

# Multi-wire arc additive manufacturing of Ti basic heterogeneous alloy: effect of deposition current on the microstructure, mechanical property and corrosion-resistance

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## Abstract

Deposition current during fabrication plays an important role in the microstructure and properties of titanium alloy components prepared by multi-wire arc additive manufacturing (MWAAM) technology. In this study, Ti system heterogeneous alloy with Ti-6.5Al-3.5Mo-1.5Zr-0.3Si (TC11) as the main component was deposited using the MWAAM method with the deposition current ranging from 360 A to 400 A. The effects of deposition current on the microstructural evolution, mechanical and

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corrosion properties of the MWAAM titanium alloys were investigated, and the process-microstructure-property relationship was analyzed. The results show that the microstructure of as-received Ti system heterogeneous alloy was mainly composed of lamellar primary  $\alpha$  phase ( $\alpha_P$ ) and transformed  $\beta$  phase ( $\beta_T$ ), and increasing the deposition current during the MWAAM process would result in the increased width of  $\alpha$  phase and the decreased aspect ratio of  $\alpha$  phase. The mechanical properties of MWAAM-deposited specimens decrease with increasing current, which means that phase composition played a dominant role in determining hardness. When increasing the deposition current during the MWAAM process the ultimate tensile strength (UTS) decreased from 843.75 to 804.38 MPa. The MWAAM-deposited Ti system heterogeneous alloy featured excellent corrosion properties, the corrosion potential of the best specimen was -311 mV SCE and the corrosion current density was  $1.23 \times 10^{-8}$  Acm<sup>-2</sup>. This study provides a better understanding of the effect of deposition current on the targeted deposition property in the MWAAM process, which will contribute to future process control, improvement and optimization..

**Keywords:** Ti-6.5Al-3.5Mo-1.5Zr-0.3Si; Multi-wire arc additive manufacturing; Deposition current; Mechanical property; Corrosion performance

## **Introduction**

Titanium alloys are widely used in national defense, military, aerospace, green energy and other industries because of their excellent properties such as high strength,

good toughness and low density [1]. Due to the poor machining performance of titanium alloy, the traditional process is difficult to meet the machining requirements of high performance and large size titanium alloy structural parts [2-3]. Conventional manufacturing of large titanium alloy components has many problems, such as complex technological process, low material utilization rate, high cost, low efficiency and insufficient flexibility in multi-process composite manufacturing [4-5]. Therefore, the development of advanced manufacturing technology for large critical components of difficult-to-machined metals such as titanium alloy is still the focus of the manufacturing industry.

Since the development of additive manufacturing (3D printing) technology, it is gradually deepening from multiple levels such as design, manufacturing, materials and equipment, various processes of process technology and many fields of industrial application [6]. In particular, the high-performance 3D printing technology of metal is widely regarded as the most difficult and promising cutting-edge development direction of the industry, and it is also the molding technology that can directly serve the equipment manufacturing industry [7]. Wire arc additive manufacturing (WAAM) technology has attracted extensive attention from experts in additive manufacturing due to its its manufacturing flexibility, high deposition efficiency, unlimited deposition capacity, relatively low cost and environmental friendliness [8-10]. The development of WAAM technology provides a new way to manufacture the low-cost green additive manufacturing of large and medium-sized complex titanium alloy metal parts.

In recent years, a large number of studies have reported that WAAM process

conditions have an important effect on the microstructure and mechanical properties of titanium alloys. Wu et al. [11] analyzed the influence of heat accumulation on microstructure and mechanical properties of Ti6Al4V alloy deposited by WAAM. They concluded that the quality of Ti6Al4V parts manufactured in other open environments using only local gas protection was acceptable when the process interpass temperature below 200 °C. Wang et al. [12] studied the effects of the travel direction and interlayer dwell time on the evolution microstructure and properties of Ti6Al4V part via WAAM. This work showed that the  $\alpha$  lath width changed little with the increase of dwell time, while the hardness, yield strength and tensile strength increase with the increase of dwell time. Chen et al. [13] reported the effect of boron on the microstructure of Ti6Al4V by WAAM. The results revealed that the TiB can be formed at the  $\beta$  grain boundary with the boron addition, and the  $\beta$  grain was significantly refined in the Ti6Al4V due to the increase in the fraction of TiB phases. As can be seen from the brief overview of the above literature, most of the current research is focused on WAAM Ti6Al4V alloy. However, there are still many titanium alloys with excellent properties that need further investigate.

