Selective Laser Melting Additive Manufacturing of Hard-to-Process Tungsten-Based Alloy Parts With Novel Crystalline Growth Morphology and Enhanced Performance

Tungsten (W), due to the unique properties such as high melting point, high tensile strength, and low thermal expansion coefficient, is very promising for the applications as high heat flux components and high-power density structural materials in radiation environments [1–3]. Nevertheless, W, as a typical hard-to-process material, demonstrates serious inherent embrittlement [4], which limits its applications as the structural material. It has been revealed that the significant embrittlement and resultant low ductility of W material typically originate from the microstructural factors including the heterogeneity in grain size and its distribution and the grain growth and coarsening by recrystallization [5]. The room-temperature ductility of W material is therefore strongly dependent on grain structure and its size and can be enhanced considerably by decreasing grain size or homogenizing grain structure [6]. On the other hand, it has been disclosed that when heated above the recrystallization temperature, the microstructure of W material tends to change considerably because of the grain growth effect, which further reduces strength and hardness and, meanwhile, causes embrittlement [4]. Fortunately, the previous work has proved that the strengthening and/or toughening of W material with the addition of ceramics, which are typically added in the discontinuous form of particles dispersed...
throughout the matrix, is a promising method to decrease the brittleness of W material [7]. In particular, as the ceramic reinforcing particles are refined to a nanometer scale to prepare W-based nanocomposites, the obtainable mechanical performance is expected to be enhanced significantly, due to the unique properties of nanoparticles including small size effect and surface/interface effect [8–10]. A uniform microscopic distribution of ceramic nanoparticles along grain boundaries is effective in handicapping grain growth and grain boundary migration at higher working temperatures, which in turn elevates the recrystallization temperature and decreases the brittleness of W material [11].

Powder metallurgy (PM) methods are typically applied to produce bulk-form W-based parts, e.g., spark plasma sintering [12], hot-press sintering [13], liquid-reactive sintering [14], etc. In the case of PM methods with limited operative temperatures, one of the significant technological problems is the formation of residual porosity, due to the considerably high melting temperatures of W-based materials and attendant limited density activation. Furthermore, nearly all PM-processed pieces are required to be preworked by some dedicated tools such as moulds or dies to obtain desired shapes. However, due to the limitation of available tools, some complex-structured W-based components are normally difficult to be produced. On the other hand, for bulk-form W-based parts condensed from ultrafine nanopowder by conventional PM methods, the uncontrolled agglomeration of nanoscale particles due to the considerably large van der Waals attractive forces tends to cause the microstructural inhomogeneity and even the coarsening of original favorable nanostructures. In this situation, differential stresses caused by heterogeneous microstructures are directly related to the propagation of internal cracks in PM-consolidated solids. Therefore, novel processing methods are required to achieve complex shaped, fully dense W-based parts with homogeneous microstructures and resultant elevated performance.

SLM, as a newly developed AM/3D printing technology [15–17], enables the rapid production of 3D parts having any complex structures directly from powder materials [18–20]. SLM builds components in a layer-by-layer fashion by selective fusion and consolidation of thin layers of loose powder, using a high-energy laser beam. SLM possesses a number of advantages including net-shape production without requirements of molds or dies, a high level of processing flexibility, and a wide range of applicable powder materials [21]. Typically, SLM process demonstrates a unique nonequilibrium physical metallurgical nature, including multiple modes of heat, mass, and momentum transfer [22]. During SLM, the high-energy laser beam focused on the powder layer surface can reach a power density up to $10^{10}$–$10^{12}$ W/cm$^2$ and can heat a material surface speedily to a temperature up to 10$^3$ K, followed by a superfast cooling at a rate up to $10^5$–$10^7$ K/s [23]. In this situation, even the high-melting-point W material tends to melt completely and, subsequently, experience laser-induced rapid solidification process. It accordingly provides a high potential for obtaining very fine microstructures with superior mechanical properties. Nevertheless, little previous work has been reported on laser processing of W-based parts through the complete melting/precipitation mechanism. A large degree of shrinkage occurs during liquid–solid transformation, which tends to produce considerable stresses and even microcracks in SLM-processed W-based parts. Furthermore, the uncontrollability of the crystallization and microstructural development of W alloy in an SLM route remains a major challenge. Recent work from Zhou et al. [24] on SLM of pure W revealed that the “balling” effect of melted droplets at the laser focal points and entrapped cavities hindered the preparation of fully dense parts. An analysis of the balling mechanism indicated that such a metallurgical defect was determined by the intrinsic W properties and laser processing parameters.

