

Review

Advancements in Additive Manufacturing for Copper-Based Alloys and Composites: A Comprehensive Review

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Abstract: Copper-based materials have long been used for their outstanding thermal and electrical conductivities in various applications, such as heat exchangers, induction heat coils, cooling channels, radiators, and electronic connectors. The development of advanced copper alloys has broadened their utilization to include structural applications in harsh service conditions found in industries like oil and gas, marine, power plants, and water treatment, where good corrosion resistance and a combination of high strength, wear, and fatigue tolerance are critical. These advanced multi-component structures often have complex designs and intricate geometries, requiring extensive metallurgical processing routes and the joining of the individual components into a final structure. Additive manufacturing (AM) has revolutionized the way complex structures are designed and manufactured. It has reduced the processing steps, assemblies, and tooling while also eliminating the need for joining processes. However, the high thermal conductivity of copper and its high reflectivity to near-infrared radiation present challenges in the production of copper alloys using fusion-based AM processes, especially with Yb-fiber laser-based techniques. To overcome these difficulties, various solutions have been proposed, such as the use of high-power, low-wavelength laser sources, preheating the build chamber, employing low thermal conductivity building platforms, and adding alloying elements or composite particles to the feedstock material. This article systematically reviews different aspects of AM processing of common industrial copper alloys and composites, including copper-chrome, copper-nickel, tin-bronze, nickel-aluminum bronze, copper-carbon composites, copper-ceramic composites, and copper-metal composites. It focuses on the state-of-the-art AM techniques employed for processing different copper-based materials and the associated technological and metallurgical challenges, optimized processing variables, the impact of post-printing heat treatments, the resulting microstructural features, physical properties, mechanical performance, and corrosion response of the AM-fabricated parts. Where applicable, a comprehensive comparison of the results with those of their conventionally fabricated counterparts is provided.



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1. Introduction

1.1. Copper Alloys and Their Applications

Although copper and its alloys are among the earliest developed engineering metallic materials, they are still extensively employed in various engineering applications primarily due to their high thermal/electrical conductivity, along with their good corrosion resistance, excellent machinability, and formability [1]. However, industrial applications of different copper alloys may vary based on the type and content of additional alloying elements, which could potentially improve or even deteriorate specific properties of the end-product. For example, pure copper with excellent thermal conductivity (5.8×10^7 S/m) is primarily

desired for induction heat coils, cooling channels, heat exchangers, radiators, or radiofrequency cathodes [2,3]. Also, pure copper is commonly used in electrical applications due to its great balance of low electrical resistivity ($1.72 \times 10^{-8} \Omega$) and reasonable price compared to precious metals such as gold and silver [4]. However, the inferior mechanical strength and wear resistance of pure copper in comparison with other engineering materials became an incentive for researchers to improve their mechanical properties [5] with the addition of different alloying elements. For instance, the addition of tin improves the mechanical strength, weldability, and wear resistance of the copper and makes it a good candidate for filler materials in brazing and soldering and a wide range of structural applications [6]. Furthermore, the excellent resistance of tin-bronze to corrosion in salt water makes it an ideal choice for applications in marine components, such as propulsion and seawater handling systems [7]. The intended in-service condition of tin-bronze highly depends on its Sn content since the mechanical strength and thermal/electrical conductivity of bronzes vary significantly by increasing the Sn content [8]. For example, in electronic applications such as electrical connectors or high-precision springs, the Sn content should be kept below 5 wt.% to retain the electrical conductivity of the material [9]. When higher strength, excellent wear resistance, and good corrosion performance are required, Sn content should be increased to more than 10 wt.% to provide the required properties for applications in machinery industries, like marine components and bearings [10,11].

Chromium is another alloying element that can be added to copper to increase the mechanical strength of the material through the precipitation hardening mechanism due to the low solubility of chrome in copper [12–14]. Precipitation and dispersion of Cr-rich phases lead to the strengthening of Cu-Cr alloys without adversely affecting the electrical conductivity of the alloy ($>80\%$ IACS in the precipitation-hardened condition) [15]. By virtue of their high strength, corrosion resistance, and excellent electrical/thermal conductivity, Cu-Cr alloys are widely used in electrical contacts, arcing resistant electrodes, and other electrical apparatuses [16]. Moreover, Cu-Cr alloys are promising materials for use in heat exchangers, cooling components of semiconductor devices, and combustion chamber linings of rockets. It is notable that higher Cr content (20–50 wt.%) in Cu-Cr alloys further improves the hardness, voltage-withstand capability, arc ablation resistance, and also decreases the chopping current, which are all ideal for contact materials used in medium-voltage and high-current vacuum interrupters [15].

As opposed to Cr, which primarily improves the mechanical strength of copper through precipitation hardening mechanisms, the addition of Ni as an alloying element can positively contribute to the strength of the material through a solid-solution strengthening mechanism. Cu-Ni alloys typically contain between 2 and 30% Ni and are known for their excellent corrosion resistance and thermal stability, making them a suitable candidate for use in the oil and gas industry, power plants, and water treatment processes [17,18]. The addition of Si to Cu-Ni alloys results in the formation of 2 to 3% δ -Ni₂Si silicide precipitates and also improves the strength, which is ideal for the production of spring contacts and lead frames that were traditionally fabricated using beryllium-containing alloys with health risks [15]. Tin containing copper-nickel alloys, such as Cu-15Ni-8Sn (C79200), are also used for electrical connectors, bearings, springs, and deep-sea pipeline applications, where high corrosion resistance, strength, and thermal conductivity are demanded.

Another important copper-based alloy is the nickel-aluminum bronze (NAB) family, which has great benefits to the shipbuilding industry, especially in the production of fatigue-resistant propellers, resulting in their increased lifetime in harsh repeated water-collision conditions [19]. Generally, the Ni-Al Bronzes contain 6–13 wt.% Al as the primary alloying element, in addition to up to 7 wt.% Fe and 7 wt.% Ni, while most industrially used alloys contain 3–6 wt.% of each of Fe and Ni [20]. In some cases, around 1.5 wt.% Mn is added to NAB alloys, which acts as a deoxidizer and also improves the strength of the material [20]. As compared to traditional brass propellers, NAB propellers are lighter, up to 19 wt.%, which increases the carrying capacity of the ship without compromising the mechanical and corrosion properties [21]. In addition, NABs show extremely excellent

performance in marine environments due to their great resistance to cavitation, erosion, and corrosion, expanding their applications to underwater fasteners, valves, and seawater pump impellers [22]. While the addition of alloying elements would be the first solution that comes to mind for strengthening copper alloys, it should be noted that alloying elements, even in very small portions, have detrimental effects on the electrical and thermal conductivities of copper alloys [23].

The development of metal matrix composites (MMCs) is a great way to benefit from the strengthening properties of reinforcement particles without changing the nature of the matrix. For instance, an MMC can exhibit a great combination of ductility and toughness from its matrix and excellent hardness and strength from its reinforcements [24]. Fabricating copper-based MMCs has been found to be an efficient approach for increasing the alloy's strength without compromising its thermal/electrical properties [5,25].

1.2. Production Methods: Subtractive versus Additive

Nowadays, the technological advancements in many industries create a high demand for machines that contain more geometrically complex parts with reduced number of assemblies [1]. However, the typical manufacturing processes for copper alloys, such as powder metallurgy (PM) and other conventional methods, for example, forging, machining, extrusion, and casting, are not quite flexible and capable of processing complex structures. In this regard, various additive manufacturing (AM) technologies can contribute to the fabrication of copper-based products with a wide range of applications that require complex geometry along with high thermal and electrical conductivity, including heat sink structures, heat exchangers, vacuum electronics, and electric motors [26,27].

AM is also a great alternative for the production of tin-bronzes with high Sn content, where the formation of the brittle δ phase leads to decreased ductility and formability of the alloy, which makes it difficult to be fabricated by conventional subtractive methods [8,28]. In addition, the conventional casting of high-Sn bronze alloys leads to different process-induced defects, including micro-segregation, shrinkage, low densification, and cavities [29]. Therefore, Cu-Sn alloys have recently drawn the attention of the AM research community, aiming to develop comprehensive AM processes capable of fabricating defect-free parts from this family of alloys.

From a metallurgical point of view, additive manufacturing is also highly beneficial for the production of Cu-Cr alloys, where it is difficult to control the size of Cr phases and the formation of dendritic structure by traditional production methods, such as powder metallurgy, vacuum casting, arc melting, vacuum induction melting, and melt spinning. Due to the low solubility, miscibility gap, and large difference in the melting points of Cr and Cu, the traditional manufacturing methods face drawbacks such as segregation and non-uniform distribution of Cr-rich phases during the casting process [30]. Mechanical alloying could be an alternative for the manufacturing of Cu-Cr alloys with great hardness, while it has been reported that the parts produced by mechanical alloying are characterized by a very poor electrical conductivity [31,32]. Rapid solidification is the key to the manufacturing of Cu-Cr alloys with excellent electrical and mechanical properties. Using a manufacturing process with rapid solidification, such as AM, reduces the segregation tendency and leads to refining the Cr-rich phases. By subjecting the rapidly solidified parts to a post-aging treatment, the desired hardness can be achieved without adversely affecting the electrical conductivity.

AM processing is also a great alternative to traditional fabrication processes for the production of huge NAB-based ship propellers with relatively complex geometrical features, which are conventionally fabricated through the assembly of separate components or through expensive and time-consuming large-scale sand casting. However, casting of huge parts usually comes at the price of microstructural inhomogeneities in different locations of the part, depending on the thickness of each section and the corresponding cooling rate. Recently, wire arc additive manufacturing (WAAM) of NAB alloys has drawn much

attention due to its large-scale manufacturing capacity and capability to produce relatively uniform microstructure and mechanical properties in large components.

Another area where AM of copper-based materials has been investigated is the fabrication of multi-materials with controlled alterations of microstructural features, chemical composition, corrosion and mechanical properties, and even porosity level at different locations of the part. In multi-materials, the content of the integrated materials and the gradual properties variations should be designed according to the required in-service conditions of the end-product. For example, in heat exchangers, a combination of mechanical, physical, and thermal characteristics of dissimilar materials are required in a single component [33–37]. Cu-Ni-graded components are excellent candidates for heat exchanger systems as, copper provides great thermal conductivity while nickel improves the hardness and corrosion resistance of the material [38]. One of the unique applications of AM is the fabrication of functionally graded materials (FGM) with a wide range of applications in different engineering service conditions, where distinct properties are required at different positions of a specific component [39].

1.3. Challenges Associated with the AM of Copper Alloys

Despite all the advantages of additive manufacturing, there are some common technological and metallurgical setbacks associated with the nature of AM processes, which could potentially be applicable to any metallic feedstock materials subjected to AM processes. The challenges are mostly related to the layer-by-layer deposition strategy in AM processes being comparable to a multi-pass welding process. The repetitive melting and solidification makes the process susceptible to the formation of solidification defects, such as discontinuities, hot cracks, pores, and a lack of fusions. Some common defects in WAAM, laser AM, and arc welding processes are shown in Figure 1 [40].

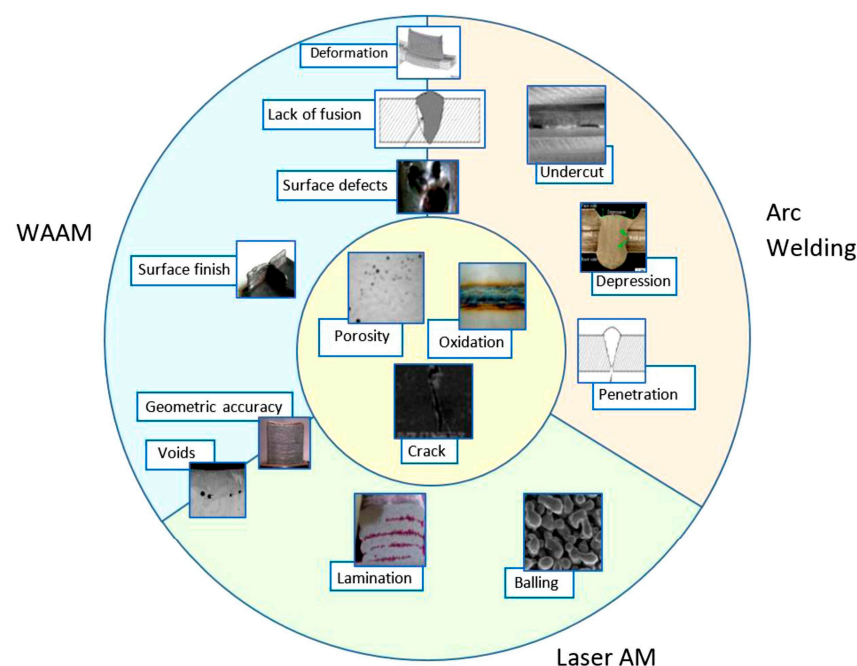


Figure 1. Different types of defects in WAAM, laser AM, and arc welding processes (Reprinted with permission from [40]).

The formation of discontinuities in a structure could potentially result in a premature fracture or a severe reduction in the formability, stiffness, and toughness of the component. Moreover, solidification-induced discontinuities, such as pores or cracks, are a strong contributor to the anisotropic performance of AM-processed products, possibly due to the presence of periodic interlayer zones in the building direction, which may contain vulnerable heat-affected zones (HAZs) and potentially a higher content of interpass defects along

the melt pool boundaries. These microstructural heterogeneities and anisotropic properties could be minimized or even annihilated through process parameter optimization or the implementation of proper post-printing heat treatment. The sequential heating and cooling cycles experienced by the material normally affect the microstructure and, consequently, the in-service performance of the fabricated parts [41]. For example, the heat generated during the deposition of each track may reheat the previous layers and adversely affect the microstructure driven by potential solid-state phase transformations [42]. Consequently, in most cases, additively manufactured parts are characterized by a heterogeneous and location-dependent microstructure [42]. These microstructural transitions could be observed from the melt pool centers to the melt pool boundaries and HAZs [43], or they may happen at a larger scale, resulting in different microstructural characteristics from the bottom to the middle or top sections of the component due to the heat buildup during the part construction [44].

The thermal history at each point of the part includes the maximum experienced temperature, the soaking time at the maximum temperature, the number of reheating cycles, and the subsequent cooling rate, which may vary at different points of the component, leading to a final product with a non-uniform microstructure [42]. In addition, the significant directional heat dissipation from the substrate usually leads to a directional solidification from the bottom to the top of the part, resulting in a textured structure along the building direction [45]. Moreover, additively manufactured parts are typically exposed to higher cooling rates as compared to other manufacturing processes, promoting their rapid solidification, and consequently the formation of non-equilibrium phases and inducing residual stress, which may lead to cracking during or after the deposition process [46]. From a metallurgical point of view, such microstructural inhomogeneities could potentially cause anisotropic mechanical properties [45,47,48].

Furthermore, it has been proven that there are certain underpinning complexities with laser-powder bed fusion (L-PBF) of copper-based materials due to their inherent characteristics, such as high laser beam reflectivity and thermal conductivity, as well as extreme affinity to oxygen [49]. The most important challenge in the processability of copper originates from its low laser absorption rate, which theoretically is 2–6% of the incident energy when subjected to Yb-fiber lasers with a wavelength of ~ 1064 nm [3]. Figure 2 compares the effect of laser wavelength on the absorption rate of various alloys, confirming the lower absorptivity of copper as compared to other metals.

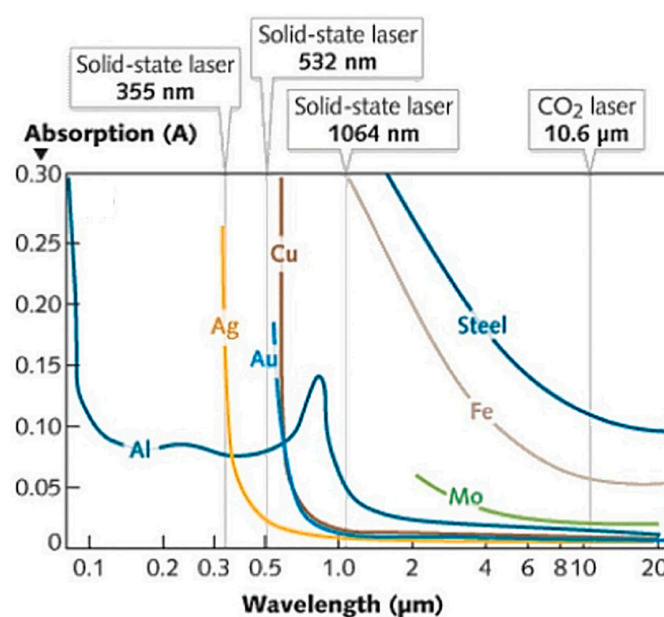


Figure 2. Effect of laser wavelength on the absorption rate of various metals (Reprinted with permission from [26]).

In addition, the exceptionally high thermal conductivity of copper, resulting in rapid solidification, in combination with the relatively low flowability of pure copper powders, could lead to the balling effect. Moreover, instant heat transfer from the fusion zone leads to a high local temperature gradient, which can potentially provoke cracking of the processed material [26]. The combination of high thermal conductivity and low laser absorption reduces the available laser energy input to melt the material, creating an unstable molten metal, and, by extension, makes the robust production of high density builds a challenging endeavor [26]. Another common issue during L-PBF of Cu alloys is the rapid formation of an oxide layer on the feedstock powder, which decomposes during processing and produces gas bubbles that can be entrapped in the end-product as porosities [50], lowering the electrical conductivity and the attained density in the L-PBF-fabricated copper as compared to the conventionally manufactured counterparts [51].

1.4. Solutions to Improve the AM Processability of Copper Alloys

To overcome the aforementioned challenges associated with the AM processability of copper and its alloys, different researchers have proposed various approaches, such as employing higher laser powers, using laser sources with lower wavelengths, preheating, adopting lower conductive materials for building platforms, and adding alloying elements, which are comprehensively discussed in the following subsections.

1.4.1. Employing High Power Lasers

In early studies on the fabrication feasibility of copper using L-PBF processing adopting low-power fiber lasers (<200 W), highly porous structures with a relatively low density were achieved (see Figure 3) [50,52,53]. As a solution to the issue of high thermal conductivity and laser reflectivity in copper, some studies investigated the adoption of higher power laser systems.

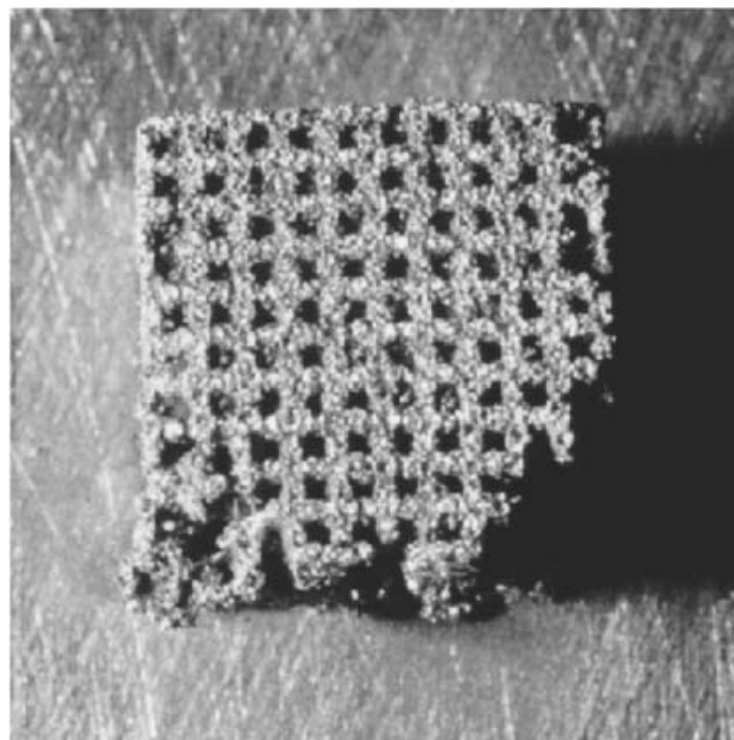


Figure 3. An example of unsuccessful L-PBF-processed copper using laser powers less than 200 W, resulting in highly porous parts (Reprinted with permission from [53]).

