tribometer (Lanzhou ZhongKe KaiHua Sci. & Technol. Co., Ltd., PR China) in air at room temperature. Before the wear tests, surfaces of specimens were ground and polished. A bearing steel GCr15 ball with a diameter of 3 mm and a
Fig. 4. Optical microscopy (OM) of the cross-sectional macrostructures of the SLM-processed parts ($P = 325$ W, $l = 30 \mu m$ and $h = 60 \mu m$): (a) $v = 3000$ mm/s, $\eta = 60$ J/mm$^3$; (b) $v = 2600$ mm/s, $\eta = 70$ J/mm$^3$; (c) $v = 2200$ mm/s, $\eta = 82$ J/mm$^3$ and (d) $v = 1800$ mm/s, $\eta = 100$ J/mm$^3$.

Fig. 5. Temperature distribution and velocity field within the cross sections of the molten pool using different processing parameters ($P = 325$ W, $l = 30 \mu m$ and $h = 60 \mu m$); (a) $v = 1800$ mm/s and (b) $v = 3000$ mm/s.
mean hardness of HRC60 was used as the counterface material and a load of 3 N was applied. The friction unit was rotated with a radius of 2 mm at a speed of 560 rpm for 15 min. During the wear tests, coefficients of friction (COF) of the specimens were recorded. And the wear volume \( V \) was conducted by:

\[
V = \frac{M_{\text{loss}}}{\rho}
\]  

(2)

where \( M_{\text{loss}} \) is weight loss of the specimens after wear tests. The wear rate \( \omega \) is determined using:

\[
\omega = \frac{V}{WL}
\]  

(3)

where \( W \) is the contact and \( L \) is the sliding distance.

2.5. Finite volume simulation

The simulation was carried out utilizing the FULENT commercial computational fluid dynamics software to conduct the thermal behavior, velocity field and cooling rate within the molten pool during the SLM processing. The thermo-physical properties of as-used Al-Mg-Sc-Zr alloy, which has been proposed by A.B. Spierings [16], are depicted in Table 2. The laser source with Gaussian configuration and various scan speeds is mathematically defined as a heat flux which is inserted in the source term for the governing equations. The heat source is identified as:

\[
Q = \frac{AP}{\rho \omega_0 d^2} \left( \frac{\omega_f}{\omega_0} \right)^2 \exp \left( \frac{2(x^2 + y^2)}{f^2} \right) u(z)
\]  

(4)

Where \( P \) is the laser power, \( d \) is the laser beam penetration depth, \( \omega_f \) and \( \omega_0 \) are the beam focal radii at the surface and at depth, \( A \) is the absorption of the material, \( u(z) = 1 \) for \( 0 \leq z \leq d \) and \( u(z) = 0 \) otherwise.

The model employed in this study has been described in our previous works [19,20]. Upon the mass, momentum and energy equation, the governing equations with regard to the Cartesian coordinate system are expressed as follows:

Mass conservation equation

\[
\frac{\partial \rho}{\partial t} + V(\rho V) = M_s
\]  

(5)

Energy conservation equation

\[
\frac{\partial (\rho T)}{\partial t} + \nabla \cdot (\rho V T) = \frac{\partial (\rho C_p)}{\partial t} + \nabla \cdot (\rho C_p V) + \frac{\partial P}{\partial t} + \frac{\partial W}{\partial t} + S_f
\]  

(6)

Momentum conservation equation

\[
\rho \left( \frac{\partial V}{\partial t} + V \cdot \nabla V \right) = -\nabla P + \mu \nabla^2 V + M_s + F
\]  

(7)

Where \( \rho \) is density, \( \kappa \) is thermal conductivity, \( \mu \) is viscosity and \( p \) is pressure. \( M_s \) is a mass source. \( V \) is the molten metal velocity.
3. Results and discussions