In the present work, bulk-form W-based alloy parts having novel microstructural features were successfully produced by SLM of a W–Ti–C system. The melting behavior and microstructural development of W-based parts at various SLM parameters were studied and the mechanical properties including densification rate, microhardness, and tribological/wear properties were assessed, with an aim to establish a relationship of process, microstructure, and mechanical performance of W-based alloy parts by SLM.

2 Experimental Procedures

2.1 Powder Materials. The starting powder materials were 99.9% purity, equiaxed W powder with an average particle size of 7 μm and 99.0% purity TiC nanopowder with a near spherical shape and a mean particle size of 50 nm. The TiC/W powder system consisting of 2.5 wt.% TiC was milled in a Pulverisette 6 planetary high-energy ball mill (Fritsch GmbH, Germany) at a rotation speed of 250 rpm for 5 hrs, using a ball-to-powder weight ratio of 10:1. The as-prepared TiC/W nanocomposite powder had a sufficiently high flowability and a sound spreading ability on powder bed, which was particularly important for a successful SLM production. For the current nano-TiC/macro-W composite system, the nano-TiC particles were dispersed and mixed uniformly during ball milling treatment. After milling process, the as-prepared composite powder was immediately used for SLM production, which demonstrated a high flowability on the powder bed and a sound laser processing ability. With the aid of ball milling process to obtain the homogeneous W-based nanocomposite powder, the agglomeration of powder after the milling process was insignificant and the powder could be transferred to the powder bed smoothly for SLM.

2.2 SLM Processing. A schematic of the entire SLM equipment used in the present study is depicted in Fig. 1(a), and a detailed SLM processing route for the fabrication of bulk-form TiC/W nanocomposite parts is illustrated in Fig. 1(b). The self-developed SLM equipment in NUAA consisted mainly of a YLR-500 Ytterbium fiber laser with a power of ~500 W and a spot size of 70 μm (IPG Laser GmbH, Burbach, Germany), a hurrySCAN® 30 laser scanner (SCANLAB AG, Puchheim, Germany), an automatic powder layering apparatus, an inert argon gas recycling and protection system, and a computer system for process control. When samples were to be prepared, a steel substrate was fixed on the building platform and leveled. The argon gas with an outlet pressure of 30 mbar was fed into the sealed building chamber and the resultant oxygen content decreased below 10 ppm. A thin layer of TiC/W nanocomposite powder with a layer thickness of 25 μm was then deposited on the substrate by the powder spreading system. For the spreading of the powder on each layer, a reciprocating mode was applied to achieve a uniform spreading of the powder in every position on the layer. Even though there was some slight agglomeration of the powder in the first place of the layer, the powder in this place would be recoated homogeneously during the reciprocation process of the powder spreading mechanism. With the aid of the reciprocating mode for powder spreading, the as-spread powder layer was uniform and could well meet the requirements of SLM production. Afterward, the laser beam scanned the powder bed surface to form a layerwise profile according to computer-aided design data of the samples. A layer power of 160 W, which was optimized by the preliminary SLM experiments, was fixed during each batch of experiment. Meanwhile, the scan speeds were settled periodically at 50, 100, 200, and 300 mm/s by SLM control program, in order to change the applied processing conditions. Basically, the laser scan-speeds and test conditions illustrate a uniform scan speed increase of 100 mm/s for SLM applied. Furthermore, in order to investigate the effects of laser scan speed and resultant laser energy density on SLM processing ability of W-based parts, a significantly low scan speed of 50 mm/s was also applied for SLM. Laser scanning of each layer was based on a linear raster scan pattern with a scan vector length of 4 mm and a hatch spacing of 50 μm between neighboring lines.
order to assess the laser energy input to the powder layer being melted, an integrated parameter LF was defined [25]

\[ \text{LF} = \frac{P}{v h} \quad (1) \]

where \( P \) is the laser power, \( v \) is the scan speeds, and \( h \) is the hatch spacing. Four different LFs of 10.7, 16, 32, and 64 J/mm² were applied to build bulk-form parts with dimensions of 8 mm × 8 mm × 5 mm, and the amount of layers that had been deposited on the substrate was 200.