Silbernagel et al. [54] reported that even with a medium-power (200 W) laser source for the L-PBF fabrication of pure copper parts, the highest achievable density was only

85.8% in the optimized process parameters window. Constantin et al. [27] used a higher laser power (400 W fiber laser), which was found to be highly effective in improving the relative density to 95%, achieved in a very narrow processing parameter window. However, increasing the laser power output to 800 W combined with a low scan speed of 300 mm/s resulted in only a slight improvement in the relative density to 96.6% [49]. On the other hand, Colopi et al. [55] reported that the adoption of high laser powers ranging from 600 to 800 W, along with using a remelting strategy and employing a baseplate with a lower thermal conductivity (316L stainless steel), led to highly solid components with a 99% relative density. Nevertheless, it is crucial to note that employing a dissimilar alloy as the base plate may pose challenges attributable to potential metallurgical incompatibility. This could result in the development of undesirable intermetallic phases at the interface of the base plate and the printed component, ultimately giving rise to issues such as hot cracks and delamination. Additionally, while it is feasible to produce nearly dense copper parts using laser beams at their high-power range, it is important to note that increasing the laser power can cause certain technological issues. Jadhav et al. [56] reported that the synergetic effect of higher laser power outputs (600 W and 800 W) and the extremely high laser reflectivity of copper can damage the dielectric coating on the optical mirror of the laser source (Figure 4). To minimize the damage, they suggested applying output powers of less than 500 W along with the adaptation of a finer laser spot size [56].

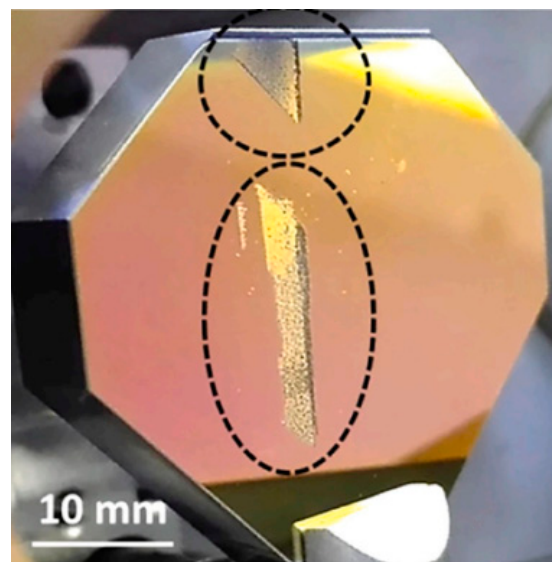


Figure 4. Breakage in the optical mirror of the laser source due to laser back reflection during the L-PBF processing of copper (Reprinted with permission from [56]).

1.4.2. Preheating the Powder Bed

Another strategy to decrease the required energy for melting copper-based feedstock powders, reduce the laser reflectivity, and ultimately prevent the potential breakage of the laser optics is to preheat the powder bed before the laser treatment [26,55]. Maly et al. [3] studied the influence of powder bed preheating using two temperatures of 200 and 400 °C and proved the positive contribution of preheating to the relative density of the end-products, with the maximum relative density of 92.2% and 99% for the preheating temperatures of 200 and 400 °C, respectively (see Figure 5). However, preheating may also come with some side effects, such as restricted powder recyclability due to the oxidation and agglomeration of the unused feedstock powders [3].

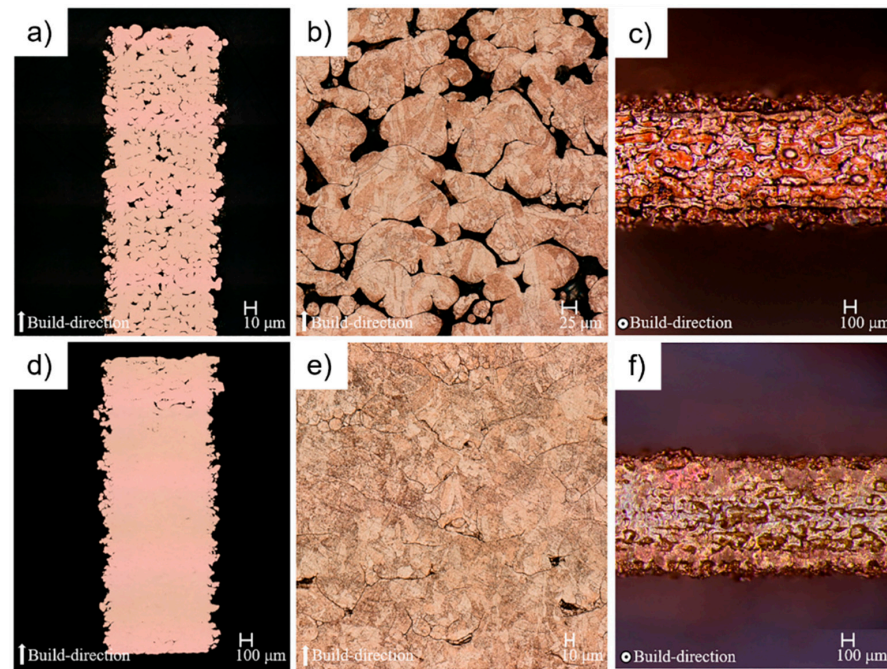


Figure 5. The effect of preheating temperature on the density of L-PBF-fabricated copper parts; (a–c) preheating temperature of 200 °C, and (d–f) preheating temperature of 400 °C (Reprinted with permission from [3]).

1.4.3. Employing Laser Sources with Lower Wavelengths

Another approach to facilitating the fabrication feasibility of copper using the L-PBF process is the adoption of low-wavelength laser sources. It is well-known that laser absorption rates increase at shorter wavelengths for most metallic materials (see Figure 2). As shown in Figure 6a, in the case of solid copper, decreasing the wavelength from 700 nm to the range of green and blue lasers at a wavelength of ~500 nm increases the laser absorptance from a negligible value of 3% up to 40%. Interestingly, in the case of copper powders, this value is reported to be even higher in the range of over 70% absorption [55,57]. As two extreme cases from previous studies with different laser wavelengths, Lykov et al. [50] employed a 200 W CO₂ laser with a wavelength of 10 μm and obtained a relative density of 88.1%, while Hori et al. [58] used a 200 W blue diode laser with a wavelength of 450 nm and achieved a relative density of 99.1%. Accordingly, in recent years, green and blue lasers with a much shorter wavelength (~500 nm) than that commonly produced with a conventional Yb-fiber unit (1070 nm) have been reported to improve the energy absorptivity of copper alloys during L-PBF processing.

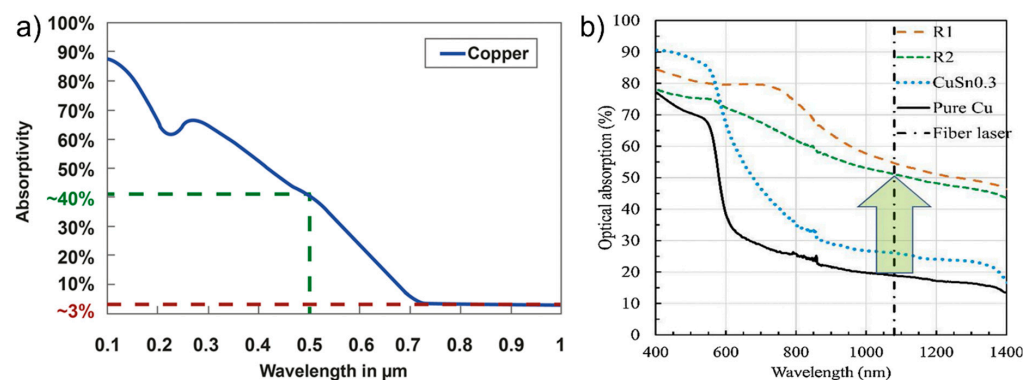


Figure 6. (a) Effect of laser wavelength on the laser absorptivity of pure copper [55], (b) comparison between the optical absorption of pure copper powders, tin-coated powders of R1 (1.36 wt.%) and R2 (0.28 wt.%), and pre-alloyed CuSn0.3 powders (Reprinted with permission from [59]).

1.4.4. Employing a Building Platform with Lower Thermal Conductivity

Employing a building platform with lower thermal conductivity could result in heat accumulation in the L-PBF-fabricated parts and consequently improve the relative density. Colopi et al. [55] studied the effect of the building platform thermal conductivity on the L-PBF processability of copper and reported that using a stainless steel substrate with lower thermal conductivity than the copper platform improved the density of the fabricated parts from 90.2% to 98.7%.

1.4.5. Addition of Alloying Elements

Another adopted strategy to enhance the L-PBF processability of copper is through the addition of alloying elements to the feedstock copper powders. Jadhav et al. [59] applied a very thin layer of tin on the outer surface of pure copper powders by an immersion plating method and showed that the addition of 0.28 wt.% of tin coating considerably improves the optical absorption of the feedstock powders. Figure 6b shows that the pre-alloying of copper powders leads to a slight improvement in optical absorption, from ~20% for pure Cu to ~26% for the CuSn0.3 alloy. However, tin-coated copper powders (R1 and R2) showed a drastic improvement in the powder optical absorption and approved the L-PBF possibility of dense and defect-free copper parts.

1.5. Aim and Structure of This Review

The present study aims to provide a comprehensive and systematic review of the existing literature on the AM of the industrially major copper alloys, including tin-bronzes, NiAl bronzes, Cu-Cr, and Cu-Ni alloys, in addition to additively manufactured Cu-based metal matrix composites using carbon allotropes and ceramics as reinforcements. This review covers different AM methods used for different copper alloys, technological and metallurgical barriers, the correlation between the manufacturing process and microstructural features, mechanical response, and corrosion properties of as-printed parts. The effects of post-printing heat treatments were also investigated, where applicable.

2. AM of Cu-Cr Alloys

According to the literature, three methods of electron beam melting (EBM), directed energy deposition (DED), and L-PBF have been used for the AM of copper-chrome alloys. In this section, the additively manufactured Cu-Cr parts with different AM techniques will be reviewed and discussed from different perspectives, including microstructure, mechanical properties, electrical conductivity, and corrosion behavior.

2.1. L-PBF of Cu-Cr Alloys

L-PBF has been the most common technique used for the AM of Cu-Cr alloys. However, as discussed in the introduction section, one of the main concerns in L-PBF manufacturing of copper alloys, especially in the case of low-chrome Cu-Cr alloys, is the feedstocks' low laser absorption rate. Accordingly, the AM of low-chrome alloys with mechanical and physical properties comparable to traditionally manufactured parts is challenging. For the family of Cu-Cr alloys, various pre/post processes have been used by different researchers, aiming to improve the mechanical and physical properties of additively manufactured parts. Table 1 summarizes different process parameters and pre/post-treatments used for the manufacturing of Cu-Cr alloys through the L-PBF technique.

Table 1. Summary and comparison of L-PBF process parameters and pre/post-treatments for copper-chrome alloys.

Alloy	Pretreatment	Process Parameters	Post-Treatment	Ref.
Cu-0.5Cr (wt.%)	None	- Laser power: 2000 W - Scanning velocity: 600 mm/s - Hatching spacing: 0.2 mm - Layer thickness: 0.05 mm	- Annealing at 480 °C for 4 h, followed by furnace cooling	[60]
Cu-0.5Cr (wt.%) with an average particle size of 35.5 µm	None	- Laser power: 2000 W - Scanning velocity: 300 mm/s - Hatching spacing: 0.14 mm - Layer thickness: 0.05 mm - Atmosphere: argon - Oxygen concentration: 200 ppm	- Heat treatment at 920, 940, 960, 980, 1000, and 1020 °C for 1 h, followed by water cooling - Heat treatment at 1020 °C for 1 h, followed by water cooling, and then aging at 480 °C for 4 h - Direct aging at 480 °C for 4 h	[61]
Cu-1.3Cr Cu-2.5Cr (wt.%) with an average particle size of 24 µm	None	- Laser power: 350 W - Layer thickness: 0.03 mm - Atmosphere: argon - Oxygen concentration: 0.1%	- Annealing at 400, 450, 500, 600, and 700 °C for 1 h under a nitrogen atmosphere, followed by furnace cooling	[62]
CuCr0.3 with an average particle size of 33.7 µm	- Mechanically mixing pre-alloyed CuCr0.3 powder with 0.05 wt.% carbon powder for 12 h in a sealed bottle in the presence of argon	- Laser power: 300–500 W - Laser scan speed: 200–1300 mm/s - Hatch spacing: 0.09 mm - Layer thickness: 0.03 mm - Atmosphere: argon - Oxygen concentration: below 50 ppm	- Solution annealing at 1015 °C for 1 h, followed by water quenching, and then age hardening at 400 °C for 0.25–12 h, followed by water quenching - Direct age hardening at 500 °C, followed by water quenching	[63]
Cu-Cr0.89 with an average particle size of 39.9 µm	- Heat treatment of Cu-Cr powders in a tube furnace under a flowing nitrogen (99.99%) atmosphere at 400–900 °C for 1 h, followed by furnace cooling	- Laser power: 200–500 W - Laser scan speed: 200–1400 mm/s - Hatch spacing: 0.09 mm, 0.105 mm - Layer thickness: 0.03 mm - Atmosphere: argon - Oxygen concentration: below 50 ppm	- Solution annealing at 1050 °C for 1 h, followed by water quenching, and then age hardening at 450 °C for 7 h, followed by water quenching	[64]
Cu-Cr1 with an average particle size of 38.5 µm	- Mechanically mixing Cu-Cr1 powders with 0.1 wt.% of carbon nano-powder for 12 h, followed by heat treatment at 750 °C for 2.5 h in an argon atmosphere	- Laser power: 500 W - Laser scan speed: 700 mm/s - Hatch spacing: 0.09 mm - Layer thickness: 0.03 mm - Atmosphere: argon - Oxygen concentration: below 50 ppm	- Solution annealing at 1015 °C for 1.5 h, followed by water quenching, and then age hardening at 450 °C for 0.25–23 h, followed by water quenching - Direct age hardening at 450 °C for 0.5–11 h, followed by water quenching	[65]
Cu-0.8Cr with an average particle size of 30 µm	- Mixture of 0.2 wt.% TiC nano-particles with Cu-0.8Cr powder by ball milling for 20 min under 300 rpm	- Laser power: 320 W - Laser scan speed: 500, 600, 700, 800, and 1000 mm/s - Hatch spacing: 0.7 mm - Layer thickness: 0.03 mm	- Annealing at 480 °C for 4 h, followed by furnace cooling	[66]
Cu-20Cr Cu-25Cr with an average particle size of 40–50 µm	- Preheating of the powder bed to 200 °C	- Laser power: 375 W - Laser scan speed: 400 mm/s - Hatch spacing: 0.12 mm - Layer thickness: 0.03 mm - Atmosphere: argon - Oxygen concentration: below 50 ppm	- Aging at 400, 500, and 600 °C for 1 h, 2 h, and 3 h, followed by furnace cooling	[67]

2.1.1. Microstructure of L-PBF-Fabricated Cu-Cr Alloys

The main purpose of adding Cr to Cu is to facilitate the formation of Cr-rich precipitates, improve the strength and wear resistance of the material, and tailor its properties for more structural applications, such as electrical contacts in the power industry [68,69]. It is well understood that the size and distribution of chrome precipitates play a dominant role in the mechanical and physical properties of Cu-Cr alloys, which are mostly controlled by

the Cr content of the alloy [70]. Accordingly, the Cu-Cr alloys can be divided into two main categories: low Cr (<2 wt.%) and high Cr (25–30 wt.%).

A typical microstructure of a L-PBF-fabricated low-Cr copper alloy (Cu-0.5Cr wt.%) is shown in Figure 7 [60]. The optical and scanning electron microscopy (SEM) images reveal the formation of large columnar grains along the building direction consisting of very fine (smaller than 1 μm) cellular sub-structures (see Figure 7a–d), along with round-shaped (Cr phase) and diamond-shaped (Cr_2O_3) particles with an average size of 30 nm in addition to dislocations (see Figure 7e–h) [60].

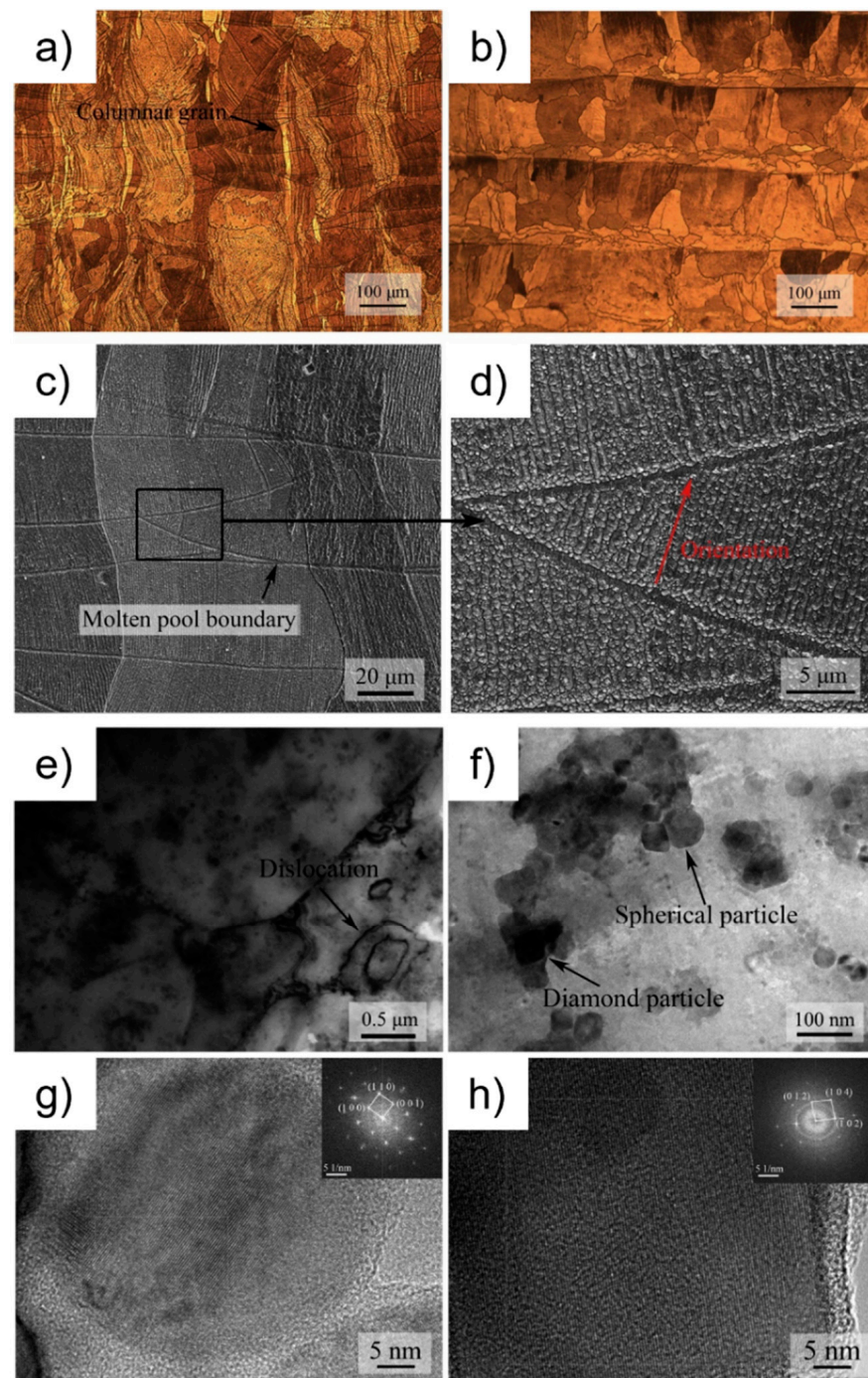


Figure 7. (a,b) Optical micrographs, (c,d) SEM images, (e,f) bright-field TEM micrographs, and (g,h) HR-TEM images taken from the L-PBF-fabricated Cu-0.5Cr alloy (Reprinted with permission from [60]).

