Abnormal interfacial bonding mechanisms of multi-material additive-manufactured tungsten–stainless steel sandwich structure

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Abstract

Tungsten (W) and stainless steel (SS) are well known for the high melting point and good corrosion resistance respectively. Bimetallic W–SS structures would offer potential applications in extreme environments. In this study, a SS→W→SS sandwich structure is fabricated via a special laser powder bed fusion (LPBF) method based on an ultrasonic-assisted powder deposition mechanism. Material characterization of the SS→W interface and W→SS interface was conducted, including microstructure, element distribution, phase distribution, and nano-hardness. A coupled modelling method, combining computational fluid dynamics modelling with discrete element method, simulated the melt pool dynamics and solidification at the material interfaces. The study shows that the interface bonding of SS→W (SS printed on W) is the combined effect of solid-state diffusion with different elemental diffusion rates and grain boundary diffusion. The keyhole mode of the melt pool at the W→SS (W printed on SS) interface makes the pre-printed SS layers repeatedly remelted, causing the liquid W to flow into the sub-surface of the pre-printed SS through the keyhole cavities realizing the bonding of the W→SS interface. The above interfacial bonding behaviours are significantly different from the previously reported bonding mechanism based on the melt pool convection during multiple material LPBF. The abnormal material interfacial bonding behaviours are reported for the first time.

Keywords: multi-material additive manufacturing, laser powder bed fusion, interfacial bonding, element diffusion, keyhole mode

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1. Introduction

The melting temperature of tungsten (W) is higher than that of any other metal on the earth. It is also featured by its excellent sputtering resistance, plasma radiation resistance and low thermal expansion coefficient [1]. Therefore, many plasma-facing components (e.g., first walls) of nuclear fusion reactors are made of W, in order to hold the strength at extremely high temperatures and shield energetic α- and γ-radiations [2]. However, high brittleness is a disadvantage of W. In the nuclear reactor’s high temperature and high radiation environment, the surface of W can be eroded by high-energy rays quickly and generates dust, which affects the plasma parameters [3].

Combining W with other metals such as nickel (Ni) and iron (Fe) can reduce the brittleness of W and increase its ductility. There are two routes to combine W with other metals. The first is to sinter W powder with other relatively low melting point metallic powders through powder metallurgy [4] and powder injection moulding [5] to produce tungsten heavy alloys (WHAs). Recently, researchers have also studied the fabrication of WHAs by three-dimensional (3D) printing technologies, including laser-based powder bed fusion (LPBF) [6] and bound metal deposition [7]. However, there has been no previous studies on additive manufacturing (AM) of W–stainless steel (SS) bimetallic structure, which requires special equipment, not widely available. The second route is to join W plates/blocks with other metals via diffusion bonding (DB) [8] or hot isostatic pressing (HIP) [9]. DB and HIP cannot manufacture parts with complex 3D geometry, so it is not feasible to fabricate complex W-involved multi-material components via these traditional methods.

The production of 3D components composed of dissimilar materials through AM methods is an emerging field, which is promising to overcome the above drawbacks of traditional processes. The latest development of multi-material LPBF technology with multi-material powder deposition functions provides an opportunity to manufacture W–SS bimetallic structures. An ultrasonic-assisted multi-material LPBF technology was developed by the team from The University of Manchester [10]. Chadha [11] investigated an iron–cobalt alloy system fabricated via LPBF. Goh et al [12] reported the recent progress of AM of multi-layered and multi-material electronics. Chao et al [13, 14] reviewed recent progress of multi-material LPBF mechanism and material characteristics. However, until now, there has been no reported work on AM-fabricated multi-material components involving W and SS, although studies on AM-production of W heavy alloys have been reported [6, 7] and a W block printed on a dissimilar material substrate [15].

W and SS present completely different physical properties, e.g. melting temperature, material density and thermal conductivity. These differences may pose a challenge to the manufacture of W–SS bimetal structures. So far, there has been no previous studies reported on how these differences affect the W–SS interfacial bonding during AM.

In this study, we investigated the feasibility of LPBF printing a sandwich structure comprised of 316L SS and W, focusing on the characteristics of the material interfaces of the sandwich structure. Modelling and simulation tool revealed the effect of deposition sequences on the molten pool’s temperature gradient and its thermodynamic behaviour. The study reveals the effect of melting point differences on the interfacial bonding mechanisms of dissimilar materials in multi-material LPBF. The high-temperature liquid phase W causes the pre-printed SS layer to enter a keyhole mode, which is the fundamental reason for the W–SS interface bonding. In the case that the pre-printed W layer is not remelted, the mutual diffusion of dissimilar metallic elements at the interface can also make SS bond to the solid W layers.

2. Experimental materials and procedure

2.1. Materials

As shown in figure 1(a1), the spherical 316L SS powder, supplied by LPW Ltd, had a particle size distribution arranging from 10 to 45 μm. The spherical W powder (particle size: 15–45 μm, as shown in figure 1(a2)) was provided by TEKNA advanced materials Inc., Canada. Samples were printed on sand-blasted 316L plates in this study.