2.3 Microstructural Characterization and Mechanical Properties Tests. Phase identification of SLM-processed parts was performed by a D8 Advance X-ray diffractometer (XRD) (Bruker AXS GmbH, Germany) with Cu Kα radiation (\( \lambda = 0.154 \text{ nm} \)) at 40 kV and 40 mA, using a continuous scan mode. A quick scan at 4 deg/min was first performed over a wide range of 2\( \theta \) = 30–120 deg to give a general overview of the diffraction peaks. A slower scan rate of 1 deg/min was further used in the vicinity of the first and second strong peaks to give a more accurate determination of 2\( \theta \) location and intensity of the peaks. Specimens for metallographic examinations were cut, ground, and polished according to the standard procedures and etched with a solution comprising HF (10 mL), HNO₃ (30 mL), and distilled water (70 mL) for 15 s. High-resolution microstructures were characterized using a LEO 1550 field emission scanning electron microscope (FE-SEM) (Carl Zeiss NTS GmbH, Germany) in a secondary electron mode at 5.0 kV. Chemical compositions were analyzed by an EDAX energy dispersive X-ray (EDX) spectroscopy (EDAX Inc., Mahwah, NJ), using a super-ultra thin window sapphire detector.

The experimentally measurable density of SLM-processed parts was defined as mass divided by volume. The mass of the specimens was measured by the analytical balance, and the volume of the specimens was determined using the Archimedes’ method. Then, the densification rate of SLM-processed parts was determined by the ratio of the experimentally measurable density to the TD of the corresponding material. The Vickers hardness was measured using a MicroMet 5101 microhardness tester (Buehler GmbH, Germany) at a load of 0.3 kg and an indentation time of 20 s. Based on the ASTM G99 standard, the wear/tribological properties of the specimens were estimated by the dry sliding wear tests conducted in a HT-500 ball-on-disk tribometer (Lanzhou ZhongKe KaiHua Sci. & Technol. Co., Ltd., Lanzhou, China) in air at room temperature. Surfaces of samples to be tested were ground and polished prior to wear tests. A bearing steel GCr15 ball having a diameter of 3 mm and an average hardness of HRC60 was taken as the counterface material, using a test load of 5.2 N. The friction unit was rotated at a speed of 560 rpm for 15 min, and the rotation radius was 2 mm. The COF was recorded automatically during wear tests. The wear volume (V) was determined gravimetrically using

\[ V = \frac{M_{\text{loss}}}{\rho} \quad (2) \]
here, the standard diffraction peaks for W, which are change due to the addition of TiC and the variation of SLM
fraction peaks of W, as depicted in Table 1, revealed that the exact
processed parts at all given LFs. The XRD characterization within
W (JCPDS Card #04-0806) were generally detected in SLM-
of 2θ of SLM-processed W-based parts obtained within a wide range
LF = 10.7 J/mm², v = 300 mm/s, (b) LF = 16 J/mm², v = 200 mm/s,
LF = 32 J/mm², v = 100 mm/s, and (d) LF = 64 J/mm², v = 50 mm/s

where  \( M_{\text{loss}} \) is the weight loss of the specimens after wear tests, and \( \rho \) is the density. The wear rate (\( \omega \)) was calculated by
\[
\omega = \frac{V}{WL} \quad (3)
\]
where \( W \) is the contact load, and \( L \) is the sliding distance during tests.

3 Results and Discussion

3.1 Phase Evolution. Figure 2 depicts the typical XRD spectra of SLM-processed W-based parts obtained within a wide range of 2θ = 30–120 deg. The strong diffraction peaks corresponding to W (JCPDS Card #04-0806) were generally detected in SLM-processed parts at all given LFs. The XRD characterization within small 2θ angles in the vicinity of the first and second strong diffraction peaks of W, as depicted in Table 1, revealed that the exact 2θ locations and intensities of W peaks showed an apparent change due to the addition of TiC and the variation of SLM parameters. Here, the standard diffraction peaks for W, which is located at 2θ = 40.264 deg and 2θ = 73.195 deg, were taken for a comparison. It revealed that as the applied LF increased by lowering laser scan speed, the 2θ locations of the W diffraction peaks generally shifted to the higher 2θ angles. The shift tendency of 2θ angles to larger values became more significant at a higher LF (Table 1). Meanwhile, the intensity of the W diffraction peaks showed a significant decrease when a higher LF was applied (Table 1), which implied the formation of considerably refined crystalline microstructures in SLM-processed W-based part in this situation.