3.1. Phase identification

XRD spectra of the raw powder and SLM-processed parts of Al-Mg-Sc-Zr alloy, obtained in a wide 2θ range of 20-90° is depicted in Fig. 3a. The diffraction peaks corresponding to the α-Al phase were detected both in the raw powder and the SLM-processed parts obtained using different laser scan speeds. While the Al3(Sc,Zr) phase was not detected due to the limited content in the matrix. The powder spectra exhibited a prominent (111) texture whereas, the XRD spectra for the as-fabricated Al-Mg-Sc-Zr parts exhibited strong Al (200) texture peaks, suggesting a dramatical texture change due to the rapid melting/solidification behavior of the SLM process (Fig. 3a). The XRD characterization in a small 2θ angle range of 37.8-38.5° for the α-Al diffraction peaks revealed that the location of the α-Al diffraction peaks changed with the increase of applied laser scan speed (Fig. 3b). The standard α-Al phase diffraction peak located at 2θ = 38.3° was taken for a comparison purpose (Table 3). For the raw powder, the 2θ location of the α-Al diffraction peak shifted to a low value. As the laser scan speed of 1800 mm/s was applied, the 2θ value of the diffraction peaks for α-Al considerably decreased compared to that of the raw powder (Fig. 3). As the application of v increased above 2000 mm/s, the 2θ location of the diffraction peaks for α-Al shifted to a low 2θ (Fig. 3). A dramatical shift of 2θ location to a small value was observed when a maximum ν of 3000 mm/s was applied.

According to the Bragg’s law [21]

\[ 2d \sin \theta = n \lambda \] (8)

the observed decrease of 2θ value in both powder and bulk samples indicates an increase in the lattice plane distance d, which was believed to be caused by the formation of solid solution of Al-Sc-Zr. Compared the raw powder with the as-fabricated samples, it was obvious that the 2θ location of the bulk parts was much lower than that of the raw
powder material, which was probably induced by the high heating/cooling rate ($10^3$-$10^8$ K s$^{-1}$). The dramatically high cooling rate during the solidification led to a significant increase in the content of Sc/Zr atoms within the Al matrix, increasing the lattice plane distance $d$ (Table 3).

### 3.2. Densification behavior

The microstructure of the cross-section of the SLM-processed Al-Mg-Sc-Zr parts using various laser scan speeds are presented in Fig. 4. The layerwise features were observed, ascribed to the layer-by-layer incremental deposition manner of the SLM process. It was noted that the configuration of the solidified molten pools, features of residual pores and layer distribution were significantly affected by the application of the processing parameters. As the applied $\eta$ was 60 J/mm$^3$, the irregular pores with an average size over 150 $\mu$m between the layers combined with the narrow microracks parallel to the building direction with an average length of $\sim 70$ $\mu$m were generated (Fig. 4a). As a result, a porosity of $\sim 9.1\%$ was obtained in the SLM processed part. As an applied $\eta$ increased to 70 J/mm$^3$, large irregular pores were disappeared with a slight decrease of microracks. Meanwhile, residual porosity of the SLM part decreased to 6.7% with the appearance of the spherical patterns of a mean size of 30 $\mu$m (Fig. 4b). For an $\eta$ of 82 J/mm$^3$, although residual spherical pores were still remained, the densification rate of the SLM parts was significantly enhanced ($> 96\%$) with absence of the microcracks (Fig. 4c). At an even low $v$ of 1800 mm/s and the attendant high $\eta$ of 100 J/mm$^3$, the dense and fine bonding layers without any interlayer pores or cracks were formed, promoting an increase in the densification rate as high as 98.5% (Fig. 4d).