It is worth mentioning that obtaining dense parts of Cu-Cr alloys with low Cr content is challenging due to the low optical absorption of copper. In order to improve the optical absorption of Cu-Cr powders, researchers have modified the feedstock powders through nitriding [64], carburizing [65], and mixing the powders with carbon [63] or TiC nanoparticles [66]. Jadhav et al. [64] modified the surface of the virgin CuCr1 powders by the nitriding process and observed a considerable improvement in the stability of the melt tracks and a lower porosity level in both top- and side-view images as a result of the nitriding process (see Figure 8).

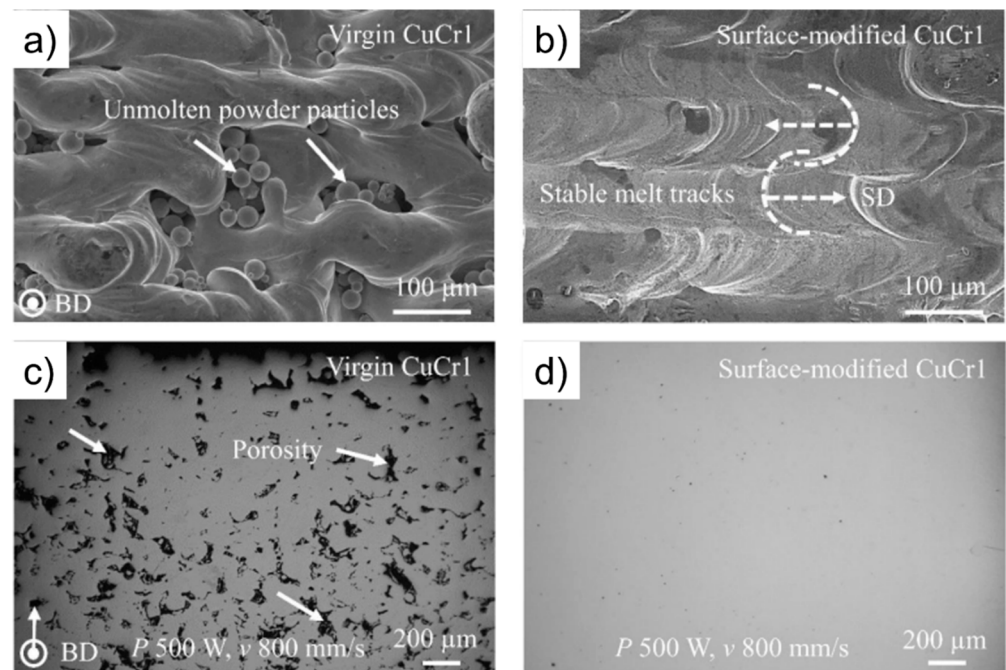


Figure 8. The top view of L-PBF-fabricated CuCr1 parts using (a) virgin and (b) nitrided powders. The corresponding side views of samples fabricated with (c) virgin and (d) nitrided powders (Reprinted with permission from [64]).

Jadhav et al. [65] also used carbon-mixed CuCr1 and carburized CuCr1 powders to produce Cu-Cr alloy using the L-PBF technique. Comparing the cross-section of the L-PBF-fabricated samples revealed the successful manufacturing of dense parts with carburized powders, while some porosities were detected in the sample produced by carbon-mixed powders (see Figure 9) [65].

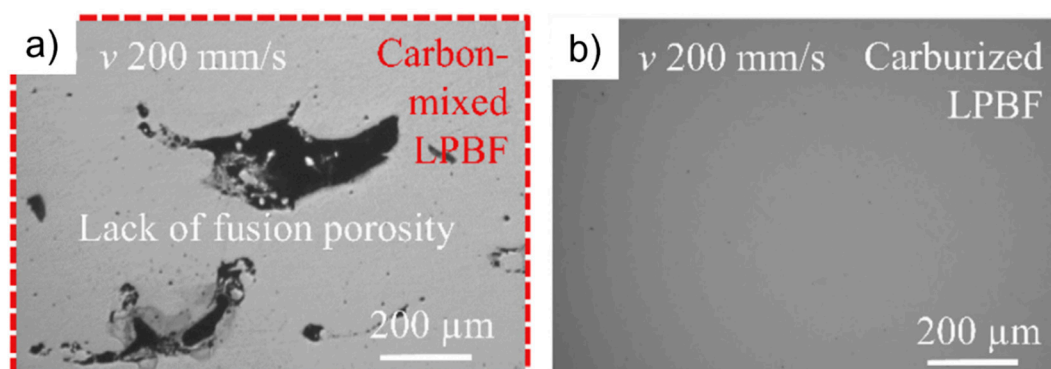


Figure 9. Optical microscopy images showing the porosity level in L-PBF-fabricated CuCr1 samples using (a) carbon-mixed and (b) carburized powders (Reprinted with permission from [65]).

The mixing of Cu-0.8Cr powder with 0.2 wt.% TiC has also been reported to be effective in manufacturing dense parts with the L-PBF method (see Figure 10), which was analogously attributed to the optical absorption improvement of virgin powders from 30.5% to 59.9% [66].

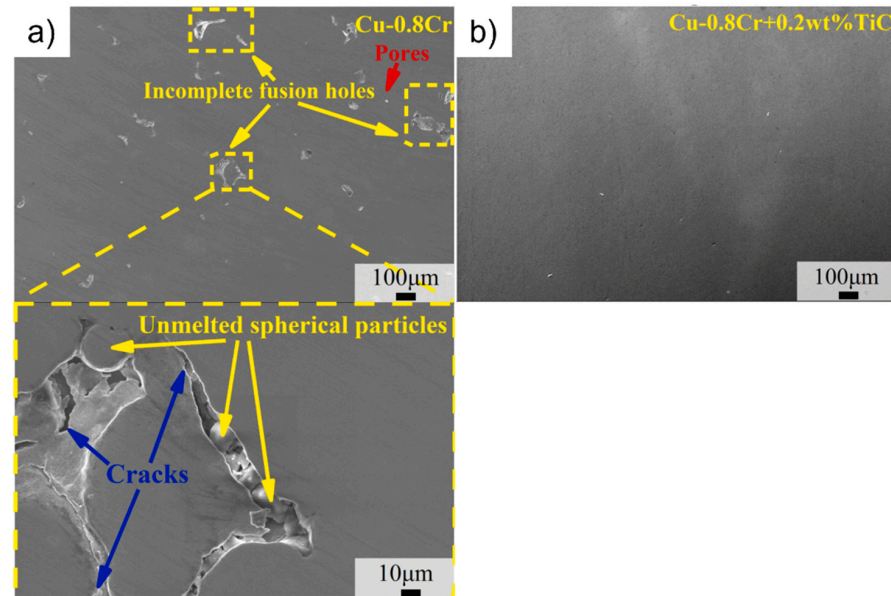


Figure 10. SEM images showing the improvement in the density level of L-PBF-fabricated Cu-0.8Cr alloy manufactured by (a) virgin Cu-0.8Cr powders and (b) Cu-0.8Cr + 0.2 wt.% TiC powders (Reprinted with permission from [66]).

SEM micrographs of manufactured samples from various modified Cu-Cr powders [63–65] are shown in Figure 11. Similar to the microstructure of additively manufactured samples with virgin Cu-Cr powders, Cr-rich precipitates were consistently reported to form in the microstructure of samples produced by carburized and carbon-mixed powders. However, no chrome precipitates were observed in the as-built microstructure of the nitrided Cu-Cr powders due to the very high cooling rate during the L-PBF process [61].

As the properties of Cu-Cr alloys are highly dependent on the size and distribution of Cr-rich precipitates, balancing the properties of L-PBF Cu-Cr alloys could be conducted through different post-printing heat treatments, such as (i) solutionizing, (ii) solutionizing + aging, and (iii) direct aging at different times and temperatures, resulting in various microstructures. The microstructure of the solution-treated L-PBF Cu-Cr0.5 samples at different temperatures is depicted in Figure 12, confirming that increasing the solution treatment temperature decreases the density of the precipitates (white spots) in the microstructure [61]. In addition to reducing the size and amount of the precipitates, solutionizing at higher temperatures can also decrease the dislocation density in the heat-treated samples (see Figure 13) [61].

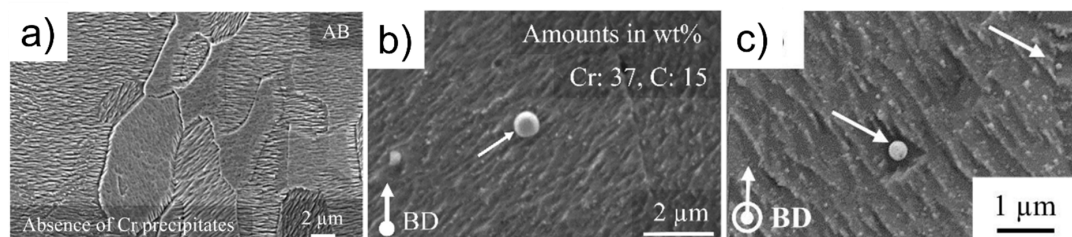


Figure 11. Microstructure of the L-PBF-fabricated Cu-Cr alloys using (a) nitrided CuCr powders (Reprinted with permission from [64]), (b) carburized CuCr powders (Reprinted with permission from [65]), and (c) carbon-mixed CuCr powders (Reprinted with permission from [63]).

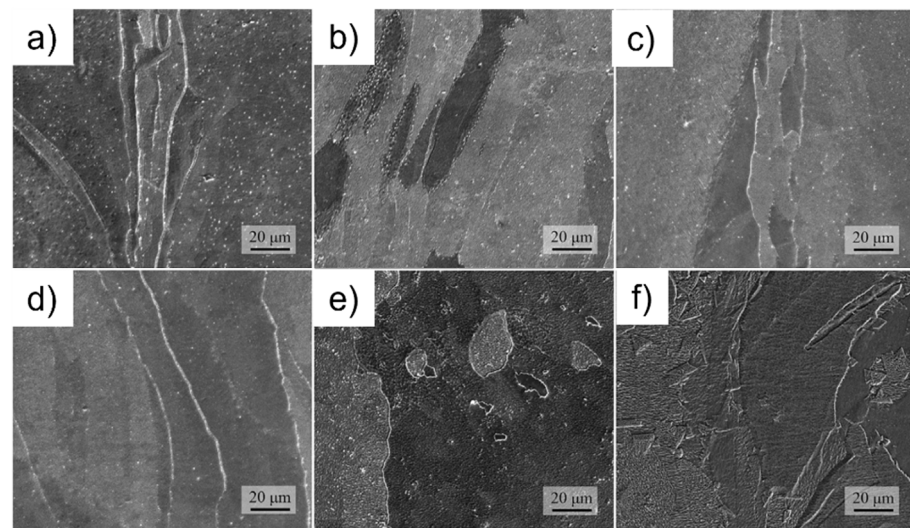


Figure 12. SEM images of the L-PBF Cu-Cr0.5 samples solution-treated at (a) 920 °C, (b) 940 °C, (c) 960 °C, (d) 980 °C, (e) 1000 °C, and (f) 1020 °C (Reprinted with permission from [61]).

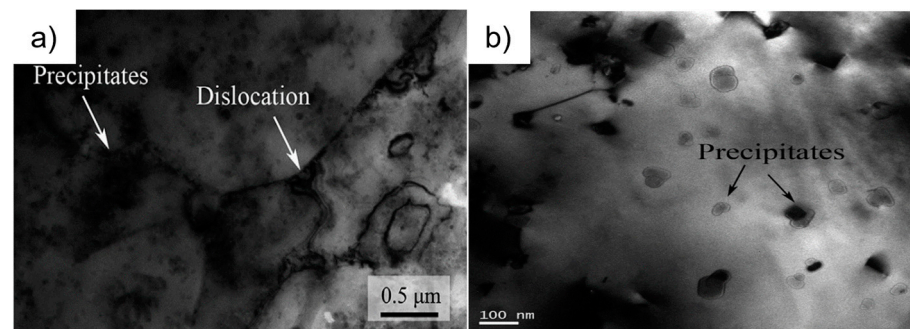


Figure 13. TEM images taken from the L-PBF CuCr0.5 sample (a) before and (b) after solution treatment at 1020 °C, confirming the reduction in dislocation density during the heat treatment (Reprinted with permission from [61]).

As opposed to the solution treatment that aims to eliminate the precipitates from the structure, the aging treatment promotes the precipitation of Cr-rich phases in Cu-Cr alloys. The microstructure of the L-PBF-fabricated Cu-0.5Cr alloy after direct aging and solution + aging is depicted in Figure 14 [61].

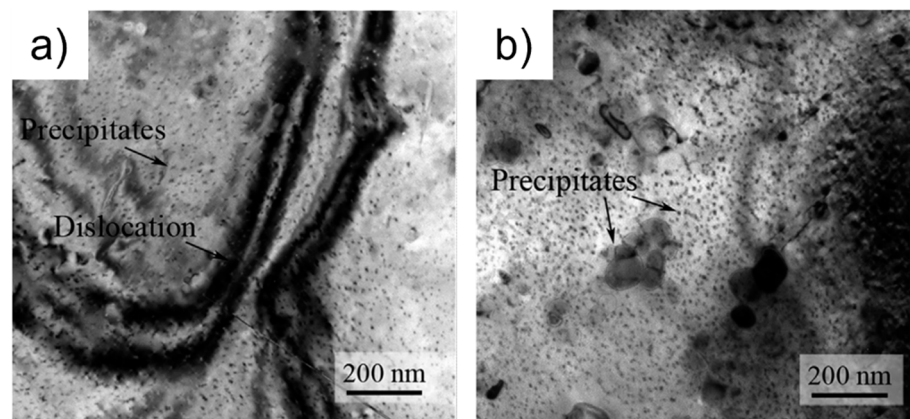


Figure 14. Microstructure of the L-PBF-fabricated Cu-0.5Cr alloy after (a) direct aging at 480 °C and (b) solutioning at 1020 °C + aging at 480 °C (Reprinted with permission from [61]).

Based on the sole study in the literature on the L-PBF of high-Cr Cu-Cr alloys, the dominant microstructure of low-Cr and high-Cr alloys is quite alike, with variations in the size and distribution of Cr precipitates. Figure 15 depicts the typical microstructure of a high-Cr alloy (CuCr20) manufactured by the L-PBF process. As observed, the microstructure features Cr-rich microconstituents with a size of around 10 μm (A), a Cu-rich area surrounding the Cr-rich microconstituents (B), a Cu-rich phase dispersed in the Cr-rich phase (C), fine round-shape Cr-rich phases with an approximate size of 50–800 nm distributed in the Cu matrix, and chromium oxides (red circles in (d)) [67].

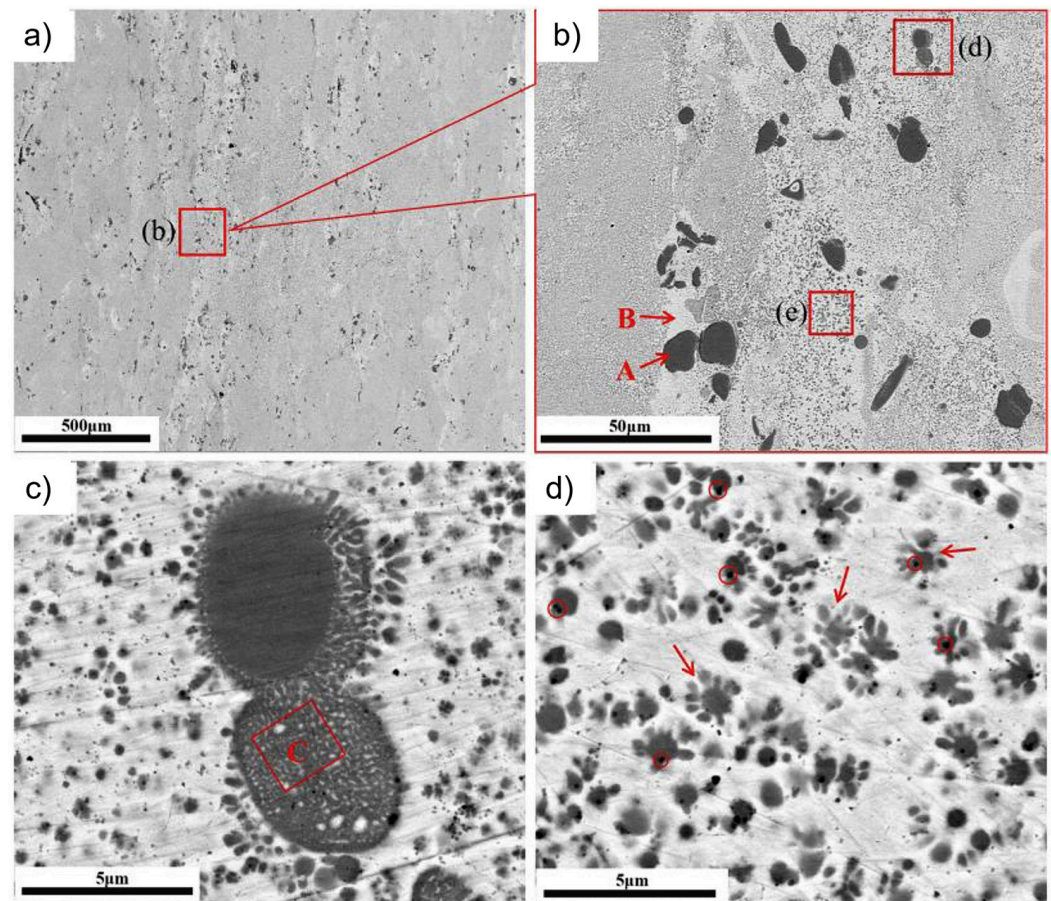


Figure 15. (a) Low-magnification image showing the distribution of Cr in the Cu matrix of a L-PBF processed CuCr20 alloy, and (b) higher magnification of the box shown in image (a). (c,d) Higher magnification images showing the distribution of Cr in the Cu matrix (Reprinted with permission from [67]).