Based on the Bragg’s law for XRD analysis [26]
\[
2d \sin \theta = n \lambda (n = 1, 2, 3, \ldots) \quad (4)
\]
the detected increase of 2θ at a higher LF (Table 1) indicates a decrease in the lattice plane distance (d), which is believed to be caused by the alloying of Ti and C atoms with W matrix. During SLM process, the high-energy fiber laser beam focused on the powder bed can concentrate a power density up to 10⁹–10¹² W/cm² and can heat the powder layer surface within 25 ms to a working temperature up to 10⁷ K [27]. SLM of the present TiC/W system is accordingly processed via a metallurgical mechanism with the complete melting of the powder. Both the W matrix powder with a melting point of 3695 K and the TiC additive powder with a melting point of 3433 K tend to become melted fully during SLM process, thereby releasing the mobile Ti and C atoms in laser-induced molten pool. During the subsequent rapid solidification process after the laser beam moves away, the solid solution alloying of Ti and C atoms in W matrix predominates during this course. The solid solution of C in W is interstitial and the rate of expansion of W lattice caused by the solid solution of C atoms amounts to 7 × 10⁻³ nm per at. % C [28]. On the other hand, the W–Ti tends to form substitution solid solution. According to the Hume–Rothery rule [29], the extensive substitutional solid solution occurs only if the atomic size factor, i.e., the relative difference between the atomic radii of the two elements, is less than 15%. If the difference is larger than 15%, the solubility is limited. The atomic radii of Ti and W are 144.8 pm and 137.1 pm, respectively, and the corresponding atomic size factor is 5.6%, which indicates an extensive solid solubility of Ti in W. Normally, the occurrence of solid solution phenomena, both the interstitial solution of C in W and the extensive substitutional solution of Ti in W, is accompanied by the microscopic volume expansion, which in turn creates stresses at grain boundaries that influence the lattice parameters of W matrix in SLM-processed W-based alloy parts.

3.2 Melting and Densification Mechanisms. Figure 3 shows the typical surface morphologies of SLM-processed W-based alloy parts at various laser scan speeds and resultant LFs. High-magnification micrographs of the corresponding surfaces, as revealed in Fig. 4, illustrate the melting and solidification mechanisms of the liquid front under different SLM conditions. The resultant densification levels of SLM-processed W-based alloy parts are depicted in Fig. 5. At a relatively low LF of 10.7 J/mm² induced by a high v of 300 mm/s, a heterogeneous, porous surface

![Fig. 2 XRD spectra over a wide range of 2θ = 30–120 deg showing constitutional phases of SLM-processed W-based alloy parts using different SLM processing parameters: (a) LF = 10.7 J/mm², v = 300 mm/s, (b) LF = 16 J/mm², v = 200 mm/s, (c) LF = 32 J/mm², v = 100 mm/s, and (d) LF = 64 J/mm², v = 50 mm/s](image)

<table>
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<tr>
<th>Samples and SLM processing parameters</th>
<th>First strong peak</th>
<th>Second strong peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2θ (deg)</td>
<td>Intensity (CPS)</td>
</tr>
<tr>
<td>Standard W sample (PDF#04-0806)</td>
<td>40.264</td>
<td>—</td>
</tr>
<tr>
<td>LF = 10.7 J/mm², v = 300 mm/s</td>
<td>40.28</td>
<td>7068.9</td>
</tr>
<tr>
<td>LF = 16 J/mm², v = 200 mm/s</td>
<td>40.30</td>
<td>5134.2</td>
</tr>
<tr>
<td>LF = 32 J/mm², v = 100 mm/s</td>
<td>40.32</td>
<td>2359.6</td>
</tr>
<tr>
<td>LF = 64 J/mm², v = 50 mm/s</td>
<td>40.36</td>
<td>2189.7</td>
</tr>
</tbody>
</table>
consisting of irregular-shaped, large-sized open pores with a mean size of ~150 µm was produced after SLM (Fig. 3(a)), resulting in a limited densification rate of 87.5% TD (Fig. 5). The solidified tracks were considerably crumpled, having the disordered liquid solidification front. A number of small-sized unmelted W particles with an average size below 10 µm appeared in the solidified liquid front (Fig. 4(a)). On increasing the applied LF to 16 J/mm² by lowering v to 200 mm/s, the SLM-processed surface was highly dense and free of any apparent pores or cracks (Fig. 3(b)), and the densification response of SLM-processed part was enhanced markedly to 93.4% TD. The solidified scan tracks had the orderly distributed liquid solidification front, exhibiting an improved microstructural homogeneity of scan tracks (Fig. 4(b)). Interestingly, at a suitable LF of 32 J/mm², the laser-processed surface of W-based alloy parts was completely dense, consisting of parallel-distributed and coherently bonded scan tracks (Fig. 3(c)). The ordered and homogeneous liquid solidification front was produced in the solidified scan tracks (Fig. 4(c)). In this situation, a near fully dense W-based part with 97.8% TD was obtained after SLM (Fig. 5). However, at an even higher LF of 64 J/mm² caused by a considerably low v of 50 mm/s, several typical metallurgical defects associated with SLM occurred on the surface of
laser-processed W-based part. First, the narrow microcracks were formed on the surface, typically in the middle of the scan tracks where the SLM working temperature is highest. Second, a number of spherical-shaped inclusions were present on the surface (Fig. 3(b)). High-magnification characterization revealed that these inclusions were the solidified liquid splashes caused by the significant liquid instability and resultant balling effect during SLM process with a high laser energy input (Fig. 4(d)). The occurrence of defects including microcracks formation and balling phenomenon lowered the densification level of SLM-processed part to 92.4% TD in this case (Fig. 5).