Ti-6.5Al-3.5Mo-1.5Zr-0.3Si titanium alloy (TC11), as a typical two-phase titanium alloy, is mainly used to manufacture parts such as aeroengine, high-pressure compressor disk and blade, which can be used for a long time below 500 °C. Lei et al. [14] explored the isothermal compression deformation behavior of TC11 alloy. Their study suggested that the flow stress was sensitive to temperature and strain soft was observed at the lower temperature. Xie et al. [15] studied the influence of

electro-shocking treatment on the crystallographic structure of TC11 alloy. Their study suggested that the texture of  $\alpha$  and  $\beta$  phase increased gradually with the energy generated by electric shock increased. Hao et al. [16] illustrated the phase evolution of TC11 alloy and its correlation with properties of different annealing time and temperatures. The result showed that the strength of TC11 alloy generally decreased firstly and then increased as the annealing temperature increased while the plasticity was the opposite. Although there have been some relevant literatures on TC11 alloy, there are few reports about WAAM TC11 alloy, and the WAAM process of TC11 alloy also needs further improvement [17-18].

As such, a square part of Ti system heterogeneous alloy with TC11 as the main component was manufactured by multi-wire arc additive manufacturing (MWAAM) at different arc current in the present study, aiming to establish the relationship between process, microstructure and property of the alloy. The evolution of microstructure with the increase of current during the MWAAM process and the effects of different microstructure on the microhardness, tensile behaviour and corrosion resistance were investigated. Furthermore, it provides the theoretical and experimental evidences for the design of process and controllability of microstructure and properties in the MWAAM titanium alloy process.

## **2. Experimental process**

### **2.1 MWAAM system and material**

The specimen was manufactured using the developed MWAAM system, consisting of a 6-axis ABB robot arm with a IRC5 controller, a shielding gas unit, the

wire feeder and other fundamental modules of the MWAAM which had been described in detail elsewhere [19-20]. The schematic diagram of the MWAAM equipment is shown in **Fig.1**. Four sets of resistance heat power sources and wire feeders were used to greatly improve the deposition efficiency in manufacturing process. The tungsten inert gas (TIG) torch was installed on a six axis robot which can move multi direction. The deposition environment was in the enclosed atmosphere with 99.99% purity argon. TC11 alloy was selected as the substrate material with dimensions of 150 mm × 150mm × 5 mm. A square-thin-walled structure was additively manufactured on the substrate using TC11 welding wires of 1.5 mm diameter, as shown in **Fig.2a-c**. And the actual chemical composition of the wires was (wt.%): 6.52 Al, 3.39 Mo, 1.74 Zr, 0.30 Si, 0.07Fe, 0.01C, 0.01 N, 0.11 O and balance Ti. The purpose of this paper was to study the changes of microstructure, tensile properties and corrosion properties with the increase of arc current in the manufacturing process of MWAAM. Based on the previous basic research, three groups of tests were set with optimized parameters, and the parameters are shown in **Table 1**. The sedimentary distribution of the three specimen is shown in the **Fig.2b**.

## **2.2 Material characterization**

After the MWAAM process, the square part was extracted from the substrate using a wire-electrode cutting machine. No post-processing heat treatment was conducted, the as-built specimens were cut into the tensile test samples, the size of the sample was shown in **Fig.2d**, and their gauge lengths were ground and polished to eliminate the influence of surface machining.