Generally, the microracks, the residual spherical pores and the attendant densification behavior were significantly associated with the combination of the melt convection and the gas escapement within the molten pool. In order to have a better understanding of the densification behavior of the SLM processed Al-Mg-Sc-Zr parts, the temperature contour and the velocity distribution using $v = 1800$ mm/s and $v = 3000$ mm/s are illustrated in Fig. 5. The simulated temperature contours of the molten pool showed a typical arc-shaped configuration (Figs. 5a and c), which was mainly attributed to Gaussian energy distribution of the laser beam. Meanwhile, the velocity vector of the thermo-capillary convection at the cross section of the molten pool was in the form of the inward pattern, caused by the temperature gradient and the resultant temperature dependent surface tension. As the scan speed increased from 1800 mm/s to 3000 mm/s, the maximum operating temperature obtained in the molten pool decreased from 1750 K (Fig. 5a) to 1600 K (Fig. 5c) and, the maximum velocity decreased from 14 m/s to 7 m/s. It was found that the depth of the molten pool at a low
laser scan speed was relatively large, implying that a drastic marangoni flow was obtained. Moreover, the simulated time-temperature dependency at 8 different monitoring points along the molten pool depth as well as the simulated time-cooling rate dependency in the center of the molten pool for $v = 1800$ mm/s and $v = 3000$ mm/s are depicted in Fig. 6. Here, the 8 monitoring points were illustrated in Fig. 5a, with a distance increment of 5 $\mu$m from the top of the molten pool. A long liquid lifetime of 0.016 ms was obtained at the scan speed of 1800 mm/s, while the liquid lifetime was supposed to be 0.006 ms at the higher scan speed of 3000 mm/s (Fig. 6a). It was noted that the maximum value of cooling rate reached $6 \times 10^7$ K/s and $3.2 \times 10^7$ K/s (Fig. 6b) at the scan speed of 3000 mm/s and 1800 mm/s, respectively.

Microcracks tended to be formed at a high $v$, which were regarded as thermal cracks caused by residual thermal stresses [22]. At a high $v$, the cooling rate of the molten pool reached $6 \times 10^7$ K/s, leading to a great temperature gradient and the resultant high residual thermal stress in the as-fabricated parts. The decrease in application of $v$ reduced the cooling rate, temperature gradient and the attendant residual thermal stress, restricting the formation of the microcracks within the as-fabricated part ($v = 1800$ mm/s). The formation of the irregular pores between layers at a high $v$ was attributed to the insufficient energy input, implying the insufficient melting of the metal powders and the poor bonding ability [23]. As the $v$ decreased, the spherical pores were obtained due to the vaporization of low melting point constituents of Mg and Al in the alloy, which generated gas bubbles within the molten pool. The nonequilibrium and unstable convection flow generated by the laser beam/powder interaction prevented the escapement of the gas, resulting in the formation of spherical defects [24]. However, as the $v$ further decreased to 1800 mm/s, the gas bubbles had enough time to escape due to an increased lifetime of liquid, leading to the formation of dense part.

3.3. Distribution of the precipitates

Fig. 7a showed the OM images of the cross-section microstructure of the single molten pool for the as-fabricated part at a relatively low $v$ of 1800 mm/s. The molten pool, marked with the white dotted line, consisted of a bright zone in the center and dark zone at the bottom of the molten pool. In order to have a further understanding of the precipitation behavior, SEM images of the parts fabricated at different laser scan speeds are shown in Fig. 8. The microstructure of a typical molten pool pattern obtained at a relatively low $v$ of 1800 mm/s is given, where the center area and the bottom area of the molten pool are depicted in Fig. 8b and c, respectively. It was obvious that a small amount of the spherical precipitates with a mean size below 100 nm, were typically found at the bottom of the molten pool. Nevertheless, only few particles could be observed in the center of the molten pool, showing a non-uniform distribution of the precipitations within the molten pool. TEM analysis has been performed to further characterize the precipitates (Fig. 9). The spherical nanoprecipitates in the matrix were identified as $\text{Al}_3(\text{Sc},\text{Zr})$ based on the SAED image in Fig. 9b. According to the...
pool, forming an aggregation zone of the Al$_3$(Sc,Zr) particles. The aggregation zone with a mean width of 10 µm was shown in a stripe-shaped configuration at the bottom boundary of the molten pool. However, only few Al$_3$(Sc,Zr) particles were observed in the center of the molten pool. As the laser scan speed was relatively high, the Al$_3$(Sc,Zr) particles was not possible to form throughout the matrix of the molten pool.

