Research on the microstructure and mechanical properties of high-entropy alloys manufactured using 3D printing technology

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ABSTRACT

In this paper, the high-entropy alloy AlMnFeCrNiCu was fabricated using 3D printing technology from a mixture of pure metal powders. The microstructure and mechanical properties of the alloy were studied on thin wall samples. The results show that the alloy has a mixed structure of two phases: face-centered cubic and body-centered cubic. Tensile strength, yield strength, and elongation are 936 MPa, 563 MPa, and 32%, respectively. The alloy obtained by the 3D printing method demonstrates outstanding mechanical properties, which are both high durability but still ensure good ductility.

Keywords: 3D printing; High entropy alloy; Microstructure; Mechanical properties.

1. INTRODUCTION

High Entropy Alloy (HEA) is a new class of materials defined as multi-element alloys (usually five or more elements) with the atomic percentage content of each component ranging from 5% to 35% [1]. This alloy is different from traditional alloys, which usually have only one element in the main content, such as Fe in steel and Cu in Latong alloy. HEA has many outstanding properties compared to traditional materials, such as good mechanical properties, corrosion resistance in harsh environments, heat resistance, good magnetism [2], etc. These properties give HEA potential applications in mold manufacturing, surface engineering, aerospace, anti-radiation materials, and other fields [3]. Currently, Additive Manufacturing (AM) technology, also known as 3D printing technology, has been used to manufacture parts made of alloys such as stainless steel, Ti alloy, and Ni alloy and is researching for HEA [4]. Laser Metal Deposition (LMD) is a widely used method in AM technology to fabricate 3D metal parts from metal powder. During this process, laser energy melts the metal powder and rapidly solidifies it to form a material layer on the substrate [5]. The following material layer is deposited by moving the laser head in a pre-designed 3D shape, eventually forming the finished part.

The CoCrFeMnNi HEA system has been extensively researched in manufacturing using 3D printing technology. Xiang [6] used the LMD technique to fabricate the CrMnFeCoNi alloy; the results showed that the fabricated alloy has a Face Center Cubic (FCC) phase structure. Mechanical properties are better than cast alloys of the same composition; tensile strength and elongation are 535 MPa and 55%, respectively. Huang [7] fabricated AlxCoCrFeNi alloy using the LMD method, and the results showed that the addition of Al to the alloy promoted the formation of the Body Center Cubic (BCC) phase and improved tensile strength. High mechanical properties are recorded in the duplex phase alloy FCC/BCC $Al_{0.7}CoCrFeNi$ with tensile strength and elongation of 1171 MPa and 11%, respectively. According to previous studies [8], the formation of FCC and BCC phase structures in high entropy alloys is predicted by that alloy's valence electron concentration (VEC) value; specifically, when VEC $\geqslant$ 8.0, the alloy tends to form an FCC phase structure. When VEC < 6.87, the alloy tends to form a BCC phase structure. A two-phase FCC/BCC mixture will form when 6.87 ≤ VEC < 8.0. Based on the VEC value as well as the preliminary study on the $FeMnNiCrCu_{0.5}$ alloy system [9], the authors chose the alloy system with composition

$Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ as the research object, and its VEC value is 7.88, suitable for forming the FCC/BCC two-phase structure.

The use of 3D printing technology to manufacture HEA typically involves the use of alloy powder as raw material, with the composition tailored to the design. Traditionally, HEA powders are prepared using the gas atomization process, a method that involves numerous production steps and high costs. However, a new, cost-effective method of making HEA powders by mixing pure metal powders into a powder mixture has recently gained attention. This method offers flexibility in changing the composition of the powder mixture and significant cost savings [10]. In this study, the LMD technique was used to fabricate a simple 3D thin wall with a composition of $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ using the mixed powder as raw material, demonstrating the potential for cost savings in HEA production. The microstructure and mechanical properties of the alloy after 3D printing were investigated.