Typically, SLM is processed based on a complete melting metallurgical mechanism of the powder, and the dynamic viscosity ($\mu$) of the molten pool consisting of the complete liquid formation is controlled by SLM working temperature ($T$) and is defined by [30]

$$\mu = \frac{16}{15} \sqrt{\frac{m}{k_{B}T^3}}$$

where $m$ is the atomic mass, and $\gamma$ is the surface tension of the liquid. Using a higher laser scan speed ($v$) results in a shorter dwelling time of laser beam on the surface of molten pool and attendant lower LF acted on the pool, thereby decreasing the operative $T$ within the pool. The dynamic viscosity of the W–Ti–C melt within the pool accordingly increases (Eq. (5)). The combined effects of a shorter liquid lifetime and an elevated viscosity of the melt result in a poor rheological property of the melt and, accordingly, a limited wettability of the melt with the neighboring scanned track and the previously processed layer. Furthermore, due to the limited SLM working temperature, the appearance of the unmelted W particles ahead the liquid solidification front (Fig. 4(a)) further decreases the wetting characteristics of the melt. Consequently, a large amount of intertrack and interlayer residual porosity tends to be remained during laser rapid solidification process (Fig. 3(a)), thereby lowering the densification response of SLM-processed W-based part (Fig. 5).

The present study reveals that as a reasonably high LF of 32 J/mm$^2$ is applied, the W-based powder system can be melted fully, which is demonstrated by the continuous and ordered liquid melting/solidification front (Figs. 3(c) and 4(c)). The complete melting of W-based powder and the subsequent stable solidification behavior of the melt play a crucial role in achieving a sufficiently high densification of SLM-processed W-based alloy parts. Nevertheless, care should be taken to control the input LF; the application of an excessive LF of 64 J/mm$^2$, although it provides a high potential for melting the W-based powder completely, exerts a detrimental influence on the densification behavior of SLM-processed part (Fig. 5), due to the presence of microcracks and balling effect in this situation (Figs. 3(d) and 4(d)). In laser-induced molten pool containing the complete liquid formation, a significant temperature gradient will be present between the center and edge of the pool. The temperature gradient in the pool gives rise to surface tension gradient and resultant Marangoni convection. As a connective stream, the formation of Marangoni flow within the pool increases the magnitude of the thermocapillary force and resultant instability of the melt [31]. It has been disclosed that a higher LF and attendant elevated SLM working temperature result in the intensified Marangoni convection and liquid capillary instability effect [18,19]. Consequently, the liquid surface flow occurs from a region of low surface tension to a region of high surface tension, changing the direction of liquid flow from a radially outward to an inward [32]. The radially inward flow causes the liquid to spheroïdize toward the laser beam center where the SLM working temperature is highest. Under this condition, a number of small-sized liquid droplets tend to splash from the surface of the molten track being solidified, due to the reduction in the surface energy of liquid at short length scales. After solidification, a large amount of micrometer-sized spherical splashes are formed and included on laser-processed surface (Fig. 4(d)), which is known as balling effect [33]. As a typical metallurgical defect associated with SLM process, the occurrence of balling effect tends to disturb the advancing liquid solidification front significantly, hence producing interrupted scan tracks and, finally, lowering the densification rate of SLM-processed part based on multitrack and multilayer laser scanning (Fig. 5).