2.2. Experimental setup

Our previous publication [16] described our home-made LPBF system in detail. Compared with commercial LPBF machines, this homemade system utilized an ultrasonic-driven powder dispensing device (figure 1(b)) to deposit different powders at desired locations on the powder bed. W and 316L powders were stored in independent cylinders with fine powder feeding nozzles (inner diameter of nozzle: 450 μm for 316L and 300 μm for W, respectively), and were...
spread on demand through vibration activated with the ultrasonic transducers; the powder dispensers moved along the computer-controlled Cartesian \( x-\gamma \) motion system to deposit pre-designed patterns comprised of different powders on the powder bed. A soft blade driven by a linear stage was used to compact, level and smooth the powder deposited by the ultrasonic dispensers.

### 2.3. Experimental procedure

As illustrated in figure 1(c), a sandwich structure comprised of three parts was printed in the order SS, W, SS.

The focus of this research was on the influence of the differences in physical properties of W–SS on their interfacial bonding behaviors. LPBF of pure W [17–19] and LPBF of pure 316L [20–23] have been extensively studied previously. Even if the processed materials were the same, the laser processing parameters reported in these studies, especially the laser energy density, often varied greatly, which might be caused by equipment differences. Our preliminary experiments found that the LPBF processing parameters of W reported in the article [17] and that of 316L reported in the article [23] were suitable on the special LPBF equipment used in the present study. Therefore, these two sets of parameters were used to produce the W and 316L parts in this study, as shown in table 1. The laser volume energy density \( E_d \) in table 1 was calculated based on the formula given by Caiazzo et al [24].

### 2.4. Material characterization

The LPBF-printed sandwich structure was cross-sectioned to 1.5 mm slabs with a precision disk cutting machine. The thin slabs were hot mounted in black conductive polymer and then ground and polished. The polished specimens were chemically etched. Kroll’s Reagent (water 91%–97%, hydrofluoric acid 1%–3%, nitric acid 2%–6%) and the etchant (potassium hydroxide 10 g, potassium hexacyanoferrate (III) 10 g, water 200 ml) were used to respectively etch the 316L part and the W part.

All optical micrographs in this study were obtained using a digital optical microscope (VHX-5000, KEYENCE) equipped with a differential interference contrast module with a universal objective lens (VH-Z100UR, KEYENCE). The element distribution patterns at the dissimilar material interfaces were characterized using a scanning electron microscope–energy-dispersive x-ray spectroscopy (SEM–EDS) system (Sigma VP FEG SEM, Zeiss). The phases of the base materials and the two interfaces were examined with a high-resolution x-ray diffractometer (XRD, Smartlab, Rigaku). Electron backscatter diffraction (EBSD) patterns of the material interfaces were acquired using an EBSD system (JSM 7800F, JEOL). A nano-hardness tester (T1950, Hysitron) measured the hardness of different regions on the specimen. Nano-hardness measurements were repeated ten times to determine the mean value.

### 3. Numerical modelling

Molten pool dynamics at the two materials’ interfaces were simulated based on computational fluid dynamics–discrete element method (CFD–DEM) integrated modelling framework developed in our previous investigation [25, 26].

Two DEM models were set up in this modelling work, including the 30 \( \mu \)m thick SS powder layer on the 120 \( \mu \)m thick solid W substrate (i.e. the SS–W interface) and the 30 \( \mu \)m thick W powder layer on the 120 \( \mu \)m thick solid SS substrate (i.e. the W–SS interface). Figures 2(a) and (b) illustrate their initial morphologies. The process parameters employed in these two simulations were the same as those used in physical experiments (see table 1).

The thermal properties of 316L SS and W used in the CFD simulation are presented in table 2.

### 4. Experimental results

#### 4.1. Macro- and micro-structures of the LPBF-printed SS–W–SS sandwich structure

As shown in figure 3(a), no visible delamination and cracks were observed on the LPBF-printed SS–W–SS sandwich sample.

#### 4.1.1. Microstructure of the base materials. The microstructures of SS at the top and SS at the bottom were both organized by overlapping and continuous melt pool tracks (a ‘fish-scale’ pattern, see figures 3(b1) and (b3)), and the typical grain structure was cellular-columnar grains oriented along the build direction of LPBF. These cellular-columnar grains grew across several build layers, a typical LPBF-fabricated SS microstructure [29, 30]. Rapid cooling and solidification of the melt pools generate the most significant temperature gradient along the build direction, leading to the fastest growth velocity of crystal grains [31].

The microstructure of the W region in the sample was comprised of columnar grains (figure 3(b2)), similar to the LPBF-printed W microstructure described in the previous investigation [32].

