Comparative study of additively manufactured samples of tungsten with molybdenum and their applications

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Abstract:

This article is a comparative study of tungsten (W) and molybdenum (Mo) samples manufactured by selective laser melting (SLM). Under the processing parameters different microstructural and mechanical properties like strain energy density, micro-hardness and surface morphology were investigated. Before the preparation of samples the SEM and XRD images were taken to calculate the size of micro particles of both the samples. These samples were further investigated by OM (optical microscopy), SEM (scanning electron microscope), EBSD (electron backscattering diffraction) and Vicker hardness to study the crystallographic structure, hardness, grain boundaries to understand a brief comparison between these two fourth group elements. It was identified as the cause of a very prominent structure with cracked features and a residual remains. During processing, different processing factors were examined, which separates at the edges of the grain, thereby creating thermal cracks. This due to the low eutectic melting compared to the matrix phase. These factors also result in a higher Ductile-to-Brittle Transition (DBTT). Later, during rapid cooling from the melting point, a combination of cracks with hot cracks on the borders of solid grain grains and cold cracks near weak grain edges forms a cracked network, which is often found in tungsten and molybdenum refined SLM. Neither does a very hot substrate plate prevent the formation of cracks in the metals formed by processing parameters. These materials are appropriate for high temperature up to more than 2000 °C such an analytic and inner wall constituents of fusion reactor or experiments. Parameters like laser power, scan speed, hatching space and the thickness of the powder layer are analyzed to achieve the high density samples. Three-dimensional printing is changing the way we make things in almost every industry, from cars to medical equipment to biotech. 3D printing to prototype one of the most critical enabling technology in a building, the heat exchanger. In comparison to current designs, this next-generation heat exchanger weighs 20% less, performs 20% better, and can be produced much faster.

Keywords: Additive manufacturing (AM); selective laser melting (SLM); Molybdenum(Mo); Tungsten(W); Surface Morphology; Cracking mechanism
1. Introduction:
Most of the transition metals have high thermal and electrical conductivities, low thermal expansion coefficient, high melting points and comparatively better metal corrosion resistance. Among all the transition metals particularly fourth group elements tungsten (W) and molybdenum (Mo) possess all these characteristics. These metals are widely used in electronics, medical applications and in aerospace due to their unique properties. Heat exchanger chip radiators are always facing deformation problems which affects the efficiency radiators and their total service life. These radiators are mainly copper based but now gradually 3D manufactured tungsten thermal exchanger has replaced them because of their low thermal expansion coefficient. SLM technique has been gradually introduced in processing and structure verification diagrams for different missile parts. Molybdenum alloys improved the performance of rocket ion thruster engine. A 3D printing scientists have estimated a huge demand for these metals, citing AM technology as a potentially revolutionary production process that will produce new opportunities for molybdenum and tungsten products[1]. But before this can happen some technological obstacles must be addressed. During the industrial treatment of these metals in molten state vulnerable defects were detected[2]. Cracks and porosity affect molybdenum and tungsten during fusion welding and Selective Laser Melting (SLM)[3]. Selective laser melting equipment have shown that the delamination defects are avoidable, but the cracks are still visible and relative densities do not exceed 97%. Plasma spheroidization powders and high laser power was used to gain the maximum density of Mo and W.[4, 5].

Cracks were detected along the building and scanning direction. For both tungsten and molybdenum, many constructed layers in height are affected. Usually transverse cracks are formed in BD(building direction) and longitudinal originates along the grain boundaries of the columnar grain[6]. These studies also showed that rotating the scanning path layer by layer decreases both the maximum and individual crack lengths[7]. Cracking can be further reduced by adding further layers of the offset between the starting point and also by adjusting the temperature accordingly. Better crack growth resistance can be obtained by rotating the laser scanning direction at 67° and by further reducing the hatching gap of the offset[8].