The schematic of the distribution mechanism of the Al$_3$(Sc,Zr) particles within the molten pool obtained at 1800 mm/s is illustrated in Fig. 10. When initial powder was irradiated by the laser beam, a molten pool with an arc-shaped configuration was formed and a peak temperature of 1750 K was obtained. Due to the high affinity of aluminum alloy to oxygen, the thin and continuous oxidation film along the boundary of the molten pool was formed during the solidification process. Meanwhile, the Marangoni flow, caused by the surface tension gradient, showed an inward pattern with a maximum velocity of 14 m/s. In such case, the oxidation films were broken into tiny pieces due to the turbulent melt stirring with a downward velocity vector. This mechanism for the formation of the oxidation debris during SLM of aluminum alloy has been reported by Gu et al. [25]. As the temperature within the molten pool decreased below the liquidus temperature (Fig. 6a), the initial phase to be solidified from molten liquid is Al$_3$(Sc,Zr), as expected from the Al-rich end of the Al-Sc equilibrium phase diagram [12] (Fig. 7b). It was interesting to point out that the broken oxidation debris could act as the nucleation sites for primary Al$_3$(Sc,Zr) precipitation, which have been investigated by Prangnell and Spierings [12,16]. From conventional nucleation theory, the nucleation current $J$, number of nuclei per unit time per unit volume, is [26,27]:

$$J^* \propto ND\exp(-\frac{\Delta G^*}{RT})$$  \hspace{1cm} (9)

where $N$ is the number of the nucleation sites, $\Delta G^*$ is the nucleation barrier, which is inversely proportional to the square of the volume free energy change $\Delta G_v$, while $\Delta G_v$ is proportional to the logarithm of the supersaturation. The supersaturation has little difference between the overall scan speeds compared to the variation of $N$. Thus nucleation current $J$ was significantly enhanced due to the presence of the oxidation debris. Meanwhile, the dynamic viscosity $\mu$, can be expressed as [28]:

$$\mu = \frac{16}{15} \sqrt{\frac{m}{K_\text{B}T}} \gamma$$  \hspace{1cm} (10)

where $m$ is the atomic mass and $\gamma$ is the surface tension of liquid. Due to the decreased temperature, the dynamic viscosity of the Al-Mg-Sc-Zr liquid within the molten pool increased accordingly, causing a dramatical slowdown of the Marangoni flow. Therefore, primary Al$_3$(Sc,Zr) particles driven by the decreased downward flow were correspondingly deposited at the bottom of the molten pool (Fig. 10b and c). As the temperature further decreased below solidus temperature (Fig. 6b), the remaining liquid solidified by the simultaneously coupled growth with the $\alpha$-Al and eutectic Al$_3$(Sc,Zr) phase according to the phase diagram. Due to a considerable increase in the dynamic viscosity and the resulted limited movement of the precipitates, the homogeneous distribution of the eutectic Al$_3$(Sc,Zr) particles throughout the molten pool could be predicted (Fig. 10d). As a result, a nonuniform distribution of the precipitates within the molten pool consisting of primary and eutectic Al$_3$(Sc,Zr) particles, was formed at a relatively low laser scan speed (Fig. 10d). It had to be mentioned that the absence of the precipitates at a relatively high laser scan speed could be ascribed to a significant enhancement of the cooling rate. As the laser scan speed declined, the velocity of Marangoni flow dropped from 14 m/s to 7 m/s (Fig. 5) and, duration time off liquid between $T_i$ and $T_f$ decreased from 0.016 ms to 0.006 ms (Fig. 6). This caused a dramatical increase of the oxidation debris and nucleation sites of the Al$_3$(Sc,Zr) precipitates, thus restricting the growth of precipitates. With an increase in the laser scan speed, the solid solubility of Sc and Zr atoms in the matrix was