To observe the surface morphology, MWAAM specimens were etched with a solution (1ml HF, 6ml HNO<sub>3</sub> and 100ml H<sub>2</sub>O) for 10 s. The optical microscopy (OM, ZEISS-Scope AI), the field emission scanning electron microscopy (SEM, JSM-IT500A) and the energy-dispersive X-ray spectrometer (EDS, JSM-IT500A) were to characterize the microstructure and elements distribution of the specimens. The phase composition was done using X-ray diffraction (XRD, D/Max 2500PC, Rigaku, Cu K $\alpha$ ). The diffraction angle range from 20° to 80°, and the scanning rate is 3°/min.

The Vicker's hardness of each MWAAM-deposited specimens was performed using microhardness instrument (Huayin, HVS-1000) with a load of 200 g and a dwell time of 15 s. Ten locations of each specimen was conducted and each location was repeated five times to reduce errors. The mechanical performances were carried out using the tensile testing system (Instron 1121). The loading rate was 1mm / min. The fracture morphology of the sample after tensile test were analyzed by SEM and ultra depth of field 3D microscope (VHX-950F).

The electrochemical corrosion tests were measured in 3.5% NaCl solution by electrochemical workstation (Gamry 600, Gamry Reference 600). The platinum electrode is auxiliary electrode, MWAAM specimen is working electrode, and the saturated calomel electrode is reference electrode.

Open-circuit potential (OCP) was measured for 4 h to obtain potential stability of 0.01 mV/min. Electrochemical impedance spectroscopic (EIS) were recorded at an AC potential amplitude of 5 mV over the frequency range of 10<sup>5</sup> - 10<sup>-2</sup> Hz. The impedance

data were evaluated by ZSimp-Win software. The polarization curves were also conducted. The polarization curves were performed by sweeping potential from -0.5 V to 2.0 V at a 1 mV/s scanning rate.

### 3. Results and discussion

#### 3.1 Macrographs analysis

It is well known that the solidification time of molten pool will affect the grain growth, the longer time will result in the larger grains. For  $\alpha + \beta$  biphas titanium alloy, both  $\alpha$  and  $\beta$  phases become coarser during nonequilibrium solidification. However, the  $\alpha$  and  $\beta$  phases will interfere with each other and thus limit grain growth. **Fig.3** reports the microstructure of the as-built specimen at different current. Due to the low current of specimen 1, the  $\alpha$  tended to grow in a long and narrow shape and formed basketweave structures during the solidification process, as shown in **Fig.3a**.

With the increase of arc current, the width of  $\alpha$  phase increased and the aspect ratio of  $\alpha$  phase decreased, as shown in **Fig.3b-c**. The reason for this phenomenon was that the curvature radius of the end face of the  $\alpha$  phase was smaller than that of the side, resulting in the solubility of the end face of the  $\alpha$  phase was higher than that of the side [21]. This solubility difference resulted in a concentration difference, which led to end-face dissolution and lateral growth of  $\alpha$  phase [22]. With the increase of current, the  $\alpha$  phase in the specimen had a more sufficient growth time, so the aspect ratio of  $\alpha$  phase gradually decreased during the solidification process. Meanwhile, the increase in current slowed down the cooling rate, resulting in a coarse colony  $\alpha$  structure (typical Widmannstatten structure) in the basketweave structures, as shown



in **Fig.3c**. Because  $\alpha$  phase belonged to densely packed hexagonal structure, the number of slip systems was 3, the number of slip systems was small, and the slip deformation ability was poor. The large colony  $\alpha$  had weak the deformation coordination ability in the sliding process, and the increase of colony  $\alpha$  structures will reduce the ductility of the as-built specimen [11].