Experiments may also be used to determine the influence of oxygen. Planetary milling of tungsten powder was used in this analysis[9]. The manufactured specimens had a maximum relative density of only 88% because it is impossible to do manufacturing exactly in an inert or reducing environment, resulting in a greater oxygen percentage in the powder[10, 11]. Different researchers used variety of parameters and scanning strategies but it is impossible to achieve crack free tungsten or molybdenum samples. Scientist tried to reduce the mechanism of cracking. Later on high magnification cameras were used to investigate the molten track produced during the selective laser melting of tungsten[5]. Many authors believed that cracks appeared in a predictable pattern behind the molten region, and that cold cracking occurs when the temperature drops below DBTT[12]. There are many reason for cracks formation mainly the Nano pores created by evaporated and separated oxides and the grain boundaries as well.

Different research groups reduced the specific crack length, but the tungsten and molybdenum grain boundaries remained thin, resulting in fabricated parts with low malleable and flexural strength, low pliability, and minimal breakage hardiness. The results of samples obtained with various parameters are presented in this paper.

2. Materials and methods:
The tungsten powder TEKMAT W-45 was used for this process. The chemical composition of the powder is given in table 1 below.in the figure 1a, b particle size distribution and surface morphology of tungsten are shown. For the additive manufacturing high density and more granular structures are most suitable[13].
The spherical shape of tungsten particles is commodious for selective laser melting. The particle size of tungsten particle is up to 25 microns. State of the art parameters were selected for manufacturing of tungsten samples. The SLM equipment was mainly included Ytterbium fiber laser with spot size of approximately 40-45 µm high speed laser scanner, an atmosphere protection system, a layering system and computer controlled software EOSPRINT Laser. The quantity of oxygen within the chamber was reduced to 0.10% to minimized oxidation and balling phenomenon. The laser power, hatching space and scanning speed was adjusted accordingly for every sample. The size of the sample was 5mm × 5mm × 5mm. Samples were prepared on a stainless steel with a preheating temperature of 180-210°C. The SLM process lasted for approximately 8 hours.

Table 1. Composition of tungsten powder (wt. %)

| Element | Tungsten (W) | Oxygen (O) | Carbon (C) | Sulphur (S) |
|---------|-------------|------------|------------|-------------|
| wt. %   | Balance     | 0.0016     | 0.0063     | 0.0022      |

Figure 2.1. (a) shows the SEM morphology of tungsten (W) and (b) shows the particle size distribution.

Molybdenum powder used in this research was spheroidized. The element size of molybdenum was slightly bigger than tungsten, it was around 10-45 µm. The metallic purities of both the particle was 99.9%. MALVERN Laser 2000 particle size analyzer was used to determine the particle size distribution. The powder chemistry and process results were assessed after a certain period of time in a plastic jar [1]. The quantity of all the contents was measured. Surface morphology of Mo was examined by Scanning Electron Microscope. All the specimens were prepared with same size to avoid possible variations through size effects. Grinding and polishing was done for the metallographic preparation. Vickers hardness was used to measure the micro hardness, optical image analyzer was used for imaging of specimens. The samples were treated chemically to avoid any errors through open porosity. The contents of oxygen, hydrogen, carbon and nitrogen in molybdenum powder are listed in table 2 and the morphology of powder is displayed in fig 2. Typically both the particles have oxygen saturation of 100-1000 µg/g but it can be increased significantly over the time depending on storage conditions[13].
The line energy density \( (E_L) \) is defined by the equation.

\[
E_L = \frac{P}{v}
\]

Where \( P \) for \( LP \) (laser power) and \( v \) is \( SP \) (scanning speed).

**Table 2. Chemical composition of Molybdenum (Mo) powder (wt. %)\( \mu \text{g/g} \) & particle size distribution (\( \mu \text{m} \))**

| Power | Bulk Density | D10 | D50 | D90 | C  | O  | H  | N  |
|-------|--------------|-----|-----|-----|----|----|----|----|
|       | g/cm\(^3\)   |     |     |     |    |    |    |    |
| Mo    | 5.71         | 18.6| 31.6| 52.0| 34 | 1216| 18 | 50 |