2.1.2. Electrical Conductivity of L-PBF-fabricated Cu-Cr Alloys

The electrical conductivity of L-PBF Cu-Cr alloys is highly impacted by the size and distribution of Cr-rich precipitates, as well as the Cu lattice distortion. The extremely fast cooling rate of the melt pools during the L-PBF process leads to the distribution of Cr atoms in the Cu matrix and distortion of the copper lattice, which results in increasing the electron scattering and accordingly decreasing the electrical conductivity of the as-fabricated L-PBF Cu-Cr samples [71–73]. Therefore, exposing the additively manufactured samples to different heat treatments affects the electrical conductivity of the as-printed parts (see Figure 16a,b).

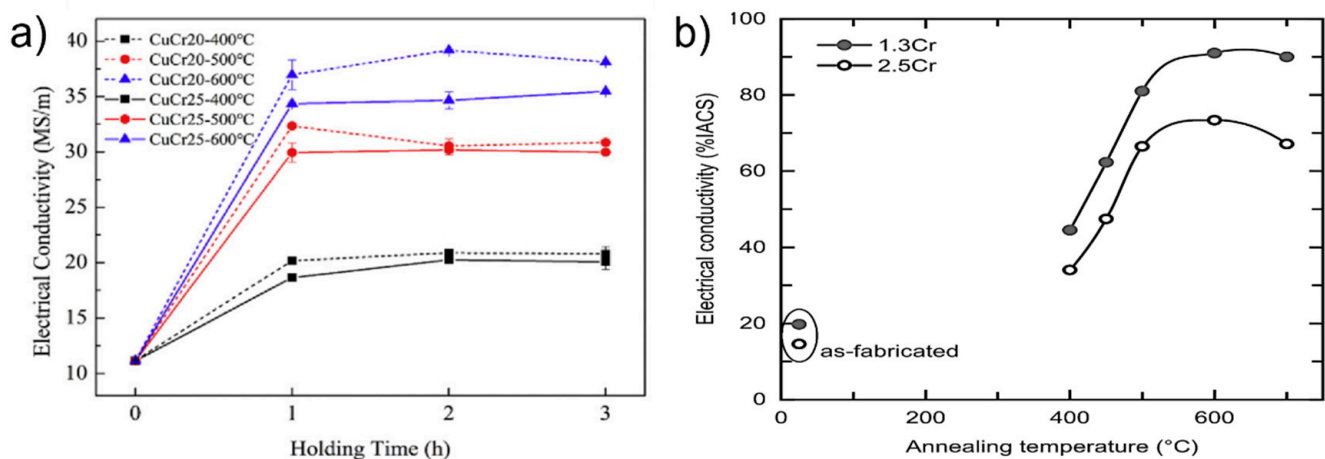


Figure 16. (a) Effect of heat treatment temperature and time on the electrical conductivity of L-PBF-fabricated CuCr20 and CuCr25 alloys (Reprinted with permission from [67]) and (b) effect of annealing temperature on the electrical conductivity of L-PBF-fabricated Cu-1.3Cr and Cu-2.5Cr alloys (Reprinted with permission from [62]).

Accordingly, if the heat treatment process is conducted below a threshold temperature, the supersaturated Cr atoms form Cr-rich precipitates, reducing the distortion in the Cu matrix lattice and leading to improved electrical conductivity. On the other hand, performing a heat treatment beyond the threshold temperature leads a decrease in the electrical conductivity due to the dissolution of Cr-rich particles and the further distribution of Cr atoms in the Cu matrix. As shown in Figure 16b, annealing heat treatment on the L-PBF-fabricated 1.3Cr and 2.5Cr alloys increased the electrical conductivity of the material up to 600 °C, followed by a drop at higher annealing temperatures due to the dissolution of Cr-rich phases in the Cu matrix [62].

It is worth noting that the precipitation of Cr-rich phases is faster at higher aging temperatures due to the higher diffusion rate of solute atoms with the aid of vacancies [74]. A six-time higher diffusivity of solute atoms has been reported by a 50 °C increase in the aging temperature [75].

2.1.3. Hardness of L-PBF-Fabricated Cu-Cr Alloys

Similar to the electrical conductivity, the additively manufactured samples provide a hardness value lower than that of the traditionally produced parts, while aging treatment raises the hardness value to a level higher than both as-printed and cast samples. The improvement in the hardness value of the L-PBF-fabricated Cu-Cr samples after heat treatment (Figure 17a) can be attributed to the Cr precipitation from the supersaturated Cu matrix [67]. Additionally, the size and distribution of Cr-rich precipitates in the copper matrix are contributing factors to the hardness value of the heat-treated samples. The highest hardness value can be achieved with fine and evenly distributed precipitates in the matrix. Exposing the samples to higher aging temperatures increases the size and inter-particle spacing of precipitates, leading to a decrease in the hardness value (see Figure 17b) [62]. Moreover, as can be seen in Figure 17a,b, there is a direct relationship between the hardness values and the content of Cr in the feedstock powder.

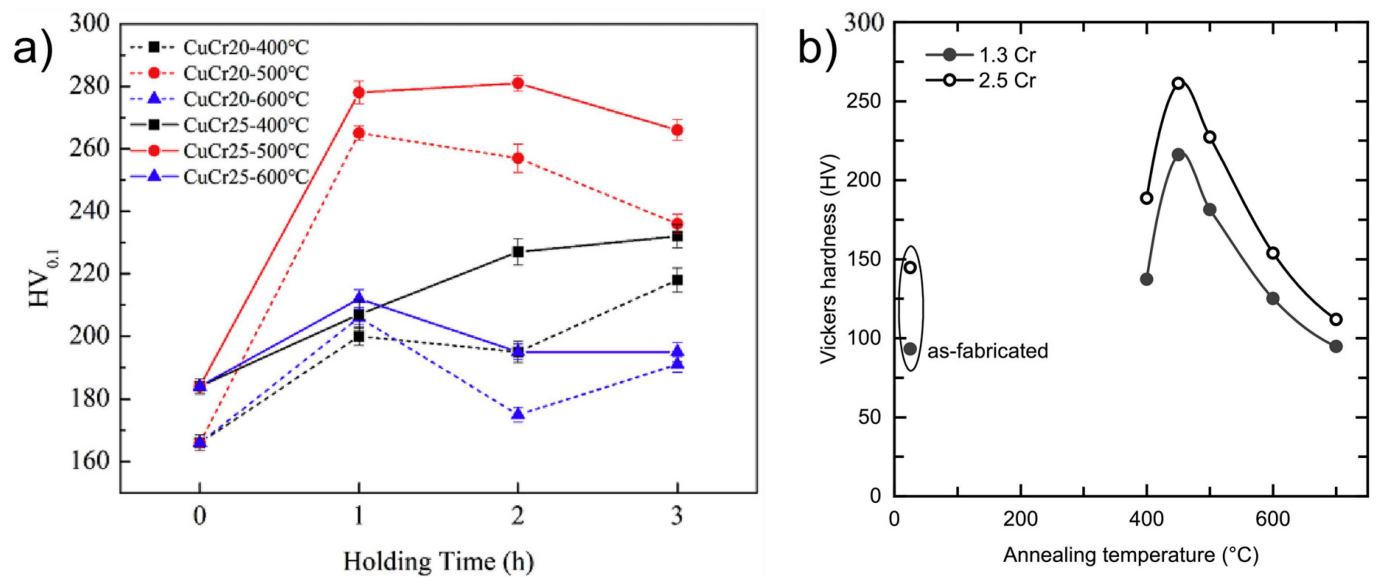


Figure 17. (a) Effect of post-printing aging time and temperature on the Vickers hardness of L-PBF-fabricated CuCr20 and CuCr25 alloys (Reprinted with permission from [67]) and (b) effect of annealing temperature on the hardness of L-PBF-fabricated 1.3Cr and 2.5Cr alloys (Reprinted with permission from [62]).

2.1.4. Strength and Ductility of L-PBF-Fabricated Cu-Cr Alloys

Generally, L-PBF-fabricated Cu-Cr alloys exhibit lower tensile and yield strengths but higher elongation values compared to their cast counterparts [60,61]. Solution heat treatment increases the elongation of the additively manufactured samples, while its effect on the strength of the samples is minimal (Figure 18a–c) [60,61,67,76].

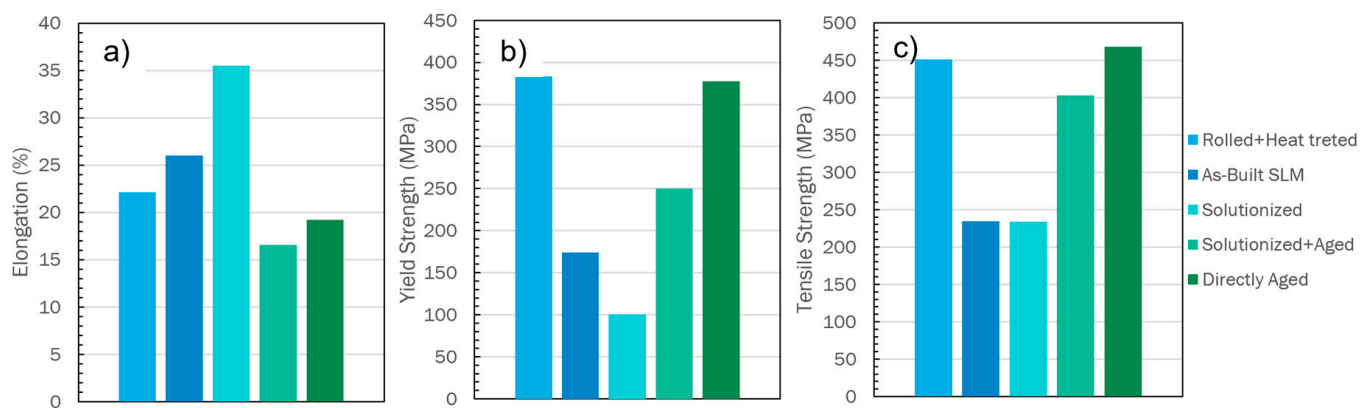


Figure 18. (a) Elongation, (b) yield strength, and (c) tensile strength of traditionally and L-PBF-fabricated Cu-0.5Cr alloy (the applied heat treatment cycles for the L-PBF sample: direct aging at 480 °C, solutionizing at 1020 °C, and solutionizing at 1020 °C + aging at 480 °C) [60,61].

Uchida et al. [62] studied the effect of aging temperature and Cr content on the tensile strength of L-PBF-fabricated Cu-Cr alloys. As shown in Figure 19a,b, the tensile strength of the samples reaches its peak values at the aging temperature of 450 °C [62].

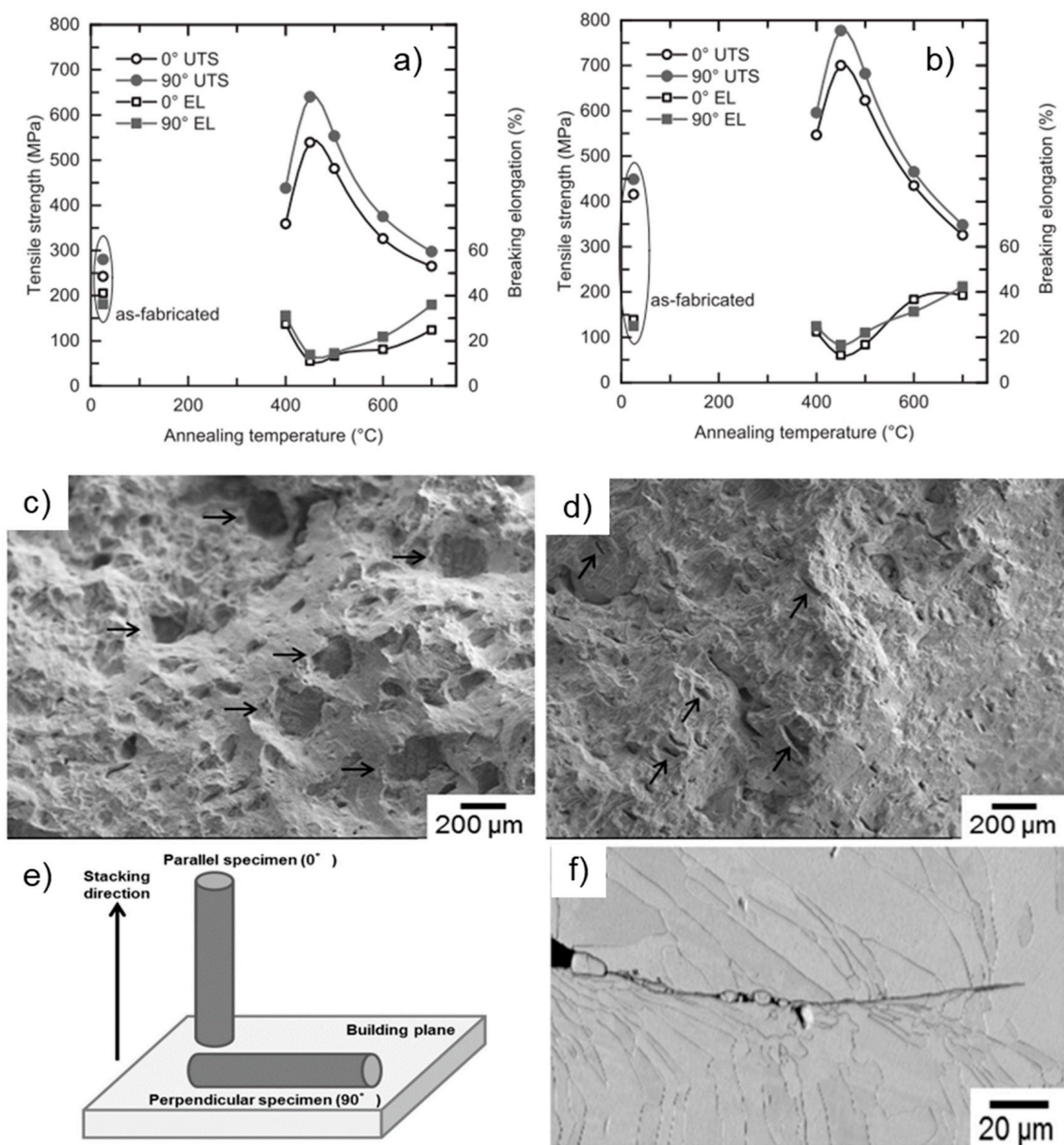


Figure 19. Effect of annealing temperature on the tensile strength and breaking elongation of L-PBF (a) Cu-1.3Cr and (b) Cu-2.5Cr alloys fabricated in parallel (0°) and perpendicular (90°) to the stacking directions, and SEM images taken from the fractured surfaces of the L-PBF Cu-1.3Cr alloy fabricated in (c) parallel (0°) and (d) perpendicular (90°) directions schematically shown in (e), and (f) a vertical cross-section image showing the crack propagation in the as-printed Cu-1.3Cr L-PBF sample (Reprinted with permission from [62]).

An initial increase in aging temperature leads to the formation of smaller, closely spaced Cr-rich precipitates, resulting in maximum strength values [77,78]. At elevated annealing temperatures, the formation of coarser precipitates with wider inter-spacing reduces their ability to block dislocations, thus diminishing their strengthening impact.

As additively manufactured parts are usually characterized by inter-layer defects, it is important to investigate their potential anisotropy in mechanical properties. In the case of L-PBF-fabricated Cu-Cr alloys, the tensile strength anisotropy has been linked to the presence of disk-shaped defects between the deposited layers [62]. The reaction between Cr powders and residual oxygen in the fabrication atmosphere results in the formation of chromium oxide and subsequent defect zones (see Figure 19c–f) [62].

Although the main purpose of modifying the Cu-Cr feedstock powders by nitriding [64], carburizing [65], and mixing with carbon nano-particles [63] is to increase the optical adsorption and produce denser parts, the modifying process also leads to improvements in the mechanical properties of the as-printed products. The elongation, yield strength, and tensile strength of L-PBF-fabricated Cu-Cr alloys using virgin and modified powders before and after different heat treatments taken from different studies are summarized in Figure 20.

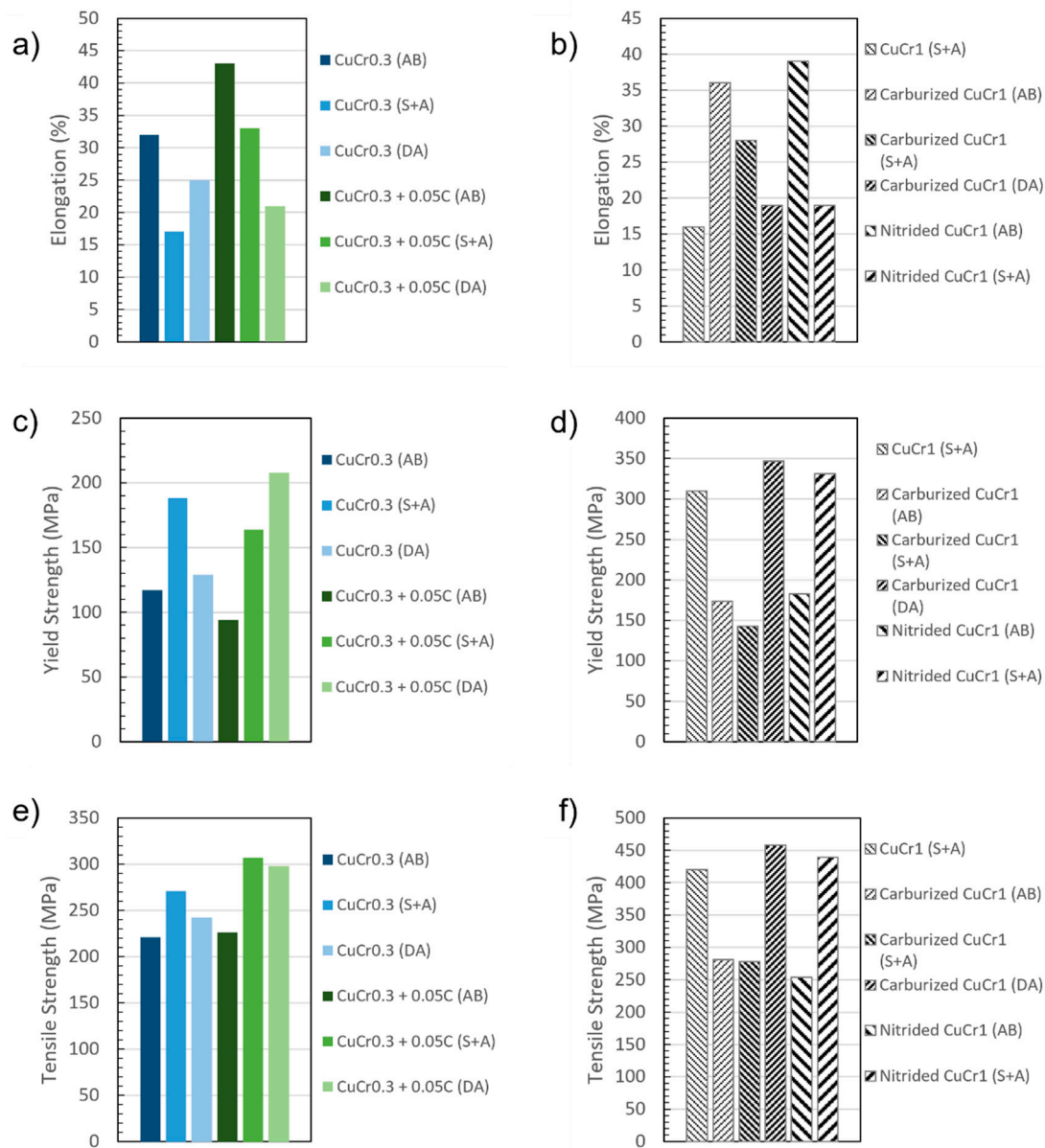


Figure 20. (a,b) Elongation, (c,d) yield strength, and (e,f) tensile strength of L-PBF Cu-Cr alloys manufactured by CuCr0.3 [63], CuCr0.3 mixed with 0.05 wt.% carbon nano-particle [63], carburized CuCr1 [65], and nitrided CuCr1 [64] before and after different heat treatments. (Note: AB, S+A, and DA stand for as-built, solutionized+aged, and directly aged, respectively.).