### 3.2 XRD and phase analysis

The XRD patterns of the TC11 wire and the as-built MWAAM specimens are shown in **Fig.4**. The wire and the as-deposited specimens had approximately the same diffraction peaks. It was obvious that there were strong diffraction peaks at the crystal planes (101), (002), (103) and (112) of  $\alpha$ -Ti from the XRD patterns.

Compared with the PDF # 44-1294 standard card of  $\alpha$ -Ti phase, the  $2\theta$  position of the sample after MWAAM was shifted to the direction of high Bragg angle, indicating that the lattice distortion of the specimens occurred after deposition. This phenomenon was caused by the thermal stress of the additive manufacturing process and the solid solution of the alloy atoms [23-25]. At the same time, weak diffraction peaks were found on the planes (110) and (200) of  $\beta$ -Ti. In contrast to the  $\alpha(101)$  peak, the peak of the  $\beta(110)$  was barely visible due to that the  $\beta$ -Ti phase was usually too small to be detected by X-rays. The intensity of  $\alpha(101)$  and  $\alpha(103)$  peak decreased significantly with the increase of the input current, indicating that the phase transformation from lamellar  $\alpha$  phases to colony  $\alpha$  phases during the MWAAM process [11].

The influence of alloying elements in titanium alloys is strong, and alloys can be divided into different types according to the content of  $\beta$  -stable elements. Therefore,

the phase transformation in titanium alloys was comprehensively affected by heating temperature, element content and cooling rate [26]. Since  $\alpha$  phase and martensite can not be distinguished by diffraction peaks due to their similar Hexagonal close packed (HCP) structure, the phase composition of MWAAM TC11 was necessary to further clarify. The phase analysis of TC11 was carried out by JPro thermodynamic simulation software, and the equilibrium phase diagram was shown in **Fig.5(a)**. It was well known that TC11 was a  $\alpha + \beta$  duplex alloy, and  $\alpha$  at room temperature and  $\beta$  at high temperature. The  $\beta$  phase was transformed into  $\alpha$  phase by slow cooling during equilibrium solidification. However, the cooling speed of MWAAM process was fast, which was a non-equilibrium solidification process. In addition, MWAAM was a layer-by-layer deposition and solidification process, the subsequent layers tempered on top of the previous layer, which further resulted in complex phase composition of the specimen. The simulated non-equilibrium phase diagram of TC11 at  $10^2$  °C/s cooling rate as shown in **Fig.5(b)**. In the non-equilibrium phase transition diagram, the phase transition process was as follows: liquid phase +  $\beta \rightarrow \beta + \alpha$  (Martensite).

### 3.3 Microstructure

**Fig.6** shows the cross-sectional microstructure of the MWAAM TC11 alloy specimens at different current. **Fig.6a-c** shows that the microstructure of TC11 alloy were mainly composed of lamellar primary  $\alpha$  phase ( $\alpha_P$ ) and transformed  $\beta$  phase ( $\beta_T$ ), and the microstructure of  $\beta_T$  region was composed of acicular secondary  $\alpha$  phase ( $\alpha_S$ ) and  $\beta$  matrix, as shown in **Fig.6d-f**.

The temperature gradient (G) and crystallization rate (R) of molten pool are

greatly affected by the heat input in additive manufacturing process [27]. According to the classical solidification theory, the composition undercooling ( $G/R$ ) determines the solidification microstructure of alloy. Generally speaking, with the increase of heat input, more heat is accumulated, resulting in the decrease of temperature gradient and the coarsening of microstructure.