2. EXPERIMENTS

2.1. Research object

The research object is a high entropy alloy with a molar composition of $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$. High-purity metal powders Fe, Mn, Ni, Cr, Cu, and Al (≥ 99.95%) with spherical particle size in the range of 50 ‑ 150 µm are used as raw materials (provided by Changsha Tianjiu Company - China). The metal powders are weighed according to the molar ratio of $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ alloy. Then, the powder mixture is mixed evenly in a planetary ball mill at a speed of 250 rpm, and the mixing time is 12 hours. SUS304 stainless steel plates with dimensions of 100 mm × 100 mm × 10 mm are used as substrate materials in the 3D printing process.

2.2. Laser metal deposition 3D printing system

Figure 1 describes the Laser Metal Deposition (LMD) 3D printing system, including the leading equipment: 1000W fiber laser, powder feeding device, control computer, shielding gas, and processing table. Powder and Ar shielding gas are synchronously supplied to the laser nozzle during 3D printing; the Ar gas environment prevents oxidation with 10 bar of pressure. The laser nozzle will move according to the set profile (via computer), during which the laser beam will melt the metal powder at the nozzle and create a thin metal layer on the substrate, thus forming a 3D profile.

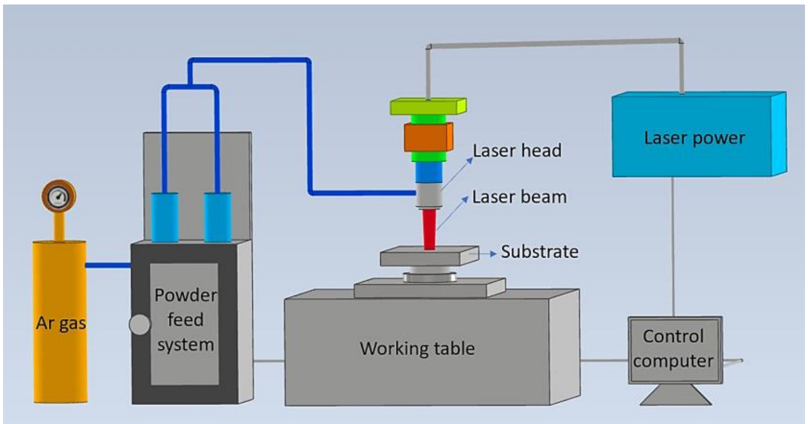

Figure 1. *Schematic of the laser metal deposition (LMD) system.*

2.3. Fabrication of high entropy alloy thin-walled samples

A simple 3D thin wall part was fabricated on a SUS304 substrate using the LMD technique. Through a series of tests, the technological parameters were selected as follows: laser power - 850 W, scanning speed - 3 mm/s, laser beam diameter - 3 mm, powder feeding speed - 3 g/min. The 3D printing process of thin-walled parts is carried out as follows: the laser head runs in a straight line, and the laser beam melts the mixed powder to form an initial printed layer. Then, the laser head is raised 0.25 mm after a single laser scan and continues to print the next layer on the alloy layer just printed on the substrate. The above process continues like this and finally creates a thin-walled part with dimensions of 60 mm in length, 10 mm in height, and 2.5 mm in thickness**.**

2.4. Method of evaluating the microstructure and mechanical properties

The phase structure of the sample was examined by X-ray diffraction on an XRD 6100 (SHIMADZU-Japan) with a scanning angle of 25°-85° and a scanning speed of 4°/min. XRD analysis was performed on the side surfaces of the thin-walled sample after grinding. The microstructure was observed under a Zeiss AxioVert A1 optical microscope. The sample's chemical composition was analyzed by energy-dispersive X-ray spectroscopy (EDS) on a scanning electron microscope.

The mechanical properties were evaluated with utmost thoroughness using a WDW-100Y universal tensile testing machine. The sheet tensile test specimens were cut with precision by a wire-cutting machine, ensuring the cutting direction was along the length of the thin wall part. Despite the challenge posed by the small size of the thin wall part, the prepared tensile test specimen size was a carefully chosen non-standard size of 20 mm (length) × 7 mm (width) × 2 mm (thickness).