### Table 1. Laser processing parameters of this study.

| Position            | Laser thickness \((t, \text{mm})\) | Laser power \((P, \text{kW})\) | Hatch distance \((h, \text{mm})\) | Scanning speed \((v, \text{m s}^{-1})\) | \(E_d = \frac{P}{v·h·t} \) \((\text{J mm}^{-1} \cdot \text{mm}^{-3})\) | References |
|---------------------|-----------------------------------|-------------------------------|-----------------------------------|-------------------------------------|-------------------------------------------------|------------|
| SS                  | The 1st–67th layers               | 0.03                          | 0.2                               | 0.07                                | 1.2                                             | 79.4       | [23]       |
| W                   | The 68th–135th layers             | 0.03                          | 0.4                               | 0.1                                 | 0.725                                           | 183.9      | [17]       |
| SS                  | The 136th–203th layers            | 0.03                          | 0.2                               | 0.07                                | 1.2                                             | 79.4       | [23]       |
4.1.2. Macro- and micro-structures of the material interfaces.

4.1.2.1. SS→SS interface. The interface between the SS part at the sample’s bottom and the SS substrate presented a typical metallurgical bonding microstructure. Neat fish-scale solidification lines appeared at the top of the substrate (see figure 3(b4)). This phenomenon indicated that the laser beam completely penetrated the powder layer and melted the powder particles around the laser beam spot to form a melt pool. Meanwhile, part of the laser energy and the heat transfer from the heat conduction of the liquid metal also remelted the surface of the substrate, enhancing the wettability between the liquid-phase material and the solid-phase base [33], avoiding the balling phenomenon. It also enhanced the mutual diffusion of elements in the powder material and the substrate material because of Marangoni convection in the melt pool [34]. It achieved good metallurgical bonding to the substrate.

4.1.2.2. SS→W interface. The SS→W (SS printed on W) interface (figure 3(b5)) was completely different from the above-mentioned SS→SS interface and did not show the solidification lines of melt pools; the pre-printed W layers still maintained their original morphology. The W particles (labelled by arrows in figure 3(b5), may have been adhered on and carried by the powder blade) remaining on the top of W layers were not able to be fused by the low energy density for SS. It may be due to the big melting temperature difference between W and SS (3695 and 1658 K respectively). No cracks, pores, and delamination defects were found at this interface, evidenced by the magnified SEM image (figure 3(c1)). The unmelted W particles were completely embedded in the molten SS layers, and no pores or cracks were found around them. All the above phenomena indicated that liquid SS presented acceptable hydrophilicity on the solid W, so liquid SS could be firmly attached to the surface of W. However, it could not explain that, after high-frequency heating–cooling thermal circles during LPBF, why the newly-printed SS layers still firmly adhered to the pre-printed solid-state W substrate without warping and delamination. The EDS result and the EBSD result will provide further insights into the causes.

Figure 2. The initial DEM model morphologies of (a) the SS powder layer deposited on the solid W substrate and (b) the W powder layer deposited on the solid SS substrate.

Table 2. Thermal properties of 316L SS [27] and W [28].

| Symbol | Nomenclature                      | 316L               | Tungsten          |
|--------|-----------------------------------|--------------------|-------------------|
| $T_s$  | Solidus temperature (K)           | 1658               | 3605              |
| $T_l$  | Liquidus temperature (K)          | 1723               | 3605              |
| $\rho_s$ | Solidus density (kg m$^{-3}$) | $8084 - 0.4209T - 3.894 \times 10^{-5}T^2$ | $19.250 - 0.266207 \times (T - 293.15) - 3.0595 \times 10^{-5} \times (T - 293.15)^2 - 9.5185 \times 10^{-3} \times (T - 293.15)^3$ |
| $\rho_l$ | Liquidus density (kg m$^{-3}$)  | $7433 - 0.0393T - 1.8 \times 10^{-4}T^2$ | $16.267 - 0.7679 \times (T - 3695) - 8.091 \times 10^{-5} \times (T - 3695)^2$ |
| $k_s$  | Solidus thermal conductivity (W m$^{-1}$ K$^{-1}$) | 9.248 + 0.01571$T$ | $149.441 - 45.466 \times 10^{-3}T + 13.193 \times 10^{-6}T^2 - 1.484 \times 10^{-9}T^3 + 3.866 \times 10^6T^2$ |
| $k_l$  | Liquidus thermal conductivity (W m$^{-1}$ K$^{-1}$) | 12.41 + 0.003279$T$ | $66.6212 + 0.02086 \times (T - 3695) - 3.7585 \times 10^{-9} \times (T - 3695)^2$ |
| $\mu$  | Viscosity (kg m$^{-1}$ s$^{-1}$)   | $10^{1.23552T - 3.5958}$ | $0.16 \times 10^{-3}e^{14672.4T}$ |
| $\sigma$ | Surface tension (kg s$^{-2}$) | 1.6 | 2.48 |
| $\frac{d\sigma}{dT}$ | Surface tension coefficient (kg s$^{-2}$ K$^{-1}$) | $-0.8 \times 10^{-3}$ | $-0.31 \times 10^{-3}$ |
| $L_m$  | Latent heat (J kg$^{-1}$)          | $2.7 \times 10^3$ | $2.84 \times 10^3$ |
| $C_p$  | Heat capacity (J kg$^{-1}$ K$^{-1}$) | 775 | 132 |
Figure 3. (a) An LPBF-printed SS–W–SS sandwich sample; (b1)–(b3) the microstructures of cross-sections at SS (top), W, and SS (bottom) parts; (b4)–(b6) the microstructures of the cross-sections at different material interfaces; (c1), (c2) the magnified SEM graphs of the cross-sections at different interfaces.