As shown in **Fig.6a-c**, the morphology and size of  $\alpha$  phase were obviously different. As the current increased, the microstructure changed from elongated lamellar  $\alpha$  phase to lamellar  $\alpha$  phase, which resulted in a decrease in the aspect ratio of  $\alpha$  phase. Due to the large aspect ratio of  $\alpha$  phase in specimen 1, it was easy to produce local stress concentration and crack at  $\alpha/\beta$  interface during tensile process, which reduced its ductility [28-29]. In addition, Imagine J software was used to calculate the proportion of the two phases of **Fig.6a-c**. The  $\alpha$  phase proportion of specimen 1-3 was 60.88%, 62.51% and 71.51%, respectively, and the proportion fraction of  $\beta$  phase was 39.12%, 34.71% and 28.49%, respectively. It can be found that the proportion of  $\alpha$  phase in the specimen microstructure increased with the increase of current thermal input. **Fig.6d-f** shows the magnified view of the  $\beta_T$  region. By comparison, the acicular martensite  $\alpha_S$  in specimen 1 was the smallest while in specimen 3 was the most coarse. This phenomenon showed that  $\alpha_P$  and martensite  $\alpha_S$  tended to grow with the increase of current. It has been reported that increasing the number of acicular  $\alpha_S$  and decreasing the size of acicular  $\alpha_S$  can effectively improve the strength of titanium alloy [30]. It was interestingly noticed that goast  $\alpha$  phase appeared in the microstructure of specimen 3 when the current reached 400A. The phenomenon can be

explained by that the  $\alpha_S$  phase annihilated due to insufficient temperature and cooling rate for forming  $\alpha$  lamellar structure, and the  $\alpha_P$  phase returned to solute state to form the  $\alpha$  phase in the remelting region of MWAAM [31]. Similar results were also reported by Chen et al. [32] on the study of MWAAM TC11-TC17 dual alloy.

In order to study the distribution of elements in microstructure of WAAM TC11 alloy, EDS plane scanning analysis was carried out on the sample section microstructure, and the analysis results are shown in **Fig.7**. It was obvious that the distribution of Mo, Al and Zr elements in WAAM was not uniform. It can be seen from the scanning results that Al was mainly enriched in  $\alpha$  phase, while Mo and Zr were mainly enriched in  $\beta$  phase. This phenomenon can be attributed to the Al element was  $\alpha$  phase stable element, while Mo and Zr elements were  $\beta$  phase stable elements [33].

**Fig.8** shows the microstructure evolution of MWAAM TC11 alloy during cooling. **Fig.8a** displays the TC11 alloy transformed from a liquid state to the coexistence of  $\beta$  and  $\alpha_P$  phases. The  $\alpha_P$  phase was preferentially formed at the  $\beta$  grain boundary. As the temperature decreased, the  $\alpha_S$  phase formed inside the  $\beta$  phase owing to the high degree of undercooling, as shown in **Fig.8b**. The most  $\alpha_S$  phases were distributed in the mixed microstructures in fine lamellar or acicular. With the temperature being further reduced, the morphological difference between the primary  $\alpha_S$  phase and the  $\alpha_P$  phase decreased, and the microstructure gradually changed into primary  $\alpha_P$  phase and  $\beta_T$  phase, as shown in **Fig.8c**. Therefore, the microstructure of the as-deposited specimens was typically a mixture of  $\alpha_P$  and  $\beta_T$  phase. Lizzul et al. had been reported

that the phase transition between the  $\beta$  and  $\alpha$  phases usually forms an angle [34]. Similar phenomenon had been observed in microstructure of MWAAM TC11 alloy, as shown in **Fig.6a-c**. This phenomenon can be attribute to the specific Burgers relation between the  $\beta$  and  $\alpha$  phases. Crystallographic correspondence between  $\beta$  phase and martensite  $\alpha$  phase as shown in **Fig.9**. The hexagonal cell size :  $a = 0.293$  nm,  $c = 0.4675$  nm,  $c/a = 1.596$ . According to the  $\beta$  and  $\alpha$  phase of Burgers relation [35]:  $(0001)_\alpha // (011)_\beta, [\bar{1}2\bar{1}0]_\alpha // [\bar{1}\bar{1}\bar{1}]_\beta$ . Therefore, the  $\alpha$  and  $\beta$  phase were formed at a certain angle due to the preferential growth of the  $\alpha$  phase parallel to the (110) family of crystallographic planes of the  $\beta$  phase.