On the other hand, the formation of microcracks on the surface at an excessive LF (Fig. 3(d)) is believed to be thermal cracks caused by residual thermal stresses. During SLM densification process, shrinkage occurs speedily once the powder material becomes fully molten. A nominal flat surface of powder bed becomes a curved surface or a recessed region due to the effect of densification caused by conversion of the loose powder to dense liquid [34]. Based on the previous studies by Dai and Shaw [35] and Xiao and Zhang [36], a dominant mechanism that induces residual stresses in laser additive manufactured part is that the cool-down phase of the molten top layer tends to shrink due to the thermal contraction; however, simultaneously, such a deformation is inhibited by the underlying previously solidified layers. The thermal shrinkage for a given metallic material increases as the input laser energy density increases [37], thereby accumulating considerable thermal stresses in SLM part being solidified. The microcracks in SLM-processed W-based alloy part, as noted in Fig. 3(d), typically belong to the hot craking, caused by the interruption of liquid film at grain boundaries in the solidification temperature range, due to the action of the complex tensile stresses [38].

### 3.3 Microstructures and Chemical Compositions

The characteristic microstructures of W-based crystals on the etched cross sections of SLM-processed W-based alloy parts using various LFs are provided in Figs. 6(a)–6(d). The chemical compositions of the corresponding W-based crystals are detected by EDX method, as revealed in Table 2. The underlying crystallization mechanisms of W crystals during SLM are schematically depicted in Fig. 7. Generally, the microstructural features of W-based crystals in SLM-processed W-based alloy parts differed entirely from the grain-structured crystals in the conventionally PM-processed W-based parts based on solid-state sintering or liquid-phase sintering mechanisms [12–14]. The complete melting/solidification processing mechanism contributed to the formation of unique microstructures of SLM-processed W-based alloy parts. EDX element analysis revealed that the crystals in SLM-processed structures were generally identified as the W crystals dissolved with Ti and C elements. As the applied LF increased, more Ti and C elements were found to be dissolved in the W matrix (Table 2). Meanwhile, it was found that the applied LF played a key role in
determining the microstructural development of W crystals during SLM. At a relatively low LF of 10.7 J/mm² combined with a high \( v \) of 300 mm/s, the directionally solidified W crystals with a cellular structure were present on the cross section of SLM-processed part. The cellular crystals were significantly refined, with the average length and diameter of cellular crystals less than 15 \( \mu \)m and 1 \( \mu \)m, respectively (Fig. 6(a)). As the LF increased to 16 J/mm², although the as-developed W-based crystals almost demonstrated a directionally solidification feature, the mixed crystal structures consisting of cellular crystals and cellular dendritic crystals were present. A fraction of W-based crystals developed into a cellular dendritic morphology, and the refined secondary dendrites start to form along the cellular crystals (Fig. 6(b)). At a sufficiently high LF of 32 J/mm², the homogenous cellular dendritic W-based crystals were produced after SLM, having a reduced crystal length of \( \sim 5 \mu m \) and a slightly coarsened cellular width of \( \sim 1.5 \mu m \) (Fig. 6(c)). The microstructural features of SLM-processed W-based alloy part changed completely at an even higher LF of 64 J/mm²; the equiaxed dendritic W-based crystals were formed after SLM, with the average crystalline size in the order of 2–4 \( \mu m \) (Fig. 6(d)). For comparison, the typical microstructure of SLM-processed pure W part without the addition of TiC is provided in Fig. 6(e). A relatively coarsened granular crystal feature was observed, which was different from the cellular/dendritic growth features of SLM-processed W-based alloy parts (Figs. 6(a)–6(d)).

It was accordingly reasonable to conclude that as the applied LF increased by lowering laser scan speed \( v \), the morphologies of W-based crystals in SLM-processed W-based alloy parts experienced a successive change from the cellular crystal to the cellular dendritic crystal and, finally, to the equiaxed dendritic crystal, as depicted schematically in Fig. 7. During laser rapid solidification process, the velocity of the solidification front is determined by the temperature field. As the velocity of the solidification front

### Table 2 EDX elemental analysis in point #1, #2, #3, and #4 in Figs. 6(a)–6(d) showing the chemical compositions of W-based crystals in SLM-processed W-based alloy parts