4.1.2.3. W→SS interface. The W→SS (W printed on SS) interface (figure 3(b6)) showed a totally different morphology compared with the SS→W interface (figure 3(b5)). The high laser energy density for melting W (183.91 J mm$^{-3}$) resulted in the remelting zone of the pre-printed SS layers as deep as 130 µm. In the remelting zone, a large number of small particles with approximately spherical shapes and large particles with irregular shapes appeared, and a mixed zone of
elements (labelled with arrows in figure 3(b6)) appeared as well.

The keyhole mode of LPBF described by Chen et al [35] could be employed to explain the above phenomena. Excessive laser energy density caused the melt pool at the W→SS interface to enter a keyhole mode. In this mode, the high temperature vaporized the material to create a cavity (i.e., keyhole) in the pre-printed SS layers, and then the laser beam directly shot into the cavity, and multiple refractions occurred in it. It allowed more laser energy to be absorbed by the SS layers, further increasing the melt pool depth and width. The cavity collapsed later, and the liquid W flew into the keyhole. Because of the Marangoni convection, liquid W mixed with the elements of SS and may produce a new phase. The thermal conductivity of W is greater than that of SS (174 W m⁻¹ K⁻¹ and 14.0–15.9 W m⁻¹ K⁻¹ respectively). According to Newton’s law of cooling, materials with high thermal conductivity cool faster [36]. Hence, W in the melt pool solidified before SS. Liquid Fe/Ni spread well on the skin of solid-state W [37]. Thus, liquid Fe/Ni could completely encapsulate the pre-solidified W particles. These explained the lack of cracks and pores around the solidified W particles.

Tiny liquid W droplets contained less heat than large W droplets; hence tiny W droplets cooled faster than large W droplets. The surface tension of the liquid increased as the temperature dropped. As a result, the small W droplets first agglomerated into spherical particles due to the smallest Gibb's surface free energy [38]. The large W droplets did not have time to completely solidify before the surrounding liquid SS solidified; as a result, the large W droplets finally solidified into embedded irregularly-shaped particles.

The magnified SEM image of this interface (figure 3(c2)) provided more clues to revealing the above phenomena, which provided the trajectory of the W droplets in the remelted SS melt pool. As shown in arrows in figure 3(c2), regardless of the size of the W droplets, the angle between the falling direction of all W droplets in the melt pool and the laser scanning direction was 153°. It may result from the combined force of gravity and the movement of the melt pool caused by laser scanning. Behind the small W droplet, an area (marked by dotted lines in figure 3(c2)) similar to the tail of a meteor appeared. The microstructure of this area (bright dots (W) on the dark background (SS)) was different from those of solidified W and SS. We speculated that W droplets reacted with liquid SS while falling in the melt pool and formed new Fe–W/Ni–W phases. This speculation was confirmed by subsequent XRD and EBSD test results.

4.2. EDS mapping of the material interfaces

4.2.1. Element diffusion at the SS→W interface. As shown in figure 4(a1), we did not find a bowl-shaped element mixing area caused by the Marangoni convention-induced circular flow in the melt pool [39]. It indicated that the pre-printed W part was not remelted during the LPBF printing of the SS part.

On the other hand, it was observed that weak signals of Ni and Fe diffused to the W side (figures 4(a3) and (a4)). The EDS line scanning plot (figure 4(a5)) based on the red scan path in figure 4(a1) provided more information on this solid-state diffusion (SSD) phenomenon. As shown by the yellow arrow and the red arrow in figure 4(a5), at the material interface, the element content of W increased and the element contents of SS decreased gradually, rather than a sharp change. It is a typical concentration profile of steady-state inter-diffusion caused by the Kirkendall effect [40]. The width of the mutual diffusion zone was around 0.6 µm, which was similar to that in the previous study [41]. As highlighted by the black arrow in figure 4(a5), the total diffusion depth of the elements in SS on the W side exceeded 20 µm.

The movement or flux of the elements (J) in SSD is proportional to the element diffusion coefficient (D) and the element concentration gradient (dC/ds), according to the Fick’s first law of diffusion (J = –D dC/ds) [42]. The diffusion coefficient of Ni–W is much greater than that of the Fe–W (6 × 10⁻¹⁵ m² s⁻¹ for Ni–W [43], 10⁻¹⁸ m² s⁻¹ to 6 × 10⁻¹⁹ m² s⁻¹ for Fe–W [44]). Therefore, the diffusion of Ni into the solid-state W area is stronger than that of Fe.

The research of Reisner et al [44] reported that the diffusion coefficient is directly proportional to temperature. Although the laser energy density for melting SS could not remelt the surface of pre-printed W layers, it could keep the printed part at high temperature, increase the active energy of Ni and Fe elements and let them migrate to the W side via SSD and archive the SS→W interface bonding.