3. RESULTS AND DISCUSSION

3.1. Morphology and chemical composition of 3D printed parts

Fig.2 shows the geometrical and surface morphology of a thin wall $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ sample fabricated by the LMD method. It can be seen that the thin wall has a length of 60 mm and a height of 10 mm without macro-defects. There are a few metal spherical particles attached to their surface. The phenomenon is that when laser scanning increases the height of the sample, the molten metal will have a small amount of adhesion on the side wall of the part.

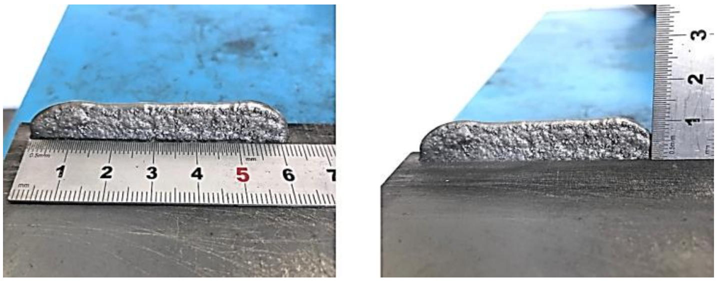

Figure 2. *The thin wall $Al_{0,25}Mn_{0,75}FeNiCrCu_{0,5}$ HEA.*

The thin wall samples, after fabrication, were analyzed for chemical composition using EDS (Energy Dispersive X-ray Spectroscopy). The spectrum analysis images and chemical content in atomic percentage (at.%) are shown in figure 3 and table 1.

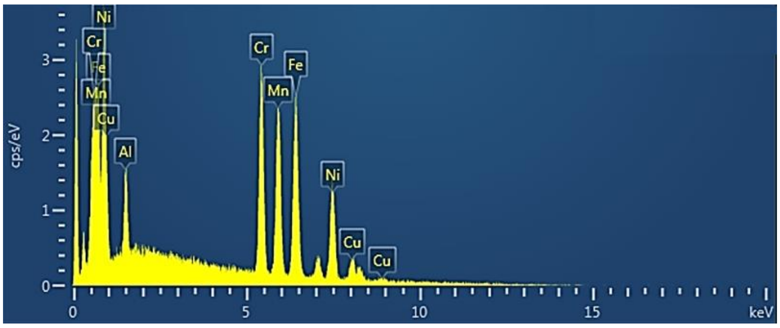

Figure 3. *EDS spectrum analysis of 3D printed sample of $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ HEA.*

Table 1. *Elemental content (at.%) in 3D printed samples of high entropy alloy.*

Element	Fe	Cr	Ni	Mn	Cu	Al
Normal	22,22	22,22	22,22	16,67	11,11	5,56
Actual	22,43	21,95	22,48	16,78	11,27	5,09

The content of elements in the actual 3D-printed sample is close to the theoretical calculation. The content of Al is lower than that of other elements because Al has a much lower melting temperature. Under the high energy of a laser beam, Al can be partially burned. The result can confirm that a mixed powder of six metal elements can be manufactured entirely according to the composition of a high-entropy alloy sample using the 3D printing method. Compared to alloy powder, mixed powder can be a suitable choice when it is necessary to change the composition flexibly during the research process.

3.2. Microstructure and mechanical properties

Figure 4 presents the results of X-ray diffraction analysis. It can be seen that diffraction peaks appear at the diffraction angle position 2theta approximately 43.4°, 50.5°, and 74.4° are determined to be the (111), (200), and (220) faces of the FCC phase lattice, respectively. The diffraction peaks at the diffraction angle position 2theta, approximately 44.7°, 64.5°, and 82.3° are determined to be the (110), (200), and (211) faces of the BCC phase lattice, respectively. The above results are similar to the study by author Hsu [11] on the $CoCrFeMnNiAl_x$ alloy system when adding and changing the Al element content; specifically, Al is the element that promotes the formation of the BCC phase. Thus, through the results of X-ray diffraction analysis, we can preliminarily determine that the phase structure of the alloy in this study is composed of a mixture of FCC and BCC phases. The phase structure of this alloy system is also consistent with the theory predicted by the electron concentration value, as mentioned above.