### 3.4 Microhardness

Microhardness was measured and the effect of current on mechanical properties of MWAAM specimens was studied. **Fig.10** shows the Vickers microhardness of the samples fabricated at different current. Different current of the samples exhibited various phases morphologies, leading to different microhardness, the hardness indentation as shown in **Fig.10a-c**. From **Fig.10**, the microhardness curves of samples showed varying degrees of fluctuation. As the arc current increases, the hardness of MWAAM sample slightly decrease. The average microhardness of the three specimens was 402.11 HV, 363.44HV and 332.95HV, respectively. One reason of this phenomenon was with increasing the current, the ratio of  $\beta$  phase increased. The  $\beta$  phase is known to have the lowest Young's modulus and hardness of all titanium phases [36]. The other reason was according to the decreasing phase boundaries due to the microstructure coarsening caused by increased current. As we all known, the

increase of phase boundary can hinder the local crystallization slip and dislocation movement, thus improving the microhardness of samples [37].

### 3.5 Tensile properties and fracture mechanism

It is known that the width of the  $\alpha$ -lath and the morphology of columnar  $\beta$  grains play a decisive role in the tensile properties of titanium [38]. The columnar  $\beta$  grains parallel to the building direction are easy to be formed during the MWAAM of titanium alloys. Li et al. [39] investigated the mechanical properties of columnar  $\beta$  grains in the different direction by WAAM titanium alloy. The results showed that the ultimate tensile strength (UTS) parallel to the growth direction of coarse columnar  $\beta$  grains was generally lower than that perpendicular to the growth direction of  $\beta$  grains. In this study, the tensile property parallel to the building direction was tested to investigate the effect of MWAAM current on the tensile property of TC11 alloy. The tensile stress-strain curves of MWAAM TC11 alloy tensile specimens in different current were illustrated in **Fig.11a**, and the related performance data were given in **Fig.11b**. The average UTS of the three MWAAM specimens with different current were 843.75 MPa, 812.5MPa and 804.38MPa, respectively. The average elongation of the three MWAAM specimens were 66.3%, 78.6% and 69.1%, respectively. As the deposition current increasing from 360A to 400A, the values of UTS showed a downward trend. From this phenomenon, it can be concluded that the change of current will affect the microstructure and mechanical properties of materials in the process of large heat input arc additive manufacturing. According to the Hall-Petch equation [31,34], the UTS will be decrease as the grain grows. In this MWAAM

process, the heat input of four wires into the molten pool was much higher than that of single wire, and the decrease of the cooling speed of the molten pool will give more time for the grain to grow, so the tensile strength was less than that of the previous single wire arc additive manufacturing work [39]. These results were primarily attributed to the differences in the microstructure.

**Fig.12** displays the typical fracture morphologies of the tensile samples under the three conditions. The SEM fractographic images revealed that the river patterns, and cleavage facets dominate the whole deformed surface of MWAAM TC11 alloy samples. As shown in **Fig.12a-c**, there was no obvious necking deformation at the fracture of the samples under the three current. In order to compare the height difference of the fracture morphology under the three current conditions, we conducted ultra depth of field observation. **Fig.12d-f** shows the three-dimensional morphology of the fracture of the three samples. From **Fig.12d-f**, the height difference of the fracture surface of the specimen 1 with current 360A was the largest in three MWAAM specimens. The fracture surface of the specimen 3 with 400A current was relatively smooth. A large number of dimples appeared in the plastic deformation zone of the the fracture surface, which clearly illustrated the existance of typical ductile fracture, as shown in the high-magnification **Fig.12g-i**. However, the dimples of specimen 1 were relatively deeper than those of specimen 2 and 3.