In this study, we observed that the diffusion of W via SSD was less than that of Ni and Fe, because the body-centred cubic (BCC) grain structure of W requires higher activation energy than the face-centred cubic (FCC) structure to achieve SSD [45]. Besides, the atomic density and diameter of the W element are higher and bigger, which also lead to higher active energy. Therefore, under the same processing conditions, the jump frequency of W atoms is lower than that of Ni/Fe [46], so the SSD-induced diffusion of W was less than that of Ni and Fe in this investigation.

4.2.2. Element distribution at the W→SS interface. The area between the two red dashed lines in figure 4(b1) was the collapsed W layer close to the W→SS interface. By comparing the EDS map of W (figure 4(b2)) with the EDS maps of Fe/Ni (figures 4(b3) and (b4)), we found that the W element shed from the bottom of the W layer widely diffused in the remelted SS layers. In addition, the Fe/Ni EDS maps (figures 4(b3) and (b4)) showed that there was an SS layer above the collapsed W layer (the area between the two red dashed lines in figures 4(b3) and (b4)). The thickness of this SS layer was uneven, and there were two tips with a spacing of 100 µm, as shown in figure 4(b3). This distance value was the same as the laser scanning hatch distance for processing W in this study. Therefore, these two tips were likely to be keyhole tips.

The EDS line scanning result (figure 4(b5)) was based on the red scan path shown in figure 4(b1). The scan path was divided into six regions (marked by R1 to R6 in figure 4(b5)). The bright regions (R1, R3, R5) were mainly distributed with W, and no obvious SS element signals were detected. In the dark regions (R2, R4, R6), strong W signal and SS element...
Figure 4. (a1), (b1) SEM micrographs of different material interface; (a2)–(a4) and (b2)–(b4) show corresponding element EDS maps; (a5), (b5) present the EDS line scanning plots according to the scanning paths in (a1), (b5).

signals were observed, indicating that W diffused into the initial SS regions. A large amount of W diffusion increased the possibility of forming the W–Fe/Ni intermetallic phases. It was notable that along the build direction, the mean values of W content of these element mixing regions gradually increased (16 At% for R6, 19 At% for R4, and 21 At% for R2). It may be due to that the melted W in R2 was near the upper W molten pool, so the concentration of liquid-phase W was higher. According to Fick's first law, a higher concentration gradient causes more elements to diffuse. Besides, compared
in XRD intensity should be caused by the phase concentration. Conditions remained unchanged in this study, so the difference is antantly higher than those at the SS interface. New Fe–W phases at the W side reacted with W and led to secondary phases, including Fe2W and Fe7W6. It was worth noting that the XRD peak intensities of new Fe–W phases at the W→SS interface were significantly higher than those at the SS→W interface. The XRD test conditions remained unchanged in this study, so the difference in XRD intensity should be caused by the phase concentration at the two interfaces. The high laser energy density for melting W caused the top surface of the pre-cured SS to be remelted, as presented in figure 3(b6), many W droplets fell into the remelted SS, significantly increasing the element reaction area, and resulting in more Fe–W phases formed.

All these new phases detected by XRD were considered as candidates in the following EBSD phase mapping.

4.3. XRD of material interfaces

As shown in figure 5(d), a typical XRD pattern of the single γ-austenite FCC structure was observed at the SS part, similar to that of LPBF-printed SS presented in a previous study [47]. Four major peaks in the diffraction pattern (figure 5(c)) of the LPBF-printed W region was the same as the original pure BCC W powder [48].

The XRD patterns at the two material interfaces (figures 5(a) and (b)) showed a significant difference compared with the above two base materials. New phases composed of elements in SS appeared at both two interfaces, such as Ni, Mo, Fe3Mn7, and Cr6Fe18Mo5; it indicated the decomposition of SS under the high laser energy density. Fe from SS reacted with W and led to secondary phases, including Fe2W and Fe7W6. It was worth noting that the XRD peak intensities of new Fe–W phases at the W→SS interface were significantly higher than those at the SS→W interface. The XRD test conditions remained unchanged in this study, so the difference in XRD intensity should be caused by the phase concentration at the two interfaces. The high laser energy density for melting W caused the top surface of the pre-cured SS to be remelted, as presented in figure 3(b6); many W droplets fell into the remelted SS, significantly increasing the element reaction area, and resulting in more Fe–W phases formed.

4.4. EBSD of the material interfaces

4.4.1. Micro-texture at the SS→W interface. Both LPBF-printed base materials presented columnar phases, see figure 6(a1). The cracks along the build direction only appeared on the W side, as highlighted by arrows in in figure 6(a1). It may be due to that the ductile–brittle transition temperature of W (500–700 K) is low [35], causing stress concentration and cracks during LPBF processing [49].