Shen et al. [66] reported that modification of Cu-0.8Cr powder with TiC nano-particles improves the mechanical properties of L-PBF samples due to improving the density of manufactured parts (see Figure 21a,b). As shown in Figure 21b, the tensile strength of the fabricated nano-TiC-modified Cu-0.8Cr alloy under the same process parameters is 225.9 MPa, which is higher than the tensile strength of samples with virgin Cu-0.8Cr

powder (198.5 MPa). The evaluation of the fracture morphology of tensile specimens fabricated from modified powders (Figure 21c–f) revealed a uniform distribution of fine plastic dimples on the fracture surface. In contrast, the fracture surface of the unmodified sample exhibited unmelted powders and a coarser microstructure [66]. The presence of unmelted powders in the microstructure of virgin Cu-Cr alloys points to poor laser absorptivity and a lower density of the manufactured samples.

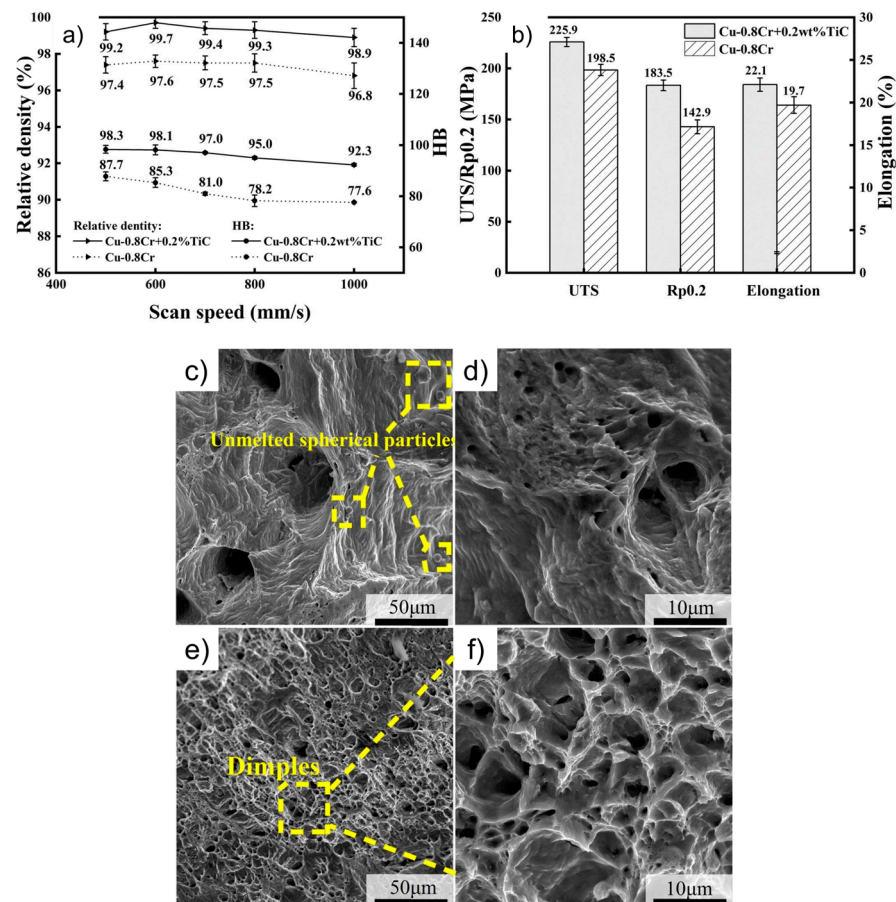


Figure 21. (a) Relative density of Cu-0.8Cr + 0.2 wt.% TiC and virgin Cu-0.8Cr samples manufactured by L-PBF process with laser power of 320 W and various scan speeds of 500 mm/s, 600 mm/s, 700 mm/s, 800 mm/s, and 1000 mm/s; (b) UTS, Rp0.2, and elongation of L-PBF samples fabricated by laser power of 320 W and scan speed of 600 mm/s. Fracture morphologies of (c,d) Cu-0.8Cr and (e,f) Cu-0.8Cr + 0.2 wt.% TiC tensile samples (Reprinted with permission from [66]).

2.1.5. Corrosion Behavior of L-PBF-Fabricated Cu-Cr Alloys

One of the key contributing factors to the corrosion resistance of Cu-Cr alloys is the homogeneity of the microstructure. The presence of phases with distinct electrochemical potentials can increase the risk of galvanic corrosion if they are electrically connected in a conductive environment [79]. For the Cu-Cr alloy, the Cu matrix acts as an anode, and the precipitates act as cathodes [61]. Dissolving the Cr-rich phases into the Cu matrix reduces the corrosion driving force, leading to higher corrosion resistance in solution-treated samples that are free from Cr-rich precipitate [61]. After aging treatment, the formation of a high volume fraction of Cr-rich precipitates in the Cu matrix results in a lower corrosion resistance due to the activation of the micro-galvanic coupling effect [61].

According to the results of the potentiodynamic polarization (PDP) measurements conducted by Zhang et al. [61] on the as-printed and heat-treated L-PBF Cu-0.5Cr alloy, the solution-treated sample provides the best corrosion resistance, followed by the as-

built sample, the solution-treated+aged sample, and then the directly aged sample (see Figure 22).

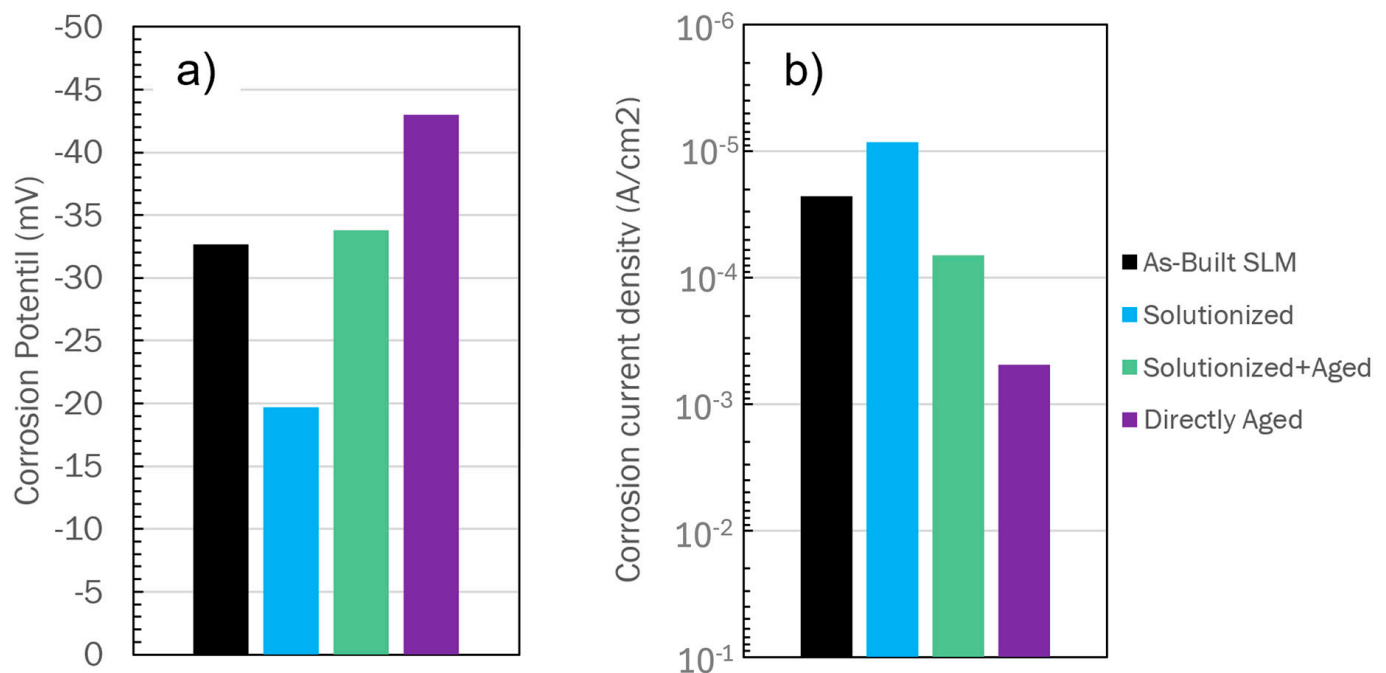


Figure 22. (a) Corrosion potential (E_{corr}) and (b) corrosion current density (i_{corr}) of the L-PBF Cu-0.5Cr samples before and after different heat treatments in 3.5 wt.% NaCl solution (applied heat treatments: direct aging at 480 °C, solutionizing at 1020 °C, and solutionizing at 1020 °C + aging at 480 °C) [61].

2.2. DED of Cu-Cr Alloys

The use of the directed energy deposition (DED) process for the fabrication of low-chromium Cu-Cr alloys is limited, with only a few studies reported in the literature. On the other hand, there has been some research on the Laser-DED (L-DED) of high-chromium alloys (CuCr30), but more investigation is needed to fully understand its capabilities and limitations in the fabrication of these alloys.

2.2.1. Microstructure of L-DED-Fabricated Cu-Cr Alloys

Rongzhou et al. [80] applied the L-DED process, followed by hot extrusion, for the manufacturing of CuCr30 alloy using a mixture of copper powder and chromium powder, with 99.95% purity and a particle size of 40–50 μm . Figure 23a,b depict the microstructure of the as-built and extruded CuCr30 samples. The dominant microstructure is similar to the L-PBF-fabricated counterparts, including Cr precipitates distributed in a Cu matrix. The Cr-rich particles were formed in the size range of 1 to 10 μm , and noticeable porosities were also detected in the microstructure of the as-built samples. The extrusion process, however, was found to effectively reduce both the size of the chromium phase to less than 4 μm and the level of porosities. Moreover, the extrusion-induced deformation caused the crushing and alignment of fibrous Cr phases along the extrusion direction [80]. The EBSD analysis (Figure 23c,d) revealed that the extruded sample exhibits a finer grain structure with a higher density of grain boundaries, particularly in the vicinity of the Cr-rich precipitates [80]. The TEM analysis of the extruded samples also indicated the formation of twins in the copper matrix, which contributes to the material's improved mechanical strength (Figure 23e,f) [80].

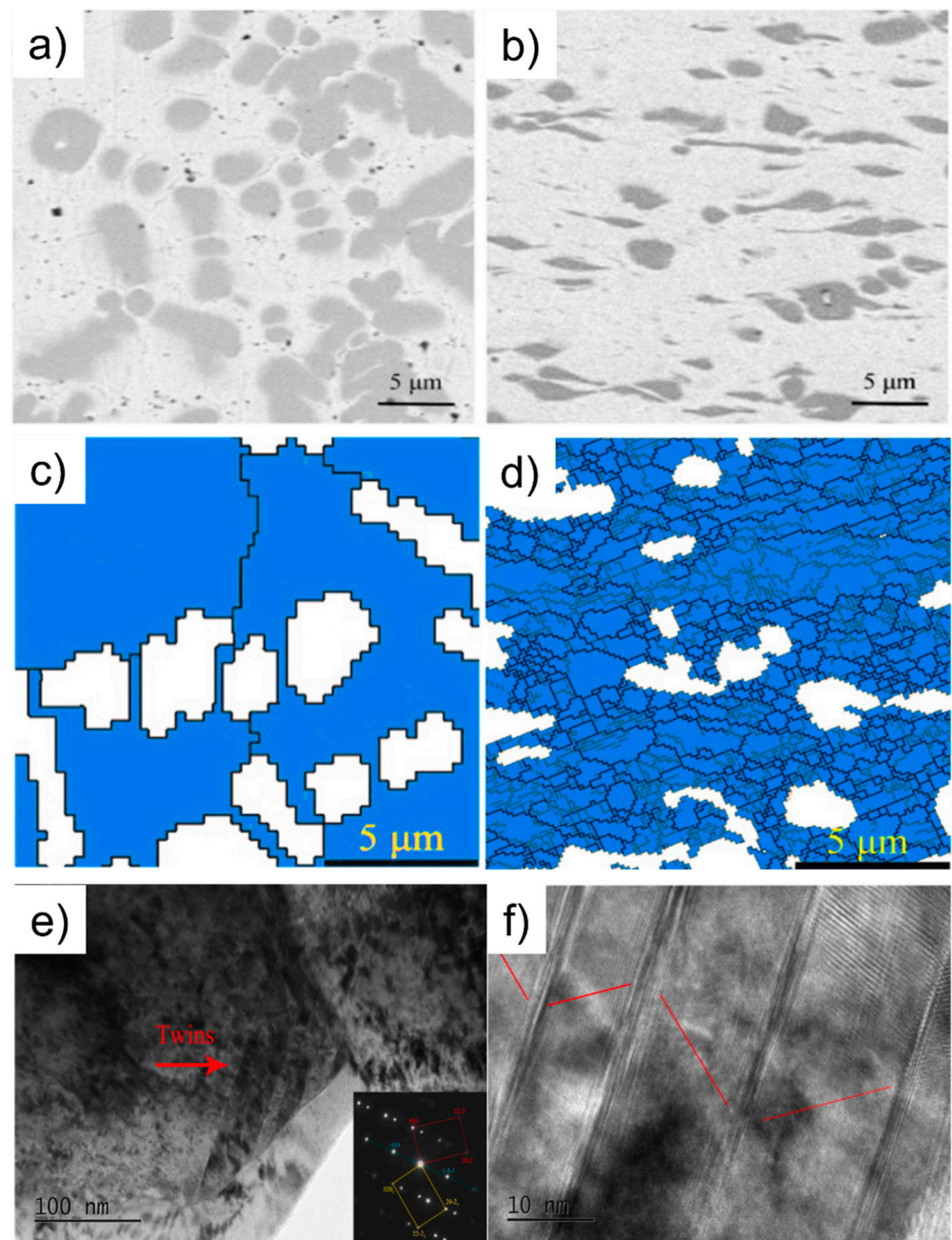


Figure 23. Microstructure of L-DED CuCr30 samples (a) before and (b) after the extrusion process, along with the corresponding EBSD analysis (c) before and (d) after the extrusion process. (e,f) Bright field TEM images taken from the L-DED CuCr30 alloy after the extrusion process indicate the formation of twins (Reprinted with permission from [80]).

2.2.2. Electrical Conductivity of L-DED-Fabricated Cu-Cr Alloys

The L-DED-manufactured CuCr30 alloy provides lower electrical conductivity than that of the counterpart fabricated through vacuum casting [81]. However, after extrusion, the electrical conductivity of the L-DED CuCr30 alloy (43.93% IACS) was increased by 6.63% to 46.84% (see Figure 24a) [80]. The improvement in the electrical conductivity of the extruded L-DED CuCr30 sample was attributed to the reduction in pores in the structure of the material during the plastic deformation (compare Figure 23a,b) [80].

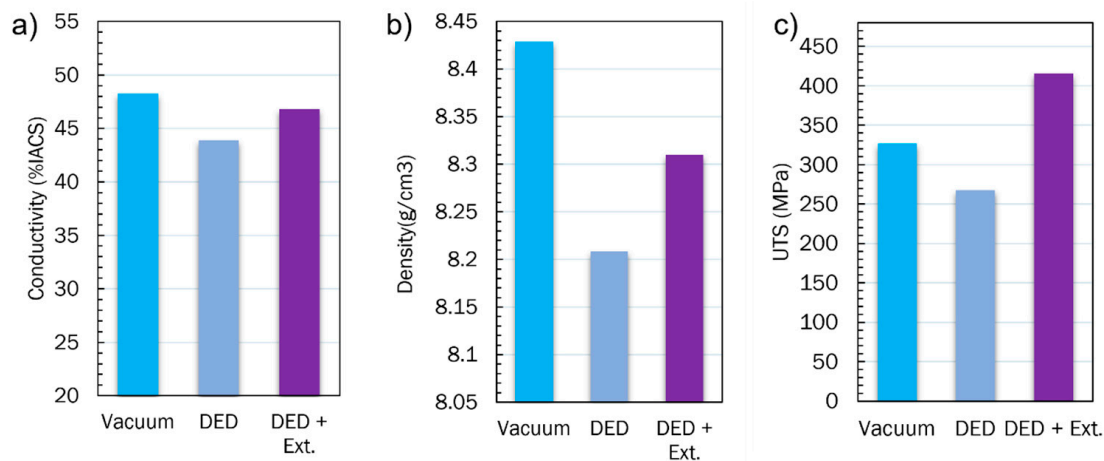


Figure 24. (a) Electrical conductivity, (b) density, and (c) tensile strength of vacuum casted, as-printed L-DED, and L-DED +extruded CuCr30 alloy [80,81].

2.2.3. Hardness, Strength, and Ductility of L-DED-Fabricated Cu-Cr Alloys

Rongzhou et al. [80] reported that the extrusion process improved the mechanical properties of the L-DED CuCr30 alloy. The Cr-rich precipitates, which serve as a second phase in the copper matrix, enhance the strength of the alloy during deformation. This is achieved not only through grain refinement in the copper matrix but also through work hardening due to the increase in dislocations during plastic deformation [80]. Furthermore, subjecting the manufactured sample to extrusion reduces pore defects and lowers stress concentrations [80]. The formation of nanoscale twins is another significant factor in improving the mechanical properties of the extruded samples [80]. According to the literature, the presence of nanoscale twins improves the strength and hardness of copper [82,83].

Overall, it can be concluded that the electrical conductivity, strength, and elongation of L-DED Cu-Cr alloys could be increased through the extrusion process [80]. However, Rongzhou et al. [80] did not study the effect of the post-printing extrusion process on the corrosion properties of the L-DED Cu-Cr alloys, and further research in this area is necessary.

2.3. EBM of Cu-Cr Alloys

The EBM technique has been used only once for the manufacturing of Cu-Cr alloys (CuCr25) in a study by Momeni et al. [84] that aimed to regulate the size of Cr-precipitates and prevent the formation of Cr-dendrites in the microstructure.

Microstructure of EBM-Fabricated Cu-Cr Alloys

Figure 25 depicts the as-printed microstructure of the Cu-25Cr alloy, consisting of uniformly dispersed fine Cr-rich particles, larger round Cr particles with diameters of a few micrometers, Cr_2O_3 particles (black dots), and Cu-rich dots within some of the Cr precipitates [84]. These microstructural features are nearly identical to those of L-PBF-fabricated high-Cr alloys investigated by Chen et al. [67] (see Figure 15). The properties of EBM-manufactured samples have yet to be investigated, and further research is necessary to evaluate the properties of EBM-produced CuCr alloys.