**Fig.13** illustrates the deformation of lamellar  $\alpha_p$  and acicular  $\alpha_s$  during tensile process. In the tensile process, the initial plastic deformation occurred in the  $\alpha_p$  phase. This was due to that the yield stress of the  $\alpha_p$  phase was lower and the stress

distribution was higher than  $\beta$  phase in the elastic deformation stage [40], as shown in **Fig.13a**. Then the plastic deformation of the  $\alpha_p$  phase was transferred to the adjacent  $\beta$  matrix and the strain of  $\alpha_s$  phase at the  $\beta$  phase boundary would further increase owing to the severe deformation happened in the  $\beta$  matrix [29], as shown in **Fig.13b**. As a result, there was a strong plastic strain concentration in the  $\alpha_s$  phase near the  $\beta$  phase boundary, eventually formed holes or cracks, as shown in **Fig.13c**. Meanwhile, these microscopic holes will gradually merge and grow up, and connect with the cracks tip front in the way of necking in the process of loading, which promoted the crack tip to expand forward, and finally caused the tensile component to fracture.

### 3.6 Corrosion characteristics

In order to reveal the chemical corrosion resistance of the MWAAM specimens, the electrochemical corrosion properties of specimens in 3.5 wt% NaCl solution were investigated. As a nondestructive testing technique, electrochemical impedance spectroscopy (EIS) is used to predict the equivalent circuit of the corrosion process by applying small amplitude sinusoidal wave interference signals of different frequencies to the system without damaging the passive film structure on the surface of the material, so as to obtain the interface structure and dynamic information of the electrode. Bode plot of the MWAAM specimens at different currents was shown in **Fig.14a-b**. So far, many scholars have used different equivalent circuits to simulate the alloy and electrolyte interface [41-42].

When only a single layer of dense passivation film was present, it was usually represented by an equivalent circuit R(QR) containing a time constant. However, the



double-layer passivation film formed after immersion in 3.5 wt% NaCl solution with loose outer layer and dense inner layer was usually represented by an equivalent circuit containing two time constants, in which R(Q(R(QR))) model was widely used to simulate the interface behavior of titanium alloy double-layer passivation film [43]. According to the impedance spectrum characteristics of TC11 alloy with two capacitance-arc reactance, R(Q(R(QR))) model was selected to describe the impedance spectrum of this material, as shown in **Fig.14a**. The equivalent circuit corresponding to the TC11 alloy material in 3.5 wt% NaCl solution was confirmed by ZsimpWin software, and the interface behavior of the titanium alloy material was simulated to interpret the above electrochemical impedance measurement results. The fitted results of circuits were listed in **Table 2**. The resistor of  $R_s$  is solution resistance,  $R_f$  is film resistance, and  $R_{ct}$  is solution resistance. The constant phase angle element of  $Q_1$  and  $Q_2$  are physical quantity which used to describe capacitance offset. The impedance value  $Q$  is given by Eq. (1) [25]:

$$Z_Q = [Q(j\omega)^n]^{-1} \quad (j = -1) \quad (1)$$

where  $j\omega$ ,  $Q$  and  $n$  are the complex variable of sinusoidal perturbation, capacitance and fractional exponent of the  $Q$ . The  $n$  ranges from -1 to 1, indicating the extent to which the actual capacitance deviates from the ideal capacitance, which is related to surface roughness, uneven distribution of potential and current, etc. When  $n$  is close to 1, the passivation film on the alloy surface is close to the ideal capacitance. As can be seen from **Fig.14a**, the Bode modulus curve presented a horizontal straight line independent of frequency in the high frequency region ( $10^3$ - $10^5$ Hz) of the Bode

diagram. In the middle and low frequency region ( $10^{-2}$ - $10^3$ Hz), the Bode modulus curve was a straight line with a slope close to -1. In addition, the impedance value in the low frequency region is close to  $10^6 \Omega \text{ cm}^2$ . It was observed from the Bode phase diagram (**Fig.14a-b**) that the phase angle was almost reduced to  $0^\circ$  at extremely high frequencies, that was, the impedance value within this frequency range was mainly affected by the resistance of the electrolyte between the specimen and the reference electrode. However, the phase angle decreased slightly in the extremely low frequency region, which was related to the passivation film resistance on the sample surface. Meanwhile, the maximum phase angle was located in the mid-frequency region. Generally, the higher the phase angle, the higher the surface passivation film stability, and the wider the frequency range of the maximum phase angle, the more dense the passivation film [44]. Therefore, specimen 1 showed the best corrosion resistance than other specimens according to the results of Bode diagram.