The grain size distribution of figure 6(a1), calculated by the HKL Tango software, showed that the average grain size of SS (mean: 98.428 µm², number of grains: 754) was smaller than that of W (mean: 212.41 µm², number of grains: 141). As mentioned in section 4.1.1, the crystal grains produced by LPBF grow along the building direction. The SS fine-grained structure in figure 6(a1) appeared in the newly printed layers close to the SS→W interface. The larger W grains were those after printing to a thickness of 2 mm, and the W grains at this position had grown. Hence, it was normal that the newly-formed SS grains shown in figure 6(a1) were smaller than the grown W grains.

The phase map (figure 6(a3)) indicated that the SS→W interface mainly consisted of Fe-FFC, W, and Ni₄W phases. Notably, the Ni₄W phase was just presented at the SS grain boundaries, for instance, the region marked by R1 in figures 6(a1) and (a3). It should be resulted from the diffusion of W upward due to the grain boundary diffusion (GBD). GBD is the most common solute migration path in polycrystalline materials. The diffusion of elements in the solid metal along the grain boundary is faster and easier than the solid diffusion through the grain lattice [50], which can occur at low and medium temperatures. The more grain boundaries, the more elements migrate through GBD, which will result in higher interface bonding strength [51]. In this study, the grain boundaries on the SS side were far more than those on the W side. Therefore, it was observed that many W migrated to the SS grain boundaries through GBD. The high temperature caused by LPBF made the diffused W react with Ni to generate Ni₄W.

4.4.2. Micro-texture at the W→SS interface. An EBSD examination was carried out on the EDS mapping area (figure 4(b1)) and its surrounding area.

As shown in the red box in figure 6(b1), the initial microstructure of pre-printed SS was comprised of fine columnar grains. The high energy for melting W caused the top surface of SS to be remelted and recrystallized (see the red circle in figure 6(b1)). There were many spherical and irregular shaped W particles embedded in these new SS grains without defects...
such as pores/cracks. It proved that liquid W solidified earlier than liquid SS.

The grain type of the W–SS mixing zones distributed on both sides of the collapsed W layer could not be identified via EBSD and was displayed in black, see the area pointed by the arrows in figure 6(b2). The phase map indicated that intermetallic phases, including Ni₄W/Fe₂W/Fe₇W₆, appeared in these element mixing zones, as marked by arrows in figure 6(b3).

4.5. Nano-hardness and elastic modulus of the material interfaces

Figures 7(a) and (b) present the original data of nano-hardness at different locations on the sample and that of measured reduced elastic modulus ($E_r$) via the nanoindentation method. The elastic modulus of test region ($E_1$) was converted from the measured $E_r$ based on the formula (1) mentioned in the article [52], and shown in figure 7(b):

$$\frac{1}{E_r} = \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2}. \quad (1)$$

In which, $v_1$ is the Poisson’s ratio. In this study, we set the Poisson’s ratio of the SS region to 0.27, and the Poisson’s ratio of the material in the other areas was set to 0.3; $v_2$ and $E_2$ are the Poisson’s ratio (0.07) and the modulus of elasticity (1141 GPa) of the diamond indenter, respectively.

4.5.1. Nano-hardness. Compared with the data of bulk materials produced by conventional methods, as shown in table 3, LPBF-printed base materials in this study always presented significant higher nano-hardness. For example, the hardness of the SS area in this study was 1.86 times that of the bulk 316L, and the hardness of the W area was 1.55 times that of the bulk W. It might be due to the fine-grained structure produced by rapid cooling cycles in the LPBF process [53]. Because of the finer metal grains, the total area of grain boundaries was larger; it led to more dislocation barriers and higher resistance to plastic deformation of the metal during the hardness test [54].

As shown in figure 7(a), the SS→W interface had similar hardness compared with the SS base (6.20 and 5.38 GPa respectively). But the hardness of the W base (8.99 GPa) was
Figure 7. (a) Nano hardness plot of the SS–W–SS sandwich structure and (b) the corresponding plot of reduced elastic modulus and elastic modulus.

Table 3. Nano-hardness and elastic modulus of the bulk 316L SS and bulk W reported in the literature.

| Reference | Nano-hardness (GPa) | Elastic modulus (GPa) |
|-----------|---------------------|-----------------------|
| Bulk 316L SS | 2.90 | 220.40 |
| Bulk W | 5.80 | 410.00 |

5. Melt pool fluid dynamics in multiple material interfaces

5.1. Morphologies of melted powder layers

5.1.1. Morphology of the SS→W interface. A continuous melted SS track is presented in figure 8(a1), indicating that SS has good wettability with the W substrate. The clear interface in figure 8(a2) showed that the W base was not melted, and no element mixing occurred.

5.1.2. Morphology of the W→SS interface. As presented in figure 8(b1), it was interesting that SS instead of W appeared on skin of the melted W track. The high energy density resulted in the keyhole mode. Figure 8(b2) clearly presented that W flew into the SS cavity and the formation of pores; the latter is a typical defect of the keyhole mode in LPBF [57]. The keyhole depth filled with W reached 88.93 µm, which was shallower than the deepest position discovering W in the experiment (>130 µm, figure 3(b6)). An explanation will be given in section 6.2. The 3D morphology of the entire W powder layer after laser melting (figure 8(b3)) revealed that W sunk into the SS base while SS floated to the top. This simulation result was similar to that of the SS region on the top of the W layer observed in the EDS maps (figures 4(b3) and (b4)). We will discuss the cause of this phenomenon in detail in section 6.2.