To summarize, the typical microstructures of Cu-Cr alloys fabricated using different AM methods are illustrated in Figure 26. This figure offers a concise comparison of how distinct processing techniques influence the material's microstructure. Moreover, Figure 27 compares the effects of pre/post-thermal and mechanical processes on the electrical conductivities and tensile strengths of different Cu-Cr alloys, fabricated both traditionally and through AM methods. It is evident that pre/post-printing processes, such as powder surface modification, heat treatment, or mechanical deformation, play a pivotal role in attaining the desired properties for additively manufactured Cu-Cr alloys.

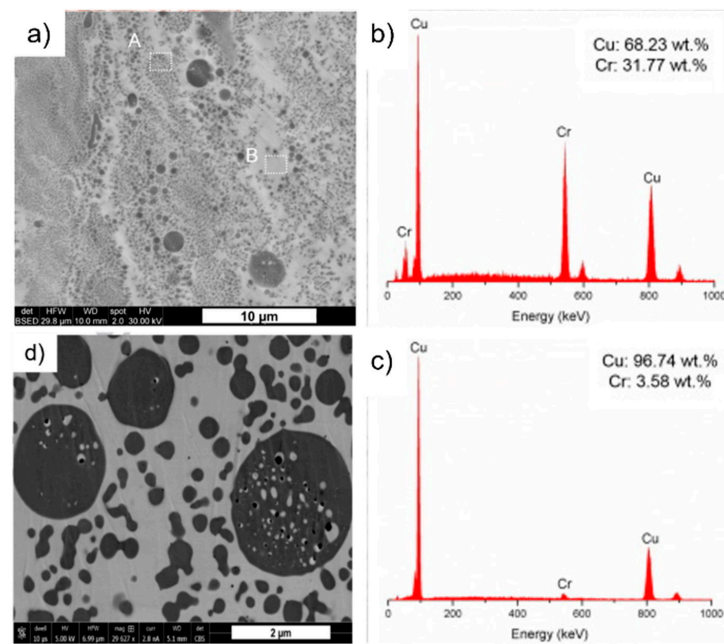


Figure 25. (a) Low-magnification SEM image taken from the EBM-fabricated Cu-25Cr alloy. (b,c) EDS elemental analysis taken from areas A and B. (d) A high-resolution FIB-SEM image taken from an EBM-fabricated Cu-25Cr alloy (Reprinted with permission from [84]).

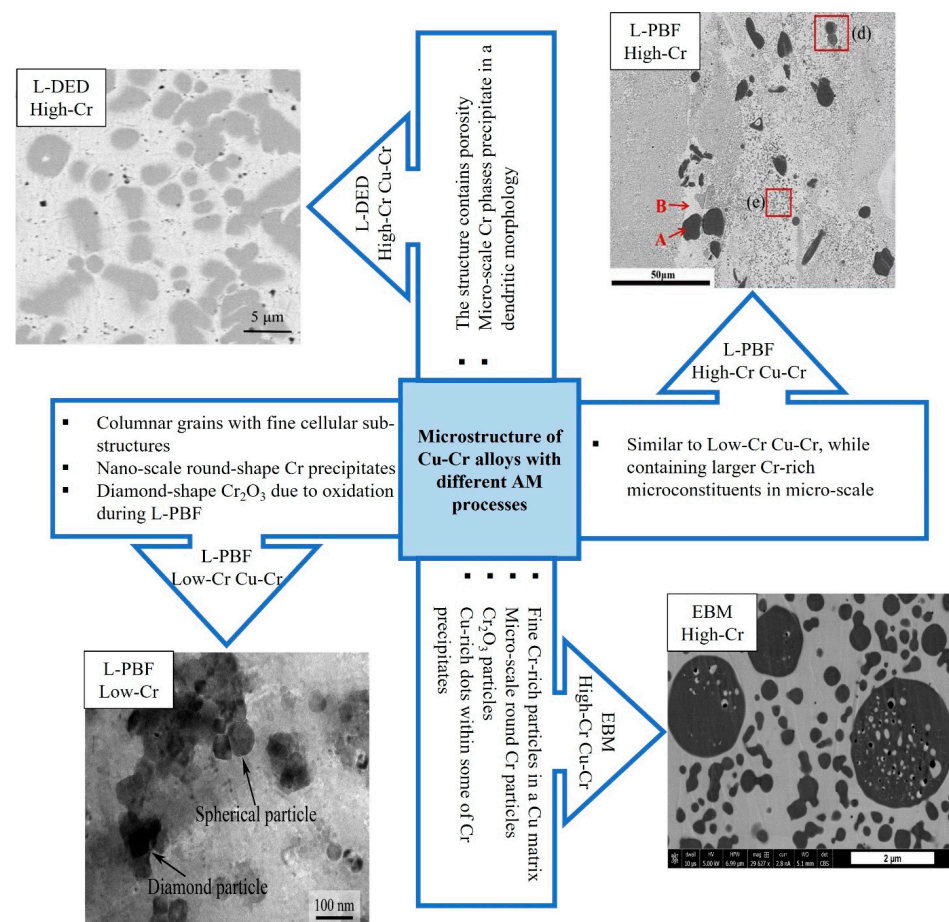
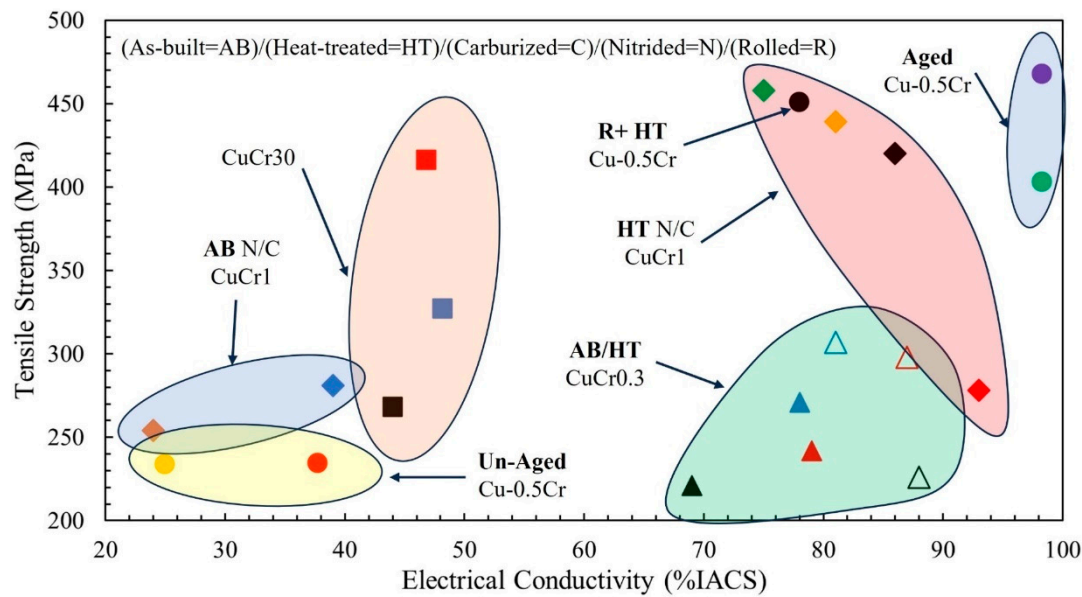


Figure 26. Typical microstructure of Cu-Cr alloys fabricated using different AM methods (Reprinted with minor edits with permission from [60,67,80,84]).



Alloy	Symbol	Ref.	Alloy	Symbol	Ref.
L-PBF CuCr0.3 (AB)	▲	[63]	L-PBF Carburized CuCr1 (AB)	◆	[65]
L-PBF CuCr0.3 (S+A)	▲	[63]	L-PBF Carburized CuCr1 (S+A)	◆	[65]
L-PBF CuCr0.3 (DA)	▲	[63]	L-PBF Carburized CuCr1 (DA)	◆	[65]
L-PBF CuCr0.3 + 0.05C (AB)	▲	[63]	L-PBF Nitrided CuCr1 (AB)	◆	[64]
L-PBF CuCr0.3 + 0.05C (S+A)	▲	[63]	L-PBF Nitrided CuCr1 (S+A)	◆	[64]
L-PBF CuCr0.3 + 0.05C (DA)	▲	[63]	L-PBF Rolled + Heat treated Cu-0.5Cr alloy	●	[60]
Vacuum Casted CuCr30	■	[81]	L-PBF Cu-0.5Cr (AB)	●	[61]
L-DED CuCr30	■	[80]	L-PBF Cu-0.5Cr (S)	●	[61]
L-DED + Extrusion CuCr30	■	[80]	L-PBF Cu-0.5Cr (S + A)	●	[61]
L-PBF CuCr1 (S+A)	◆	[65]	L-PBF Cu-0.5Cr (DA)	●	[61]
[61] DA: Direct aging at 480 °C, S: Solutioning at 1020 °C, S+A: solutioning at 1020 °C + aging at 480 °C					
[63] S+A: Solution Annealing at 1015 °C and aging at 400 °C, DA: Direct aging at 500 °C					
[64] S+A: Solution Annealing at 1050 °C and aging at 450 °C					
[65] S+A: Solution Annealing at 1015 °C and aging at 450 °C, DA: Direct aging at 450 °C					

Figure 27. Effect of pre/post-printing processes on the electrical conductivities and tensile strengths of different Cu-Cr alloys fabricated by traditional manufacturing and AM methods.

3. AM of Cu-Ni Alloys

AM of Cu-Ni alloys is implemented for producing complex shapes, bimetallic components, graded materials, and certain functional devices, such as thermocouples, thermopiles, and heat flux sensors [85]. L-PBF and DED are the only AM methods that have been applied for the production of Cu-Ni alloys.

3.1. L-PBF of Cu-Ni Alloys

L-PBF is the most common AM technique used for producing complex-shaped Cu-Ni components with low porosity levels and superior mechanical properties. Table 2 summarizes the existing studies in the literature on the L-PBF of Cu-Ni alloys.

Table 2. Summary and comparison of the powder size, pretreatment, and process parameters used for the fabrication of different Cu-Ni alloys using the L-PBF technique.

Alloy	Powder Size	Pretreatment	Process Parameters	Ref.
Cu76-Ni14.8-Sn7-Pb1.6	20 μm	80 °C preheating of steel base plate	- Laser power: 240 W - Scanning velocity: 100, 200, and 300 mm/s - Hatching spacing: 0.2 mm - Layer thickness: 0.02, 0.04, and 0.06 mm - Atmosphere: nitrogen - Oxygen concentration: 1.5%	[86]
Cu-5Ni Cu-10Ni Cu-15Ni	20–43 μm	80 °C preheating of steel base plate	- Laser power: 240 W - Scanning velocity: 200, 300, 400, and 500 mm/s - Hatching spacing: 0.2 mm - Layer thickness: 0.06 mm - Atmosphere: nitrogen - Oxygen concentration: 1.5%	[87]
Cu-19Ni	40 μm	Not reported	- Laser power: 200 W - Layer thickness: 0.02 mm	[88]
Cu-22.82Ni-4.72Sn-1.43P	Not reported	Not reported	- Laser power: 190 and 260 W - Scanning velocity: 25, 50, and 80 mm/s - Hatching spacing: 0.15 mm - Pattern angle: 0, 30, 45, 60, and 90° - Atmosphere: argon	[89]

3.1.1. Microstructure of L-PBF-Fabricated Cu-Ni Alloys

In one of the initial studies on the L-PBF of Cu-Ni alloys, Baraz et al. [88] manufactured Cu81-Ni19 alloy on an annealed conventionally produced Cu-Ni alloy platform with an identical chemical composition to the feedstock powder. The optical images of the manufactured sample depicted no obvious dendritic and grain structure, while the substrate microstructure was characterized by equiaxed grains (see Figure 28) [88]. The formation of a quasi-amorphous (metal glass) microstructure in the as-printed part was attributed to the suppression of the recrystallization process due to the extremely high cooling rate during the L-PBF process [88].

To the best of the authors' knowledge, the grain structure and microstructural details of L-PBF Cu-Ni alloys have not been thoroughly studied in previous research, and there is a need for further investigations in this area.

Investigations on the effect of laser scan speed on L-PBF of Cu-Ni alloys have shown the adverse effect of higher scan speed on the density and dimensional accuracy of the as-printed material [86,87]. As can be seen in Figure 29 [86], the lowest density and dimensional accuracy were achieved at the highest scan speeds due to inadequate melting of powders and consequently the formation of a more porous structure with poor dimensional accuracy at high scan speeds. However, a study by Sabelle et al. [89] on the L-PBF manufacturing of Cu-Ni monolayers found that increasing the scan speed leads to the formation of a thinner and denser layer (see Figure 30a,b), without providing a clear justification for this phenomenon. They merely stated that higher scan speeds result in reduced heat accumulation and a less porous structure, but they did not provide any supporting microscopy evidence to prove the porosity level of the samples fabricated at different scan speeds.

Sabelle et al. [89] also reported that using a higher laser power leads to the formation of thicker and denser monolayers of Cu-Ni alloys (Figure 30c,d). They attributed this to the fact that more powders fully melt at higher laser power, which in turn reduces defects and porosities [89].

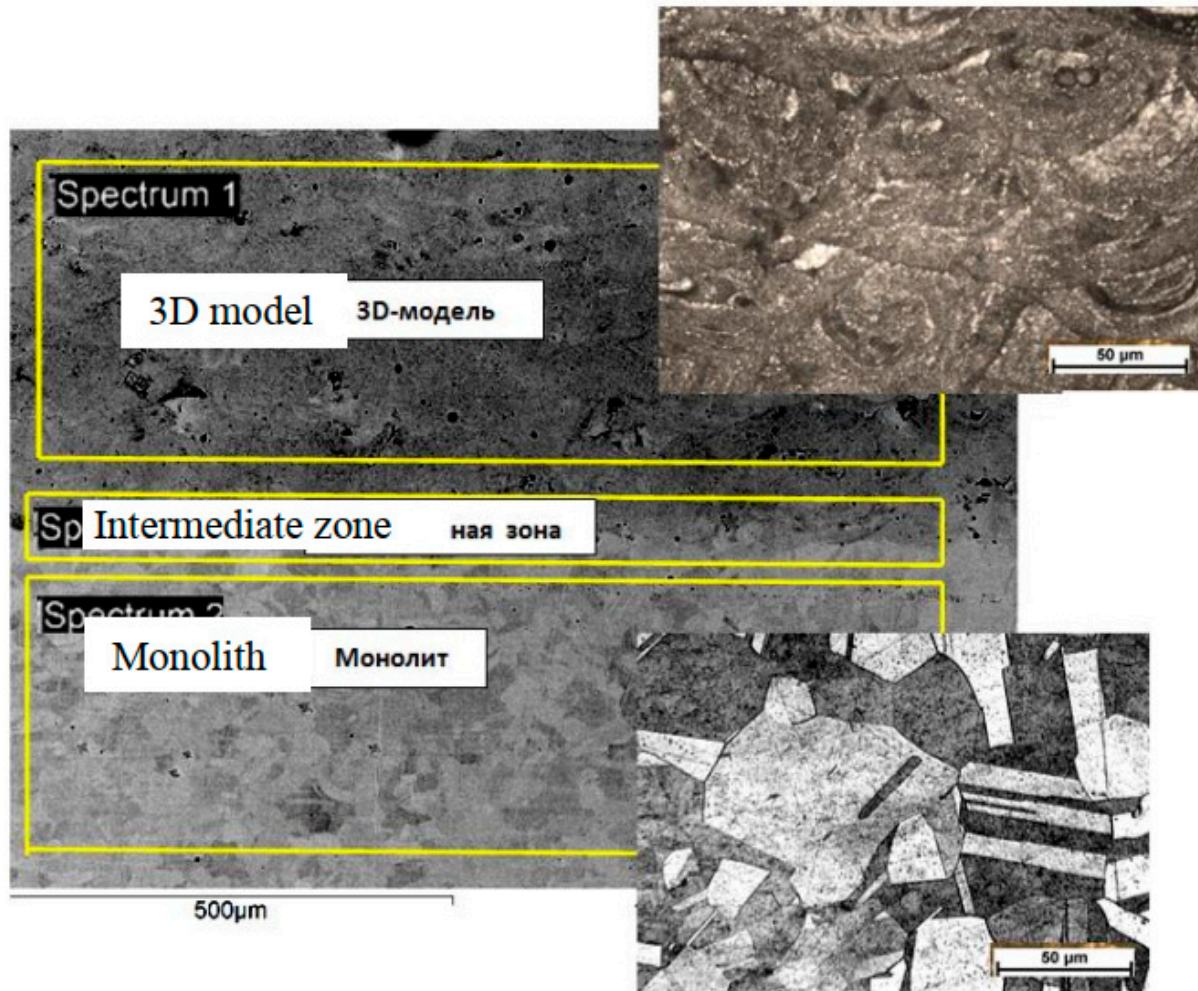


Figure 28. Microstructure of the L-PBF-fabricated Cu81-Ni19 alloy (labeled as a 3D model) and the substrate in the annealed state (labeled as a monolith) (Reprinted with permission from [88]).

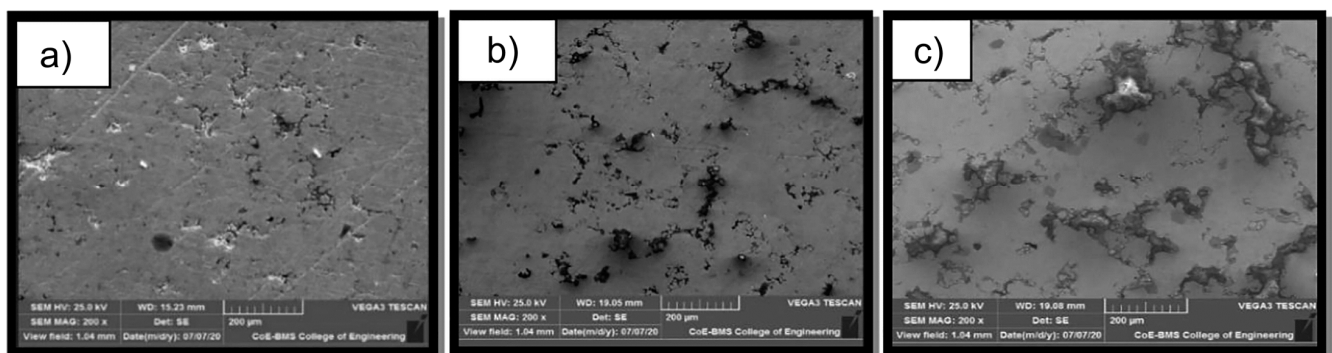


Figure 29. SEM images of L-PBF Cu-Ni alloy (Cu76-Ni14.8-Sn7-Pb1.6) with laser scan speeds of (a) 100 mm/s, (b) 200 mm/s, and (c) 300 mm/s (layer thickness: 20 µm) [86].