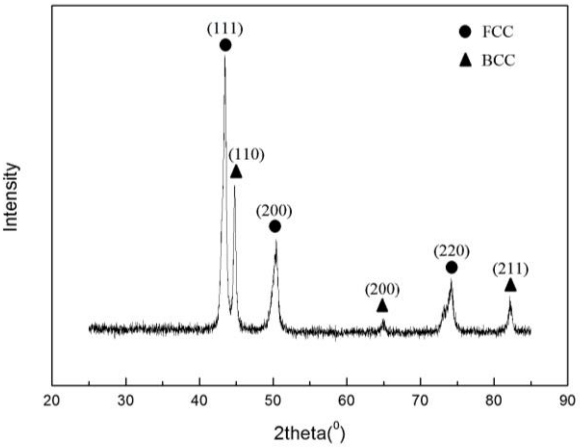

Figure 4. *X-ray diffraction pattern of $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ HEA.*

The microstructure was observed at two positions of the thin wall sample by optical microscopy, including vertical and horizontal cross-section, as shown in figure 5. Basically, it can be seen that the microstructure is clearly divided into two regions distinctly consisting of dark crystalline grains distributed on a light background. In horizontal cross-section (figure 5a), the dark grains have a small size of about 3-10 µm. Small grains are a typical feature of 3D printing technology, the main reason being that the melting and solidification process occurs at a very fast speed. On the vertical cross-section (figure 5b), the microstructure morphology is different from the horizontal cross-section. The dark grains are arranged into a columnar structure that extends along the direction of printing the thin-wall sample. This is because when the laser beam interacts with the metal powder, the metal powder melts rapidly, forming a thin layer and causing a large temperature gradient. This temperature gradient is oriented perpendicular to the surface, which promotes the formation of a columnar crystal structure.

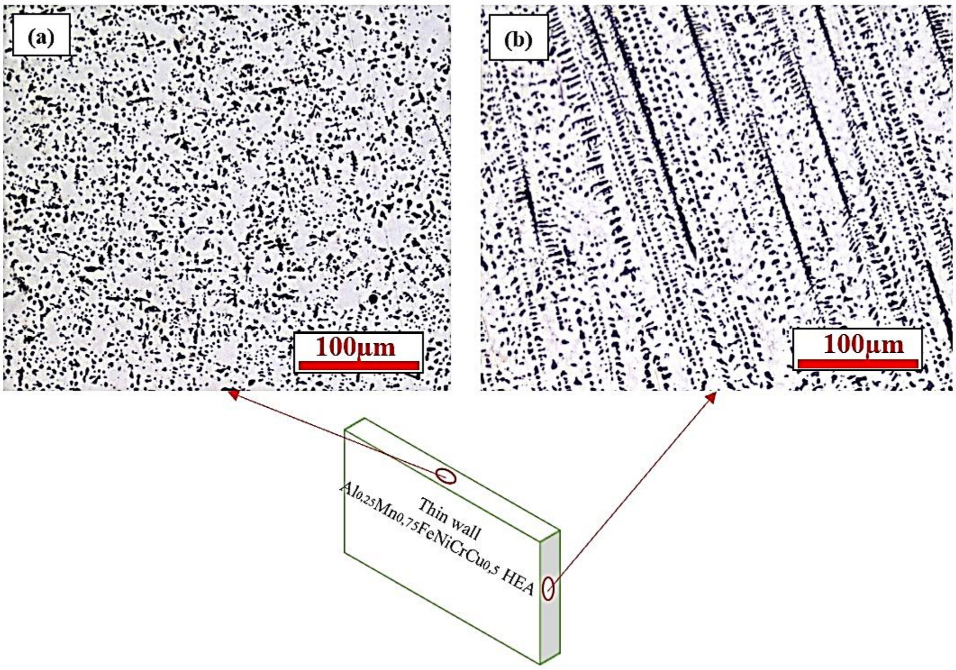

Figure 5. *The microstructure of thin wall 3D printed* $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ *HEA.*