HRTEM images of Al$_3$(Sc,Zr) precipitates (Fig. 9c), coherent lattice between the Al$_3$(Sc,Zr) particles and $\alpha$-Al was obtained. The FFT (Fast-Fourier transformation) was applied to the HRTEM image of the precipitation and it was found that the orientation consisting of (111) and (200) was involved, indicating the formation of a FCC structure similar to $\alpha$-Al. The lattice plane distance of (200) was measured equal to 2.33 Å, which is approximately similar to the lattice plane distance $d$ of 2.34 Å of the matrix $\alpha$-Al. The typical microstructure observed by SEM for the part fabricated at a high $v$ of 3000 mm/s, are exhibited in Figs. 8d and e. It was apparent that no nano-precipitate was found both in the center (Fig. 8e) and the bottom (Fig. 8d) of the molten pool, indicating a different precipitation behavior with the increase in the laser scan speed.

At a relative low laser scan speed, the distribution behavior of nanoprecipitation particles within the molten pool can be summarized as follows: a small amount of nano-precipitation particles with a radius of 10 ~ 40 nm were distributed in the matrix at the bottom of the molten
increased, leading to the increase in the interplanar crystal spacing.

3.4. Hardness and wear performance

Fig. 11 depicts the variations of microhardness of the SLM-processed Al-Mg-Sc-Zr specimens at different laser scan speeds. The microhardness of the most dense part \((v = 1800 \text{ mm/s})\) was 94 HV\(_{0.2}\), which was higher than the cast ones [18]. It was obvious that the microhardness was influenced by the applied laser scan speed. As \(v\) decreased from 3000 mm/s to 1800 mm/s, the mean microhardness values showed a slight enhancement from 87 HV\(_{0.2}\) to 94 HV\(_{0.2}\) with a limited fluctuation. The increased hardness could be attributed to the formation of the fine nano-scaled Al\(_3\)(Sc,Zr) precipitates while, the slight fluctuation could be ascribed to the irregularly shaped pores formed due to the insufficient melt of the powder under a relatively high \(v\). The results is interestingly consist with the results of XRD, SEM and TEM.

Fig. 12 depicts the variations of COF and resultant wear rate with sliding time for the SLM-processed Al-Mg-Sc-Zr specimens at different laser scan speeds and, the corresponding worn surfaces are given in Fig. 13. The COF values of the parts, at a relatively low scan speed of 1800 mm/s and 2200 mm/s, showed a steady-state behavior. However, the parts fabricated under a higher scan speed of 2600 mm/s and 3000 mm/s, displayed larger fluctuations. Meanwhile, the applied laser scan speed exhibited a remarkable influence on the obtained wear performance. At a relatively low \(v\) of 1800 mm/s, the average COF value and wear rate were 0.61 and \(1.74 \times 10^{-4} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}\), respectively. A fairly smooth worn surface covered with the adhesion tribolayer absent of the apparent protruding particles was obtained, indicating a good wear property. By increasing \(v\) to 2200 mm/s, the worn surface became rather rough and some abrasive fragments were observed, resulting in the increase in the mean COF and resultant wear rate to 0.65 and \(2.86 \times 10^{-4} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}\), respectively. As \(v\) further increased to 2600 mm/s, it was interesting to find that the worn surface primarily consisted of parallel and deep grooves with the appearance of the abrasive fragments, demonstrating an abrasion wear behavior as well as a deterioration in the wear property. Therefore, the value of COF and the wear rate dramatically increased to 0.81 and \(3.82 \times 10^{-4} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}\), respectively. As \(v\) further increased to 3000 mm/s, an even worse worn surface was bestrewed with broken oxide layers and, the COF value of 0.85 and wear rate of \(4.41 \times 10^{-4} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}\) were obtained.