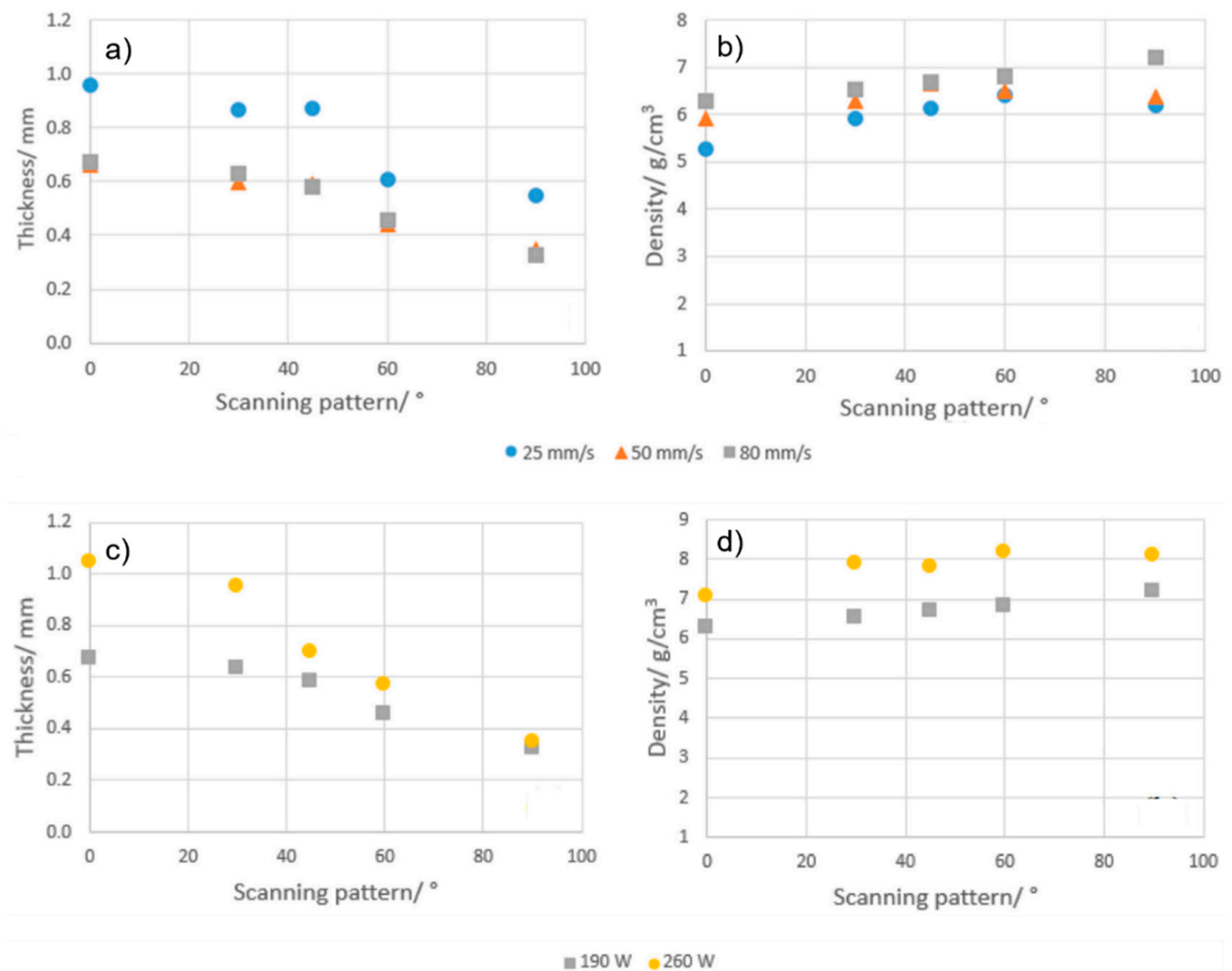


Figure 30. Thickness and mass density of L-PBF Cu-Ni monolayers (Cu71-Ni22.8-Sn4.7-Pb1.43) fabricated at (a,b) laser power of 190 W with different scan speeds of 25, 50, and 80 mm/s, and (c,d) at different laser powers of 190 and 260 W with the scan speed of 80 mm/s [89].

Regardless of the scanning speed, Cu-Ni alloys with a higher content of Ni provide higher density and dimensional accuracy [87]. The improvements in density and dimensional accuracy of produced parts with a higher content of Ni are due to the increased wettability and reduced balling effect at higher weight percentages of Ni [90].

3.1.2. Corrosion Behavior of L-PBF-Fabricated Cu-Ni Alloys

There is limited research on the corrosion of L-PBF-fabricated Cu-Ni alloys, with only one study conducted by Rajesh et al. [86]. In this study, the effects of layer thickness and scan speed on the weight loss and topography of an L-PBF Cu76-Ni14.8-Sn7-Pb1.6 alloy exposed to seawater (3% NaCl) and an acidic environment (1 M HCl) were investigated. Their topography examination revealed that greater corrosion resistance could be achieved by using a lower scan speed and the thinnest layer thickness [86]. According to SEM images of the corroded samples in NaCl medium (Figure 31), more corrosion products formed on the samples with faster scan speeds and thicker layers [86].

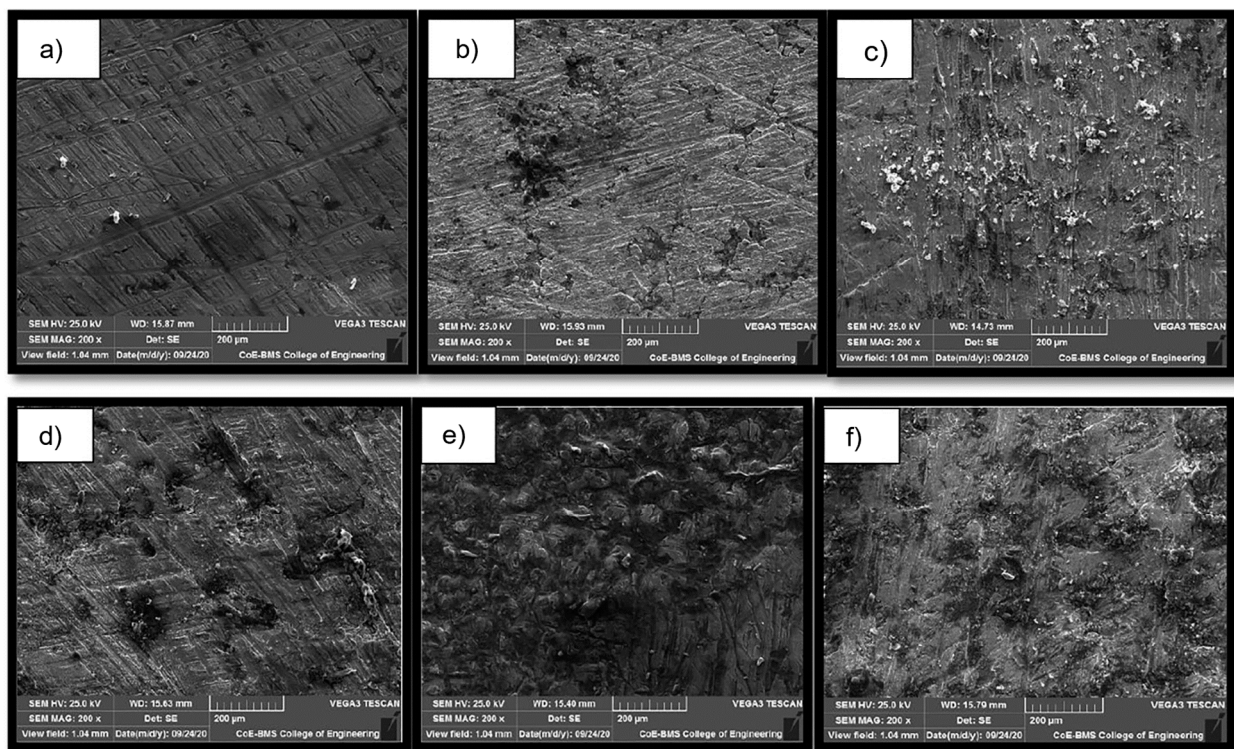


Figure 31. After-corrosion (in NaCl) topography of the L-PBF-fabricated Cu76-Ni14.8-Sn7-Pb1.6 alloy with a layer thickness of (a–c) 20 μm and different laser scan speeds of (a) 100 mm/s, (b) 200 mm/s, and (c) 300 mm/s, and a layer thickness of 60 μm and different laser scan speeds of (d) 100 mm/s, (e) 200 mm/s, and (f) 300 mm/s (Reprinted with permission from [86]).

The weight loss results supported the topography observations, as the samples manufactured with a slower scan speed and a lower thickness showed the lowest corrosion rate [86]. It should also be noted that L-PBF-fabricated Cu-Ni alloys generally provide great corrosion resistance in NaCl solutions due to a slower cathodic reaction. This slows down the corresponding anodic reaction and subsequently reduces the overall current flow and chemical attack, making them a suitable candidate for different applications in marine environments [86,91].

While Rajesh's study [86] sheds light on the general corrosion behavior of L-PBF Cu-Ni alloys produced with varying laser scan speeds and layer thicknesses, additional electrochemical analyses, such as PDP and electrochemical impedance spectroscopy (EIS) tests, are necessary to more thoroughly understand the corrosion behavior of these alloys.

3.1.3. Hardness and Strength of L-PBF-Fabricated Cu-Ni Alloys

Baraz et al. [88] deposited Cu81-Ni19 layers on an annealed conventionally produced counterpart and reported that the hardness of the L-PBF-deposited layer is 19% higher than that of the annealed substrate. They merely correlated this increase in hardness to the quasi-amorphous structure of the deposited layer without providing any further justifications or evidence.

Rajesh et al. [86] conducted parametric investigations and found that higher laser scan speed and layer thickness not only deteriorate the corrosion resistance of the material but also decrease the hardness of L-PBF Cu-Ni alloys. This was attributed to the lower energy density obtained by increasing the laser scan and layer thickness, resulting in a reduction in the hardness of the end-product [86].

Another contributing factor to the mechanical properties of L-PBF Cu-Ni alloys is the scan pattern. Sabelle et al. [89] evaluated the effect of scan pattern angle on the properties of the Cu-Ni monolayer produced by the L-PBF process. Regardless of the scanning speed

and laser power used in the manufacturing process, the maximum tensile strength was achieved at a scanning pattern angle of 60° . However, even at 60° , the tensile strength was still four times lower than the strength of the bulk alloy (see Figure 32). Increasing the scanning angle to 60° reduces the concentration of heat and the overlap of heating for consecutive tracks, leading to a less porous structure [89]. Generally, the monolayers produced at each scanning angle show a higher tensile strength at higher print speeds and laser power, resulting from the formation of denser monolayers.

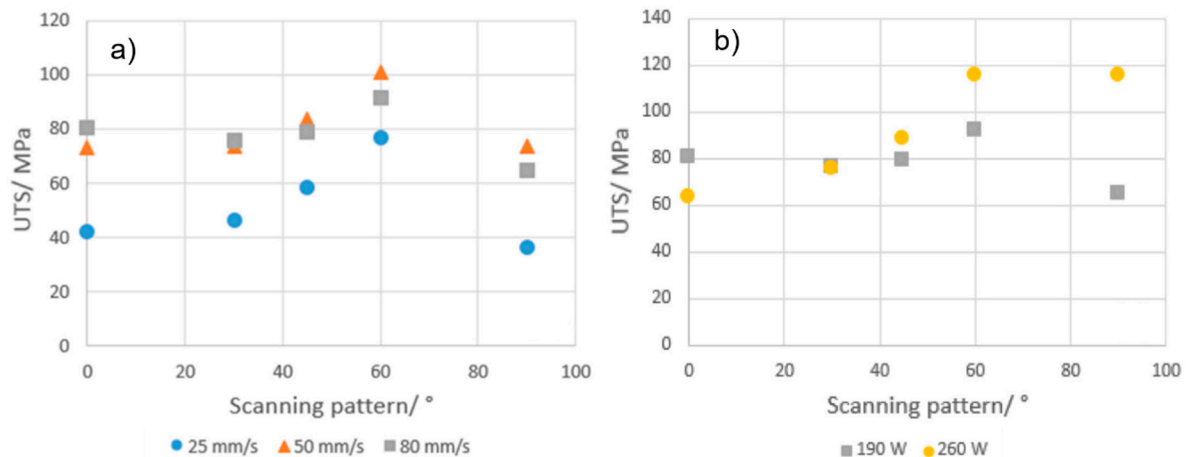


Figure 32. Tensile strength of L-PBF Cu-Ni (Cu71-Ni22.8-Sn4.7-Pb1.43) monolayers fabricated at (a) laser power of 190 W with different scan speeds and (b) different laser powers with a scan speed of 80 mm/s (Reprinted with permission from [89]).

Further investigations are necessary to better understand the mechanical properties of L-PBF Cu-Ni alloys, including the effects of inhomogeneities at different locations of the fabricated parts and anisotropy in building and deposition direction.

3.2. DED of Cu-Ni Alloys

The DED processing of Cu-Ni alloys has been investigated through both wire-based systems (WAAM) and powder-based systems (L-DED).

The only study on WAAM processing of Cu-Ni alloys was carried out by Guo et al. [85] using a feedstock wire with a diameter of 1.2 mm and a chemical composition of Si(0.082), Mn(0.89), S(0.01), P(0.04), Fe(0.64), Ti(0.25), and Ni(30.13). The process parameters used for the study are listed in Table 3.

Table 3. The process parameters used for WAAM processing of Cu-Ni alloy [85].

Parameter	Value
Voltage	18 V
Current	80 A
Feeding speed	5 m·min ^{−1}
Printing speed	14 mm s ^{−1}
Contact tip for working distance	15 mm
Gas flow rate	10–15 L·min ^{−1}
Interlayer temperature	≤150 °C
Overlap rate	50%

Yadav et al. [33] used the L-DED process to produce a graded Cu-Ni alloy (Cu/Cu-25Ni/Cu-50Ni/Cu-75Ni/Ni) using different laser powers (1200, 1500, and 1800 W) and

scan speeds (0.3, 0.5, and 0.7 m/min) for different Cu-Ni powder compositions (wt.%) with a powder feed rate of 2.8 g/min on a preheated (250 °C) Cu plate. The sequence of the deposition process and the visual appearance of the produced structure are shown in Figure 33.

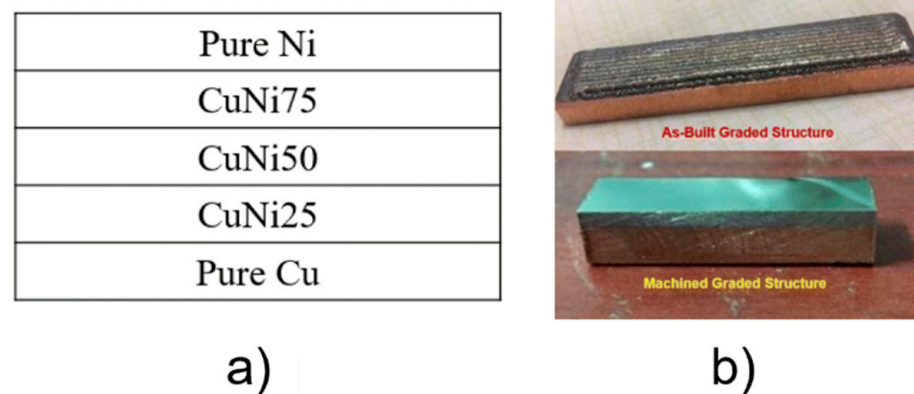


Figure 33. (a) The order of the deposition and (b) a photographic view of the as-built structure of the graded Cu-Ni alloy fabricated by the L-DED process (Reprinted with permission from [33]).

In another study, the feasibility of L-DED processing of copper-nickel alloys using two types of powders, including different blends of pure copper and nickel powders (see Table 4), and different blends of pure copper and pre-alloyed Delero-22 (0.4 wt.% Fe, 2.4 wt.% Si, 1.3 wt.% B, and Bal. Ni) feedstock powders (see Table 5) was assessed by Karnati et al. [92].

Table 4. The chemical composition of powder blends used for manufacturing copper-nickel alloys [92].

Element	Blend1	Blend2	Blend3	Blend4
Cu (wt.%)	0	25	50	75
Ni (wt.%)	100	75	50	25

Table 5. The selected sets of powder blends of pure copper and Delero-22 alloy [92].

Element	Blend1	Blend2	Blend3	Blend4	Blend5
Copper (wt.%)	0	10	30	50	70
Delero-22 (wt.%)	100	90	70	50	30

In a different study, Karnati et al. [93] also manufactured graded materials using L-DED processing of 70–30 copper-nickel alloy on Delero-22 alloy and vice versa. They aimed to optimize the deposition condition using different duty cycles of power. The deposition was conducted at a scan speed of a 500 mm/min and a powder feed rate of 15 g/min. After conducting a preliminary optimization study, all depositions were performed at a peak power of 1 kW and a duty cycle of 43% at 500 Hz modulation frequency. At the interface of dissimilar materials, the duty cycle of power was gradually ramped down from a higher value to the optimized conditions.

In a recent study, Li et al. [94] produced a copper-nickel alloy for active cooling applications using the L-DED method. The industrial powder mixture, consisting of 65% Cu and 35% Ni (wt.%), was used as the feedstock powder. The parameters employed in the production of different samples are listed in Table 6 [94].

Table 6. Manufacturing parameters of various copper-nickel alloys produced by Li et al. [94].

Sample	Laser Power (W)	Scan Speed (mm·s ^{−1})	Powder Feed Rate (g·min ^{−1})	Stepover Distance (mm)	Density (g·cm ^{−3})
B1S1	800	550	5	1.05	8.25 ± 0.20
B1S2	800	550	5	1.05	8.34 ± 0.02
B2S3	800	500	5	1.05	8.36 ± 0.16
B2S4	800	550	5	0.95	8.46 ± 0.13

The major findings of the abovementioned studies are reviewed and discussed in the upcoming subsections.

3.2.1. Microstructure of DED-Fabricated Cu-Ni Alloys

Yadav et al. [33] explored the impact of varying laser parameters during the L-DED of a graded Cu-Ni alloy and discovered interruptions in the tracks deposited at lower laser powers and higher scan speeds, which they attributed to insufficient laser energy for deposition as well as the lower laser absorption and higher thermal conductivity in the Cu-rich tracks.

They also studied the effect of the feedstock powder compositions on the surface morphology of the deposited tracks and concluded that an uneven surface morphology forms for pure Ni in the as-built condition, while increasing the Cu percentage in composition decreases the spattering on the surface due to an increase in wetting of pre-deposited layers [95] and lower surface tension [96] (see Figure 34a,b). On the other hand, increasing the Cu content was found to have an adverse effect on the relative density of the fabricated samples, plausibly due to incomplete fusion and melting of the feedstock powders (Figure 34c–e) [33]. It is notable that the higher reflectivity and thermal conductivity of Cu also play a role in the increased porosity content in Cu-rich alloys due to the wastage of laser energy [33]. However, no cracks or inclusions were found in the microstructure of the graded deposits in all layers (Figure 34a–e) [33].

Contrary to the findings of Baraz et al. [88], who reported the formation of a quasi-amorphous structure during L-PBF of Cu-Ni alloy, Yadav et al. [33] confirmed the formation of a crystalline structure by obtaining clear XRD patterns from the L-DED-deposited graded Cu-Ni samples. These patterns revealed the presence of pure Cu and Ni peaks (as seen in Figure 34f). It is notable that the Cu-Ni system does not form intermetallic compounds, as their isomorphous phase diagram exhibits infinite solubility in both liquid and solid states.

According to the microscopy images taken from different locations of the L-DED-produced graded Cu-Ni alloy along its building direction, the bottom (Figure 35a) and middle layers (Figure 35b,c) were characterized by a mix of cellular and dendritic growth [33]. The high cooling rate during the L-DED process, along with a higher concentration of Cu in the lower/middle layers, resulted in rapid solidification and, subsequently, fine dendritic growth [97]. Conversely, the thermal gradient at the top layers decreases due to pre-heating from the previous layer and a lower concentration of Cu, leading to the formation of equiaxed grains (Figure 35d) [33].