5.2. Melt pool temperature distribution at the material interfaces

The molten pool temperature contours of the two material interfaces in the ‘300–1658 K’ range are shown in figures 9(a1) and (b1) respectively; and those in the ‘300–3695 K’ range are shown in figures 9(a2) and (b2) respectively. 1658 and 3695 K are the solidus temperature of 316L SS and W, respectively, as presented in table 2.
5.2.1. Melt pool temperature profile at the SS→W interface. The melt pool depth of SS achieving the melting point of SS (1658 K) was only 32.65 µm, see figure 9(a), slightly greater than the SS powder layer thickness (30 µm in this study). The heat in the molten pool dissipated quickly through heat conduction of the W base because of its good thermal conductivity. Besides, the molten pool depth with a temperature no less than the W melting temperature (3695 K) was only 20.26 µm (figure 9(a2)), lower than the powder layer thickness. It was clear that the low laser energy density (79.37 J mm$^{-3}$) for melting SS could only melt a single layer of SS powder. It was impossible to remelt the surface of the W base and further lead to element mixing inside in the molten pool.

5.2.2. Melt pool temperature profile at the W→SS interface. The high energy density for melting W powder layer (183.91 J mm$^{-3}$) resulted in the keyhole mode (see figure 9(b1)), which not only melted the 30 µm thick W powder layer, but also deeply remelted the SS substrate; the molten pool depth with temperature greater than the melting point of SS was 127.49 µm. As shown in figure 9(b2), the region where the temperature reached the melting point of W was the front of the melt pool, which caused the liquid W to flow into the keyhole cavity. As mentioned earlier, the SS base was also deeply melted. Therefore, the liquid W could mix and react with the elements (i.e. Ni, Fe) in the liquid SS.

5.3. Melt pool velocity field at the W→SS interface

Despite having negative surface tension coefficients (table 2) for both W and SS materials, the velocity distribution in the laser beam centre presented a downward flow attributed to the high recoil pressure induced by keyhole formation, as shown in figure 10(a). Consequently, the melted W in the melt pool...
Figure 9. Melt pool temperature profiles at the SS→W interface in the range (a1) 300 °C–1658 °C and (a2) 300–3695 K; melt pool temperature profiles at the W→SS interface in the range (b1) 300 °C–1658 °C and (b2) 300–3695 K.

Figure 10. (a) Melt pool velocity field at the W→SS interface along the longitudinal cross-section, and (b) stacked views of simulated cured W→SS interfaces with different longitudinal sections (position 70–130 µm).

front would tend to flow towards the bottom of the keyhole cavity with the combined effects of surface tension forces, recoil pressure and gravity, as illustrated in figure 10(b). The Marangoni convection in the molten pool led to the rapid evolution of the fluid flow [58]; the W phase mixed with liquid SS at the subsurface of the SS base (figure 10(b)). W have higher density and higher thermal conductivity compare with SS, so the W phase first solidified in the melt pool and sank due to gravity [59], leading to element segregation. The compressibility of liquid metal is poor [60] (i.e. the total volume of W and SS participating in the reaction was almost unchanged), so falling W particles occupied the space of SS located initially below. Subsequently, liquid SS was forced to float up and brought back to the top of the melt pool through circulating flows and solidified there. This melt pool behaviour should be the cause why we observed SS instead of W on the initial W scanning track (figure 8(b1)). The above-mentioned ups-down migration of elements takes time to complete, so we only found a completely floating SS at the beginning of the scanning track that melted and solidified first.

6. Discussion of interfacial bonding mechanisms

We proposed the following dissimilar material interfacial bonding mechanisms according the above experimental results and simulation results.

6.1. Bonding mechanism at the SS→W interface

Figure 11(a) illustrates the bonding mechanism at the SS→W interface. When laser melting SS on the W surface, the melt pool depth caused by the laser irradiation cannot melt the pre-printed W (figures 3(b5), (c1) and 8(a2)). However, at high temperature and argon environment, the wettability of liquid Fe/Ni is good on the solid-state W surface [37], hence liquid Fe/Ni can spread into a thin layer without warping and balling phenomena at the SS→W interface. It is a prerequisite for the subsequent occurrence of SSD and GBD phenomena. In this study, SSD and GBD are the fundamental mechanisms to achieve SS→W interface bonding without melting W.

In the presence of material concentration gradients [42] and high-temperature heating to increase the activation energy of atoms [61], SSD can occur in solid metals. The sharp SS→W interface in this investigation provided the material concentration gradient required by SSD. Meanwhile, during LPBF processing, the laser beam repeatedly scanned the powder bed to maintain the powder bed at a high temperature, despite
temperature fluctuations. Hence, bonding SS to W via LPBF met the two requirements of SSD, so Ni and Fe with high diffusion coefficients migrated to the W side (figure 5(a5)). Due to the high activation energy of solid W, much less W migrated to the SS side via SSD (figure 5(a5)).