Fig. 2. a) Plasma spheroidized, b) Conventionally sored Mo powder

3. **SLM (selective laser melting) results of molybdenum and tungsten**

The tungsten and molybdenum powder were additionaly extracted by SLM in an argon process condition. Samples of molybdenum with a comparative density of 96.0\% and tungsten (W) with a relative density of 97.5\% percent were generated using processing parameters. In the fig 3 crack network was found in the tungsten samples. Most of the cracks were found at the border of the molten track and few were discovered in the intergranular structure. The formation of the cracks defines the scanning strategy.
Laser power=LP, Scanning Speed=SS, Hatching Space=HS

Figure 3  SEM images of tungsten manufactured under different parameters,[14]

Figure 4 shows of EBSD inverse pole figure (IPF) orientation map of pure tungsten specimen designed by SLM technique by using different parameters. The above-given tungsten sample was designed at a laser power of 150 watts with a scan speed of 300 mm/sec
Figure 4(a) EBSD inverse pole figure (IPF) orientation map of sample one is shown in figures. The IPF coloring is the plane's normal direction parallel to X, Y, and Z direction. (b) EBSD(IPF) orientation map of sample 2 is shown in figures. The IPF coloring is the plane's normal direction parallel to X, Y, and Z direction[13].

The figure 4a and b shows that the tungsten has high angle grain boundaries (HAGBs) as compared to Molybdenum.

There is a similarity in the crack network of tungsten and molybdenum. Fig. 5a, d represents the crack network of molybdenum[15]. EBSD measurements of Molybdenum were shown in the (Fig. 5b, e). Columnar grain structure is evident in the metallographic cross section. The high angle grain boundaries (HAGBs) were located at melt track borders which are prone to cracking (Fig. 5c, f). Grain boundaries between the angles of 2 to 5° are not visible at (111) orientation. But few boundaries are visible between 5 to 15° small angles boundaries (SAGBs). the color shift within the grain arises below 2°.
Fig. 5 Electron back scattering and scanning electron of molybdenum (Mo)
4. Mechanism of Defects Formation:

During the 3D manufacturing these materials can get exposure of oxygen and due to this exposure these metals cannot form passive layers. Different pores nucleation, contamination of oxygen and stabilization occurred during the process because of Marangoni convection from inward to outward flow[16]. Because of their low melting oxides and high evaporation pressure, both of these results refer to molybdenum and tungsten. It has been discovered that changing the scan path layer by layer by 67 degrees increases the intertwined grain boundaries and, as a result, the crack growth resistance of both materials [17]. This is due to a more distorted heat gradient, improved grain boundary interlocking, and a lower match between metallographic preferred directions and heat gradients for epitaxial grain growth, as previously discussed. In general, by heating the substrate layer, the heat gradient can be reduced, resulting in less induced thermal stresses. During the SEM analysis two types of pores were detected. These pores are known as lack of fusion pores and keyholes pores. Fusion pores can be removed by using high energy density parameters but keyholes pores cannot be addressed by processing parameters. Oxidation behavior of these materials cannot be ignored in this regard.

5. Conclusions:

Both the metals have very low solubility of oxygen at ambient temperature and a very minimum size defect below DBTT. All the impurities should be controlled by alloying the material or by avoiding the contact of the powder with oxidizing atmosphere. Crack free molybdenum and tungsten can achieved by alloying them with different other components. In dense metals like Mo and W cracks can be longitudinal and transverse direction. The transverse cracks are perpendicular to the surface ripple but longitudinal cracks are along the growth direction parallel to molten tracks. Layer by layer scanning rotation is helpful in removing the cracks. EBSD (electron back scattering) has revealed that columnar grain boundaries are along the building direction. The columnar grain structure evolved into an interlocked structure as a result of scanning rotation, which ultimately reduced crack growth[18].It was realized in comparison that Molybdenum can achieve relative density 97% at a laser power of 200W but it’s difficult to achieve the same relative density in case of tungsten(W). Microstructure cracks could be avoided by introducing a designed supporting structure. It was revealed during the experimental analysis that the high scanning speed did not increase in the density of the samples. Higher density samples can only be achieved if the energy input per unit volume needs to be increased by higher laser power and lower layer thickness.

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