It was concluded that both hardness and wear performance were highly dependent on the nano-precipitation behavior, which was primarily dominated by the variation of the laser scan speeds. As hardness was essentially a measure of the plastic yield stress of the metal, the traditional theory of the strengthening mechanism for the yield strength can be used to explain the variation of the hardness [29]. In the case of a high scan speed, the solid solution strengthening played a dominate role due to the absence of the precipitates, which can be assessed by [14,30]:

![Fig. 13. High-magnification FE-SEM images showing the typical morphologies of the worn surfaces of the SLM-processed Al-Mg-Sc-Zr parts at the different laser scan speeds: (a) \(v = 1800 \text{ mm/s}\); (b) \(v = 2200 \text{ mm/s}\); (c) \(v = 2600 \text{ mm/s}\); (d) \(v = 3000 \text{ mm/s}\).](image-url)
\[
\sigma = \frac{3.1Ge^{1/2}}{700} \times 3.8 \times 10^{-7}
\]
where \( e = 3.8 \times 10^{-7} \) is an experimental constant, \( G = 26 \text{ GPa} \) is the shear modulus of Al at room temperature and \( c \) is the concentration of the solute in atomic percent. As there were no precipitates formed, it was reasonable to assume that all the Mg, Sc and Zr atoms were solubilized in the matrix. Due to the little difference among the radius of these three atoms, \( c \) is estimated to be in the range of 3–5% and the estimated increment of strengthening was about 75–100 MPa \([1,4]\).

The antisite boundary strengthening, in which \( Al(Sc,Zr) \) particles resisted the dislocation motion by the formation of an antisite boundary (APB) strengthening, could be the main reinforcement mechanism due to formation of the coherent, ordered structure. The APB strengthening \( \Delta \sigma_{\text{APB}} \) was given by \([14,31]\):

\[
\Delta \sigma_{\text{APB}} = (3.1 \frac{d^{1/2}}{G}) \times 3.8 \times 10^{-7}
\]

where \( \gamma = 0.5J/m^2 \) is the APB energy of the precipitate phase, \( b \) is the magnitude of the Burgers vector of Al (0.286 nm), \( r \) is the mean precipitate radius which could be identified as 25 nm, \( f \) is the volume fraction of \( Al(Sc,Zr) \) precipitates, which could be identified as 0.75\% (the error introduced by this approximation is negligible \([1,3]\)). Then the theoretical stresses were estimated as 210.1 MPa, which was much higher than that of solid solution strengthening dominated at a low scan speed. Therefore, an increased microhardness as well as the good wear performance was obtained for the reduction of the scan speed.

4. Conclusion

In this study, the Al-Mg-Sc-Zr alloy prepared by SLM at various processing parameters was studied. The following conclusions could be drawn:

(1) The diffraction peaks of the SLM-processed parts showed a prominent (200) texture compared to the (111) texture of the raw powder. A significant shift of diffraction peaks towards a low angle and an increment of lattice plane distance were obtained as the scan speed increased, due to the rapid cooling rate of the SLM process and subsequent formation of the supersaturated solid solution. The densification was enhanced, owing to the elimination of microcracks and pores as the scan speed decreased from 3000 mm/s to 1800 mm/s.

(2) The distribution mechanism of the precipitates at various scan speeds was revealed and summarized in details. At a relatively low scan speed of 1800 mm/s, a small amount of coherent, spherical \( Al(Sc,Zr) \) precipitates with a radius of 10–40 nm were obtained at the bottom of molten pool, while very limited precipitates were found in the center of the molten pool. No precipitates were observed throughout the matrix at a very high scan speed of 3000 mm/s. This was probably attributed to the dramatical change of heat-mass transfer as well as the short liquid lifetime with the change of scan speed.

(3) The microhardness and wear performance were sensitive to the scan speeds and the resultant precipitate distribution. A high hardness of 94 HV0.2, a reduced COF of 0.61 and wear rate of 1.74 \times 10^{-4} \text{ mm}^2\/\text{m}--1 were obtained at a relatively low scan speed due to the formation of the coherent and spherical \( Al(Sc,Zr) \) precipitates. A change of dominate strengthening mechanism from solid solution strengthening of 75–100 MPa to antisite boundary strengthening of 210.1 MPa took place as the scan speed decreased.

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