On the other hand, the activation energy required for GBD through grain boundaries is much lower than the activation energy required for SSD through grain lattices [62]. Metals with more grain boundaries are more prone to GBD [63]. The SS in this study presented fine columnar grains with many grain boundaries spreading along the build direction (figure 6(a1)). Therefore, W with low activation energy could migrate to the SS side through GBD (figure 6(a3)). Because of the powder-bed’s high temperature caused by repeated laser irradiation, the migrated W reacted with Ni and Fe to produce new phases (i.e. Ni₄W in figure 6(a3)).

6.2. Bonding mechanism at the W→SS interface

The keyhole-mode molten pools during printing the first W layer and the second W layer made W to bond to the pre-printed SS base.

6.2.1. Printing the first W layer. The simulation result showed that the high laser energy for melting W caused the melt pool at the material interface to become an excessive keyhole mode (figure 8(b2)). The pre-printed low melting point SS base was melted and evaporated due to that the boiling temperatures of Ni and Fe in SS (2913 °C and 2862 °C) are lower than the W melting temperature (3422 °C). The SS evaporation process generated a recoil pressure on the SS molten pool’s liquid surface. Subsequently, the recoil pressure deformed the above-mentioned liquid surface and pushed the liquid material in the SS melt pool sidewards, allowing the laser beam to penetrate to a deeper liquid–gas interface inside the pre-printed SS layers, and ultimately resulted in the deep SS keyhole cavity [64], as shown in figure 9(b1). The liquid W flew into and filled the keyhole cavity (figure 9(b2)). During such a process, the liquid W was continuously mixed with the liquid SS (figure 10(a)) and solidified before the liquid SS (figure 6(b1)) and finally embedded in the SS matrix (figure 10(b)). Meanwhile, the low-density liquid SS was carried by the melt pool circulating flows to the molten pool’s top surface and solidified, forming a thin layer of floating SS (figures 4(b3), (b4) and 8(b1)). According to the simulation result, the depth of the melted SS subsurface layer (i.e. the thickness of the SS layer embedded with W particles) was 88.93 μm.

The above bonding mechanism is illustrated in figure 11(b1).

6.2.2. Printing the second W layer. During printing the second layer of W, the high energy density again led to the keyhole-mode molten pools; the keyhole tips penetrated into the solidified first W layer (figure 4(b3)). The good thermal conductivity of W caused a large amount of heat in the W melt pool was quickly transferred to the underlying SS layers. The solidified SS layers were remelted for the second time, which further caused the solidified first W layer to collapse. Many W particles, including large ones with irregular shapes, fell from the bottom of the first W layer and gradually sunk in the liquid SS, which made the thickness of the SS layers embedded with W particles reach over 130 μm (figure 3(b6)). Falling W droplets continuously mixed and reacted with the liquid Fe/Ni (figures 3(c2) and 4(b5)) to produce intermetallic phases such as Ni₄W and Fe₂W (figure 6(b3)).

The above bonding mechanism is illustrated in figure 11(b2).

7. Conclusion

A SS→W→SS sandwich structure was additively manufactured using a multi-material LPBF technology. The material characterization results indicated that the morphology, element distribution, phase distribution, hardness at the two
material interfaces were significantly different. Modelling and simulation tool were used to reveal the molten pools’ thermodynamic behaviour and their temperature distribution during laser melting the above two material interfaces. Two material interfaces’ metallurgical bonding mechanisms in the multiple material LPBF process were proposed based on the above experimental and simulation results.

The experimental and the simulation results show verified that the pre-printed W base cannot be re-melted by the laser energy for printing SS. Fortunately, Ni and Fe with low activation energy migrates to the W side through SSD. These two diffusion phenomena contribute to the bonding of SS and W. No secondary phase is found on the W side, that of SS and much lower than that of W. Its elastic modulus (233.07 GPa) is between SS and W.

This study shows that the high energy for melting W causes molten pools at the W→SS interface to enter an excessive keyhole mode. The keyhole tips deeply penetrate into the pre-printed SS base. The liquid W with high density in the melt pool flows into the keyhole cavity, sink in the liquid SS, and is finally embedded in the SS matrix. The low-density SS is forced to float up, forming a thin layer above the W scanning track. In the above process, the liquid W mixes and reacts with the liquid SS, resulting in secondary phases (Ni4W, Fe5W, Fe6W6). These new phases cause the nano-hardness of the SS→W interface to be higher than that of W (9.73 and 8.99 GPa, respectively). The elastic modulus of the SS→W interface (265.85 GPa) is between those of SS and W.

This research may apply to the AM of W–SS bimetallic components used in the nuclear industry. After revealing their interfacial bonding mechanisms, the subsequent investigation will optimize the process parameters, especially suitable laser energy density at the material interface [65], to improve the mechanical performance of the real W→SS bimetallic components fabricated via multi-material LPBF.

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