The Nyquist plots of the WAAM specimens are displayed in **Fig.14c**. The arc radius of capacitive reactance for three specimens decreased with the increase of current. Meanwhile, the value of  $R_{ct}$  also decreased gradually with the increase of current, indicating that the protection of passivation film formed on the surface of alloy was gradually weakened, and the corrosion resistance was decreasing. **Fig.14d** demonstrates the potentiodynamic polarization curves of MWAAM specimen at different current. In the 3.5 wt% NaCl solution, oxygen uptake reaction occurred in the cathode region of alloys specimens. With the increase of potential, the anodes of the three MWAAM specimens showed activation-passivation behavior. The current

density and self-corrosion potential were analysed by Tafel fitting. The the values of current density of the three MWAAM samples were  $1.23 \times 10^{-8}$ ,  $2.34 \times 10^{-8}$  and  $3.36 \times 10^{-8}$  A cm<sup>-2</sup>, respectively, while the values of self-corrosion potential were -311, -315 and -329 mV, respectively. The self-corrosion potential was the stable potential of the corroded system without external polarization [45]. Specimen 1 had the highest self-corrosion potential (-311mV) and the lowest corrosion tendency, while specimen 3 had the lowest self-corrosion potential (-329mV) and the highest corrosion tendency. The self-corrosion potential can only reflect the surface state and thermodynamic stability of the metal on the surface of the material, but not the corrosion rate of the metal [46]. The corrosion current density was a kinetic parameter of the reaction corrosion rate. By comparing the corrosion current density of the three specimens, it can be seen that the corrosion speed of the WAAM alloy specimen will gradually increase and the passivation film formed was easier to dissolve with the increase of the current.

#### **4.Conclusions**

In this study, Ti system heterogeneous alloy thin-walled square component has been deposited using the multi-wire arc additive manufacturing method with deposition currents of 360A, 380A and 400A. The influence of deposition current on the microstructural evolution, mechanical responses and corrosion performance of MWAAM deposited TC11 alloy were studied. The main conclusions are given below:

(1) The microstructure of as-received Ti system heterogeneous alloy was mainly composed of lamellar primary  $\alpha$  phase and transformed  $\beta$  phase, and increasing the

deposition current during the MWAAM process would result in the increased width of  $\alpha$  phase and the decreased aspect ratio of  $\alpha$  phase. The proportion of  $\alpha$  phase in the microstructure of TC11 alloy increased with the increase of deposition current thermal input.

(2) The MWAAM TC11 specimen fabricated at 360 A had the highest microhardness of 402.11 HV. The tensile results indicated that for increasing deposition current from 360 A to 400 A, the UTS was lowered from 843.75 to 804.38MPa. Such a trend could be explained by the combined evolution of microstructure and the effect of grain size during deposition. The fracture surface of MWAAM deposited specimens resembled a typical mixed type of brittle fracture and ductile fracture.

(3) The corrosion experiment results displayed a stable passive film formed on the surface of the MWAAM TC11 specimen. The potentiodynamic polarization results showed that the corrosion resistance of TC11 specimens decreased gradually when the deposition current was increased from 360 A to 400 A, which the self-corrosion potential of the MWAAM specimen was lowered from -311 to -329 mV and current density was increased from  $1.23 \times 10^{-8}$  to  $3.36 \times 10^{-8}$  A cm<sup>-2</sup>.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## **Data availability**

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study

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