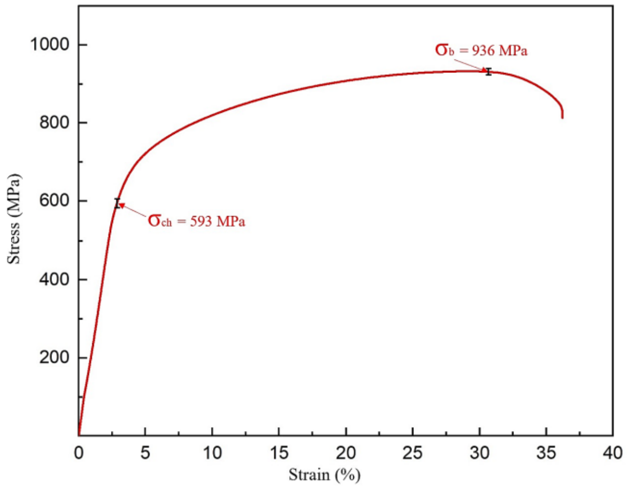

Figure 6. *The tensile curve of thin wall 3D printed* $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ *HEA.*

The tensile test was conducted at room temperature, and the results are presented in the tensile strain-stress curve (figure 6). The tensile strength σ_b reaches a value of approximately 936 MPa, the yield strength σ_{ch} (calculated at an elongation value of 0.2%) reaches a value of roughly 593 MPa. A notable point is that the elongation of the sample has a relatively high value of approximately 32%. The above values show that the 3D-printed alloy sample has high strength but maintains good ductility with an elongation of over 30%. The good comprehensive mechanical properties of the above alloy sample are attributed to the combination of its FCC and BCC two-phase structure. As we know, the FCC phase is ductile, and the BCC phase is high-strength. That combination creates properties similar to traditional dual-phase steels. In addition, the fine crystalline grain structure when 3D printing is also a factor that increases the durability of the alloy. When compared with the 3D printing alloy system $AlCrCuFeNi_{3.0}$ [12], it was found that the strength of the alloy in this study was equivalent, but the ductility was much higher. This tensile properties can also be compared with known high-strength steels such as dual-phase and TRIP steel [13]. This opens up the potential for further in-depth research on the microstructure and mechanical properties of the $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ high-entropy alloy.

4. CONCLUSIONS

The $Al_{0.25}Mn_{0.75}FeNiCrCu_{0.5}$ HEA has been successfully produced by 3D printing technology from a mixed powder. The microstructure of the thin wall sample shows a small grain size and columnar crystal grain morphology formed along the 3D printing direction. The phase structure of the alloy is a mixture of two phases, FCC and BCC, consistent with theoretical predictions. The alloy exhibits good comprehensive properties with tensile strength, yield strength, and elongation of 936 MPa, 563 MPa, and 32%, respectively. The research results open up the potential for future in-depth studies on the microstructure, mechanical properties, and manufacturing methods of this alloy system.

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TÓM TẮT

Nghiên cứu tổ chức, cơ tính của hợp kim entropy cao chế tạo bằng công nghệ in 3D

Trong bài báo này, hợp kim entropy cao hệ AlMnFeNiCrCu đã được chế tạo bằng công nghệ in 3D từ hỗn hợp của các bột kim loại nguyên chất. Tổ chức và cơ tính của hợp kim đã được nghiên cứu trên mẫu thành mỏng. Kết quả chỉ ra rằng hợp kim có tổ chức hỗn hợp hai pha lập phương diện tâm và lập phương thể tâm. Giới hạn bền kéo, giới hạn chảy, độ giãn dài tương đối lần lượt là 936 MPa, 563 MPa, 32%. Hợp kim thu được bằng phương pháp in 3D thể hiện tính cơ tính tổng hợp nổi trội vừa có độ bền cao nhưng vẫn đảm bảo độ dẻo dai tốt.

Từ khoá: In 3D; Hợp kim entropy cao; Tổ chức; Cơ tính.