<table>
<thead>
<tr>
<th>Test position</th>
<th>W</th>
<th>C</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1, Fig. 6(a)</td>
<td>95.71 ± 4.3</td>
<td>2.99 ± 1.2</td>
<td>1.30 ± 0.1</td>
</tr>
<tr>
<td>Point 2, Fig. 6(b)</td>
<td>92.04 ± 3.6</td>
<td>6.19 ± 1.5</td>
<td>1.77 ± 0.1</td>
</tr>
<tr>
<td>Point 3, Fig. 6(c)</td>
<td>91.53 ± 3.3</td>
<td>6.88 ± 1.6</td>
<td>1.58 ± 0.1</td>
</tr>
<tr>
<td>Point 4, Fig. 6(d)</td>
<td>93.40 ± 3.9</td>
<td>4.96 ± 1.4</td>
<td>1.65 ± 0.1</td>
</tr>
</tbody>
</table>

![Fig. 6 Characteristic microstructures (FE-SEM) on the etched cross sections of SLM-processed W-based alloy parts using different SLM processing parameters, showing laser-controlled crystallization features of W-based crystals: (a) LF = 10.7 J/mm², \( v = 300 \) mm/s, (b) LF = 16 J/mm², \( v = 200 \) mm/s, (c) LF = 32 J/mm², \( v = 100 \) mm/s, and (d) LF = 64 J/mm², \( v = 50 \) mm/s. Typical microstructure of SLM-processed pure W part at LF of 32 J/mm² is provided for a comparison purpose (e).]
where \( n \) is the unit direction normal to the solid–liquid interface (i.e., parallel to \( v_s \)), \( v \) is the laser scan speed, and \( \theta \) is the angle between the scan direction and normal to the liquid–solid interface. The crystallization and growth of crystals along with the advancing solidification front are further controlled by the undercooling of melt being solidified. The thermal undercooling \( \Delta T_{t} \) and the constitutional undercooling \( \Delta T_c \) within the molten pool are expressed as follows [40]:

\[
\Delta T_{t} = \frac{\Delta H_f}{v_p F_{iv}(P_i)} \\
\Delta T_c = m c_p \left( 1 - \frac{m^2/m}{1 - (1 - k(v_s))F_{iv}(P_i)} \right)
\]

Here, \( F_{iv}(x) \equiv x \exp(x) E_1(x) \) denotes the Ivantsov function (with \( E_1 \) as the first exponential integral function), \( P_i = v_p R/2D_l \) the thermal Pélet number (with \( R \) as the curvature radius of the crystal tip and \( D_l \) as the thermal diffusivity), \( \Delta H_f \) the heat of fusion, \( c_p \) the specific heat of the liquid, \( m^2 \) the velocity dependent liquidus slope, \( m \) the liquidus slope, \( c_i \) the nominal concentration of the metal, \( P_i = v_p R/2D_l \) the chemical Pélet number (with \( D_l \) as the diffusion coefficient), and \( k(v_s) = [(k_{a} + v_s/v_D)/(1 + v_s/v_D)] \) is the velocity dependence of the partition coefficient (with \( k_a \) as the equilibrium partition coefficient and \( v_D \) as the diffusive speed that is treated as a free parameter). At a lower \( v \) and resultant higher LF, the interfacial velocity of the advancing solidification front \( (v_s) \) decreases (Eq. (6)). In this situation, the thermal undercooling \( \Delta T_{t} \) shows a decrease, whereas the constitutional undercooling \( \Delta T_c \) is elevated, as revealed by Eqs. (7) and (8). With the enhancement of constitutional undercooling \( \Delta T_c \), the smooth parabolic-shaped interfaces of cellular crystals (Fig. 7(a)) become significantly unstable and, therefore, the primary dendrites tend to be bulged along the cellular crystals, leading to the formation of cellular dendritic crystal structure (Fig. 7(b)). Furthermore, due to a decrease of thermal undercooling \( \Delta T_{t} \) and a significant thermal accumulation within the pool caused by the combination of a low \( v \) and a high LF, the effect of quenching that occurs by conduction of heat through the previously processed layers is not significant in this situation. A large amount of heat is accordingly accumulated around the growing secondary dendrites, which are formed due to a significant interfacial instability caused by a high \( \Delta T_c \), hence resulting in the formation of equiaxed dendritic crystals at an excessively high LF (Fig. 7(c)).

### 3.4 Microhardness and Tribological/Wear Performance

Figure 8(a) depicts the microhardness and its distribution measured along the SLM building direction on the cross sections of SLM-processed W-based alloy parts at different LFs. With an increase of the applied LF from 10.7 J/mm\(^2\) to 16 J/mm\(^2\), the average microhardness increased from 700.4 HV0.3 to 757.6 HV0.3 and, meanwhile, the fluctuation of the microhardness distribution was weakened significantly. At a suitable LF of 32 J/mm\(^2\), a uniform distribution of the microhardness with a considerably enhanced mean value of 825 HV0.3 was observed (Fig. 8(b)).

![Morphological change of W-based crystals during SLM](image)

**Fig. 7** Morphological change of W-based crystals during SLM with the increase of LF.
809.9 HV0.3 was achieved, due to the combined effects of the nearly full densification of SLM-processed part (Fig. 5) and the formation of homogeneous, refined cellular dendritic microstructures of W-based crystals (Fig. 6(c)). A further increase in the applied LF to 64 J/mm², however, decreased the obtained microhardness to 778.3 HV0.3 and, meanwhile, intensified the fluctuation of hardness values. In this instance, the limited densification level of SLM part caused by balling effect and microcracks formation (Figs. 3(d) and 4(d)) and the presence of relatively coarsened, heterogeneous equiaxed dendritic crystals (Fig. 6(d)) were responsible for the decrease in hardness performance. Here, Arshad et al.’s work [13] on hot-press sintering of W–5 wt. % V alloy was taken for a comparison, in which the obtained maximum microhardness was 589.8 HV0.2. The microhardness of SLM-processed W-based alloy parts with the novel crystalline microstructures, accordingly, showed a maximum 27% increase upon the conventionally PM-processed W-based materials.

The variations of COFs and resultant wear rates of SLM-processed W-based alloy parts are depicted in Figs. 8(b) and 8(c), respectively. It revealed that the applied LF exerted a significant effect upon the wear/tribological properties of W-based parts. An enhancement of LF from 10.7 J/mm² to 16 J/mm² lowered the average COF slightly from 0.58 to 0.52 and the resultant wear rate decreased accordingly from 8.36 × 10⁻⁷ m³/(N m) to 7.02 × 10⁻⁷ m³/(N m). The W-based alloy part processed at LF of 32 J/mm² demonstrated the superior wear performance. An apparently decreased COF of 0.41 was obtained, leading to the lowest wear rate of 5.73 × 10⁻⁷ m³/(N m). A further increase of LF to 64 J/mm², however, worsened the wear properties; the mean COF and attendant wear rate of W-based alloy part increased markedly to 0.49 and 6.85 × 10⁻⁷ m³/(N m), respectively.

In order to disclose the underlying wear mechanisms responsible for the variations of wear/tribological properties, the typical morphologies of worn surfaces are provided in Fig. 9. At a relatively low LF of 10.7 J/mm², the worn surface was considerably rough and wavy, consisting of parallel grooves (Fig. 9(a)). Such wear morphology revealed that the sample suffered a heavy abrasive wear, thereby producing a relatively high wear rate (Fig. 8(c)). Both the low densification level of SLM-processed part caused by the residual porosity (Figs. 3(a) and 5) and the formation of directionally solidified cellular W crystals with intercellular shrinkage porosity (Fig. 6(a)) were responsible for the decrease of wear performance in this instance. As the applied LF increased to 16 J/mm², the grooves on the worn surface became shallow (Fig. 9(b)). When a sufficiently high LF of 32 J/mm² was applied, the worn surface was covered completely with the dense and smooth adhesion tribolayer, without the local plowing or fracturing of the worn surface (Fig. 9(c)). During dry sliding tests, the counterpart ball slid against the surface continuously. The worn surface experienced the sufficient plastic deformation at a temperature below its recrystallization temperature. The material strengthening was expected to occur, due to the movement and pinning of dislocations within the crystalline structure of the material, which was known as strain-hardened tribolayer [41,42]. The formation of significantly refined cellular dendritic crystals of W-based alloy part (Fig. 6(c)) contributed to the formation of strain-hardened tribolayer to enhance wear resistance of the surface. However, at an excessive LF of 64 J/mm², although the strain-hardened, smooth worn surface was still visible, the tribolayer underwent a severe fragment and the interconnected, thin, and deep cracks were present on the worn surface (Fig. 9(d)), resulting in a significant increase of COF and wear rate (Figs. 8(b) and 8(c)). In this situation, the limited densification caused by both balling effect and thermal cracking (Figs. 3(d) and 4(d)) and the coarsening of equiaxed dendritic crystals of W-based alloy part (Fig. 6(d)) were responsible for the spalling of tribolayer and, accordingly, the decrease in wear performance.

4 Conclusions

SLM AM of W-based alloy parts was performed in this study and the following conclusions were drawn:

1) The applied LF played a significant role in determining densification behavior of SLM-processed W-based alloy parts. The densification response of SLM-processed parts
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