It should be mentioned that the microstructural analysis carried out by Yadav et al. [33] was limited to optical microscopy, and further investigation through SEM, EDS, and EBSD analyses is necessary to determine any potential segregation, compositional inhomogeneity, preferential texture, etc.

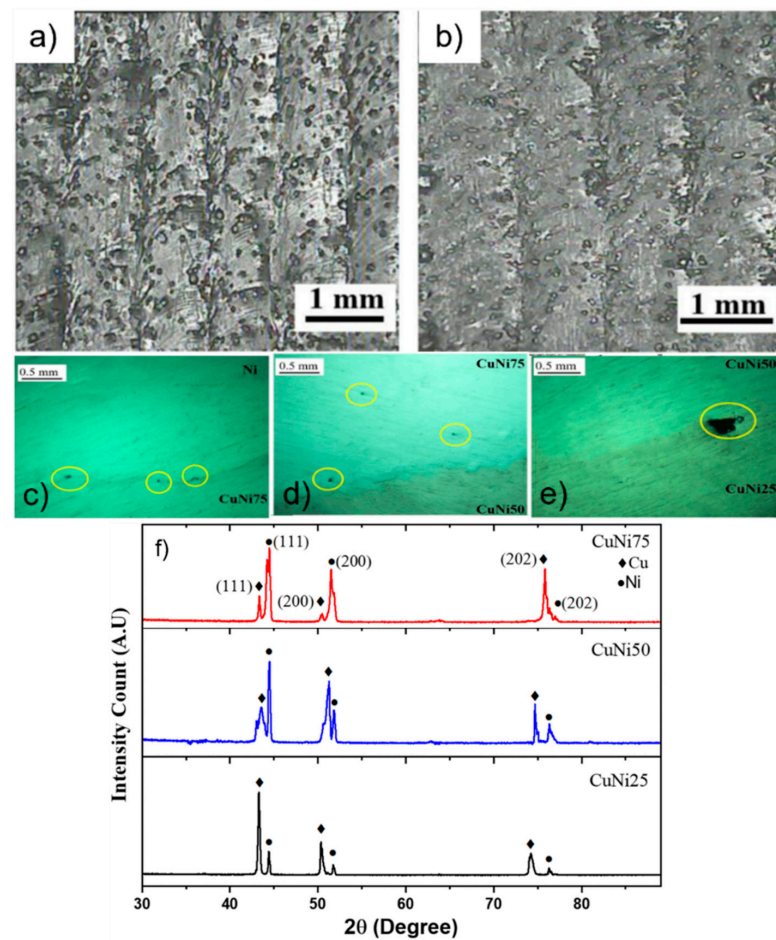


Figure 34. Surface morphology of L-DED-fabricated (a) pure Ni and (b) Cu-Ni alloy. The porosity distribution at the interface of (c) Ni-CuNi75, (d) CuNi75-CuNi50, and (e) CuNi50-CuNi25. (f) The XRD patterns of a L-DED-deposited graded Cu-Ni alloy (Reprinted with permission from [33]).

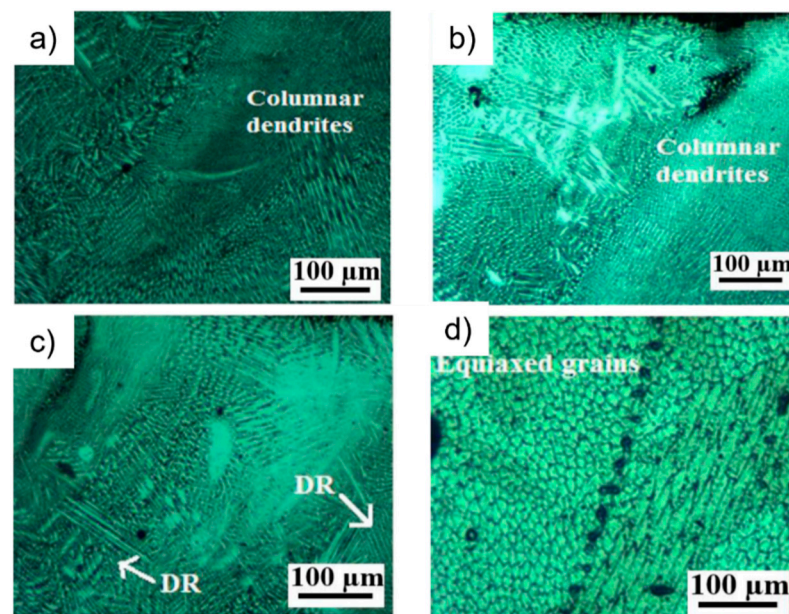


Figure 35. Microstructure of the L-DED-deposited graded Cu-Ni alloy at different locations of (a) the bottom layer, (b,c) the middle layers, and (d) the top layer (Reprinted with permission from [33]).

Guo et al. [85] found that the WAAM process is capable of producing a more defect-free Cu-Ni alloy as compared to the L-DED Cu-Ni alloys fabricated by Yadav et al. [33], which were characterized by discontinuities, surface irregularities, and internal porosities. Guo et al. [85] also addressed the lack of study by Yadav et al. [33] and performed a more detailed microstructural characterization using EBSD, TEM, and EDS. Their high-magnification EBSD maps (Figure 36a–h) revealed that the microstructure of samples consists of lamellar grains and irregular blocks. The inverse pole figures (IPFs) and pole figures (PFs) showed that the crystal orientation was elongated in the $\langle 101 \rangle$ direction (see Figure 36d–h) [85]. Further TEM analysis along with the corresponding SAED patterns also confirmed the presence of a blocked microstructure in addition to spherical crystalline inclusions characterized as TiO_2 surrounded by a high density of dislocations, which can positively contribute to the mechanical properties of the as-printed material (see Figure 36i–l).

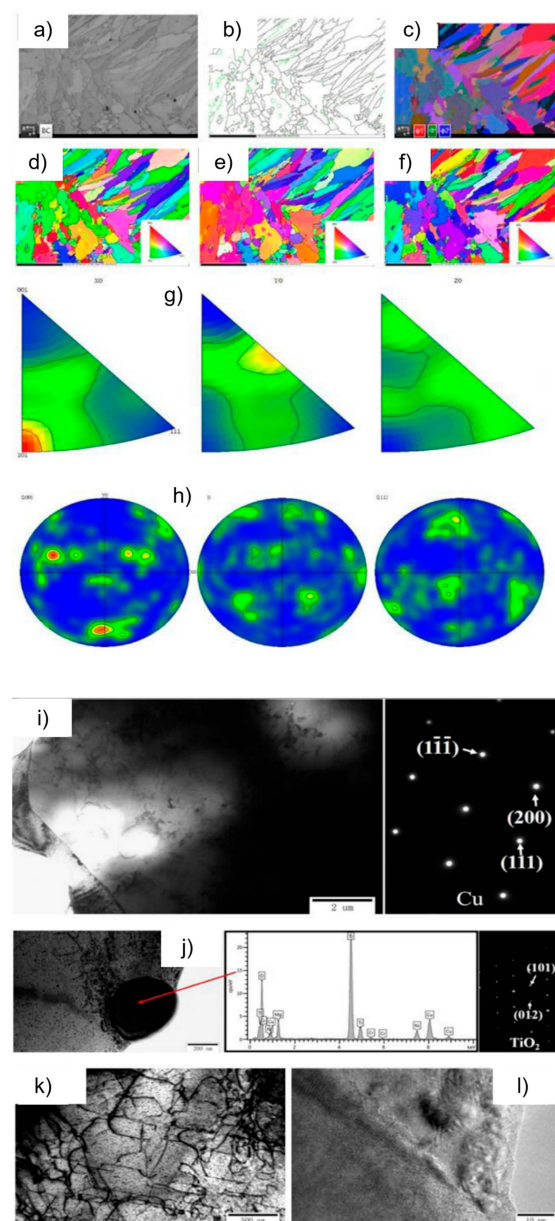


Figure 36. (a–h) EBSD data and (i–l) TEM analysis of WAAM-fabricated Cu-Ni alloy (the composition of filler: Cu-Si(0.082), Mn(0.89), S(0.01), P(0.04), Fe(0.64), Ti(0.25), and Ni(30.13) (wt.%) (Reprinted with permission from [85]).

As indicated by the findings of Karnati et al. [92], the deposition of blends of elemental copper and nickel powders produced solid solutions (shown in Figure 37), containing a significant amount of gas (spherical) and shrinkage porosities (irregular). The appearance of gas porosities was attributed to the entrapment of the oxygen gas that evolved upon the dissociation of nickel oxide, resulting from its low thermal stability [98]. The gas entrapment in the microstructure was promoted by the rapid cooling and solidification in the laser metal deposition process [99]. Modifying the process parameters and adding chromium as a gettering agent were also not effective in the elimination of porosities. Therefore, Delero-22 alloy was used as a potential alternative to elemental nickel powder, as it was believed that the presence of silicon and boron elements in Delero-22 alloy would enhance the fluidity of nickel and provide oxygen gettering during deposition [92,100]. Interestingly, a near fully dense microstructure was obtained from the deposition of Delero-22 alloy [92].

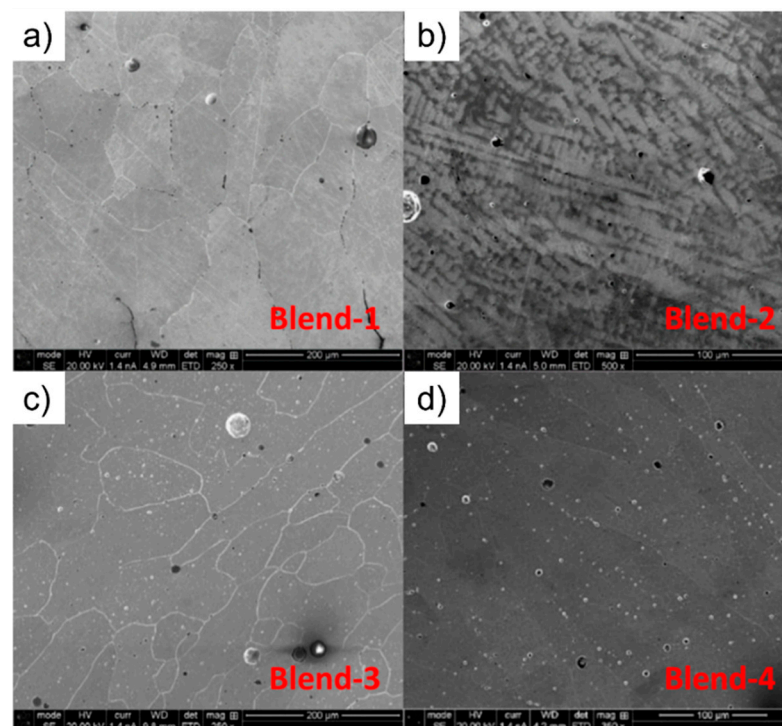


Figure 37. As-deposited microstructures of the L-DED-fabricated copper-nickel alloy using different elemental powder blends of (a) blend 1, (b) blend 2, (c) blend 3, and (d) blend 4, which are listed in Table 4 (Reprinted with permission from [92]).

Unlike the single-phase microstructure of deposited tracks using elemental blends, deposits using a mixture of elemental copper and Delero-22 alloy consisted of a dual-phase microstructure, including the Cu-Ni solid solution and Ni_3B intermetallics [92]. According to Figure 38, all deposits exhibit a dendritic microstructure, where increasing copper content leads to the coarsening of dendrites due to increasing superheat in the melt pool [92]. In their deposition of 70–30 Cu-Ni alloy on pure Ni, Karnati et al. [93] observed a dendritic dual-phase microstructure consisting of a copper-nickel solid solution and nickel boride phases.

Li et al. [94] reported that L-DED processing of a 65–35 Cu-Ni powder blend resulted in heterogeneous texture and the formation of cavities in the alloy blocks. The EDS line scan spectrum of the L-DED copper-nickel sample represented distinct regions along the line, consisting of a Cu-Ni alloy with approximately 65–35 composition and a pure Ni particle surrounded by the Cu-rich matrix (see Figure 39). During the L-DED process, the copper-nickel alloy formed at the center part of the laser line. However, the energy received by the mixed powder at the edge of the laser spot was insufficient to melt the

Ni powder. Conversely, the received energy caused the melting of Cu powder and the formation of a Cu-rich matrix. Moreover, the mismatched thermal expansion of the sample, originating from the heterogeneous nature of the material, can contribute to the formation of cavities. The authors suggested that fine-tuning the laser and mixing parameters and using pre-alloyed powders could reduce the inhomogeneity of the microstructure [94].

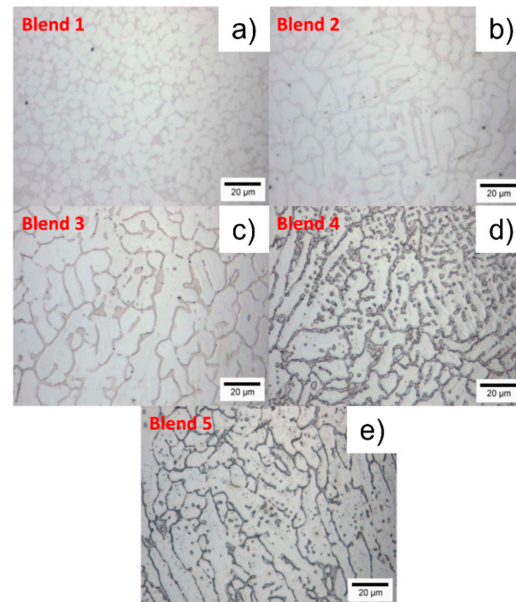


Figure 38. Optical micrographs of the as-deposited microstructure of the L-DED-fabricated copper-nickel alloys using different sets of powder blends of pure copper and Delero-22 alloy, including (a) blend 1, (b) blend 2, (c) blend 3, (d) blend 4, and (e) blend 5, which are listed in Table 5 (Reprinted with permission from [92]).

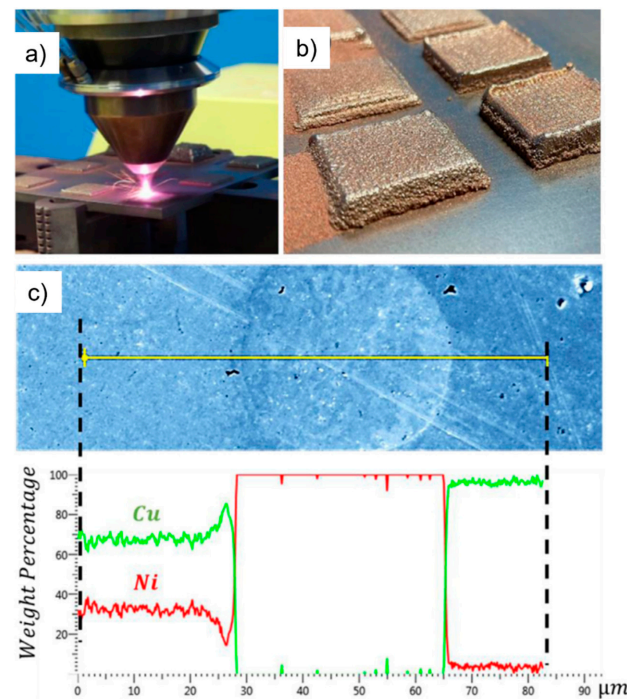


Figure 39. (a) L-DED nozzle used for mixing and melting Cu-Ni powders to produce samples shown in (b). (c) The SEM-EDS of an area from the B1S1 sample (see Table 6) (Reprinted with permission from [94]).

3.2.2. Hardness, Strength, and Ductility of DED-Fabricated Cu-Ni Alloys

As shown in Figure 40, Yadav et al. [33] evaluated the microhardness variation along the building direction for two conditions: (i) the L-DED-graded Cu-Ni alloy (refer to Figure 33 for the deposition sequence), and (ii) the pure Ni-Cu joint, in which pure Ni was deposited on top of pure Cu. Two notable differences can be observed in the microhardness profiles: (i) the maximum hardness value is higher for the graded Cu-Ni alloy, and (ii) there is a steep gradient in the pure Ni-Cu joint, which is absent in the graded Cu-Ni alloy and is instead replaced by a gradual increase from pure Cu to pure Ni [33].

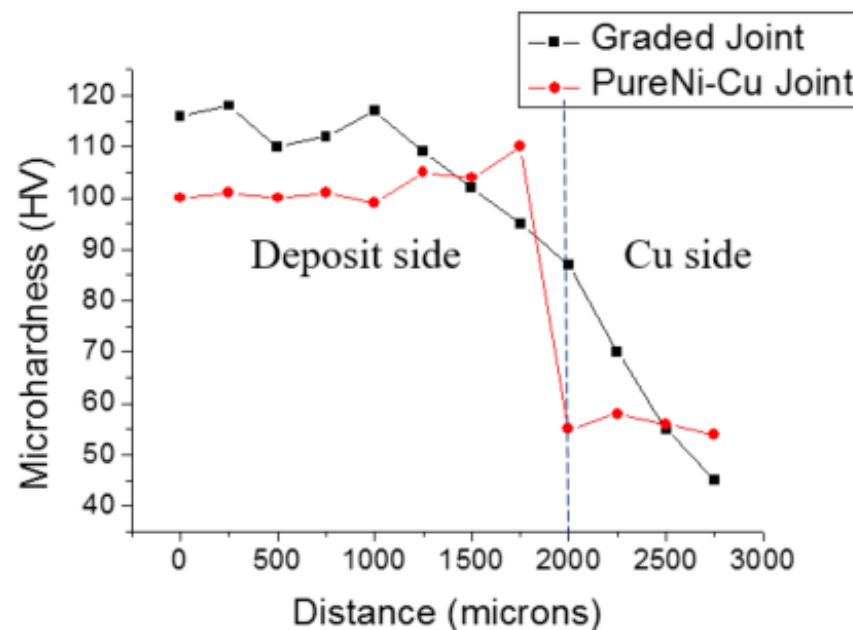


Figure 40. Microhardness variations along the building direction for two samples of L-DED-graded Cu-Ni alloy and pure Ni-Cu joint (Reprinted with permission from [33]).

The higher maximum microhardness value of the graded Cu-Ni alloy was attributed to the presence of Cu with a higher thermal conductivity, resulting in a faster cooling rate and consequently a finer microstructure. As the Hall-Petch relation suggests, a finer grain structure leads to a higher hardness value [101]. Another contributing factor to the increased hardness of the graded Cu-Ni alloy may be linked to the differences in the lattice size of pure Cu and Ni, promoting solid solution strengthening [102].

Despite the well-documented microhardness variations in the L-DED-graded Cu-Ni alloy by Yadav et al. [33], further exploration into the potential heterogeneities and anisotropy in its tensile properties is necessary to fully comprehend the tensile strength of the Cu-rich (bottom) and Ni-rich (top) sides, as well as the material's ductility in both the building and deposition directions.

The anisotropy in mechanical properties of WAAM-fabricated Cu-Ni alloys was studied by Guo et al. [85], and it was reported that microhardness measurements in the transverse and longitudinal directions showed uniform hardness distribution. However, the yield and tensile strengths, elongation, and impact energy values in the transverse direction were lower compared to those in the longitudinal direction (Figure 41) [85]. It is important to note that the tensile strength, yield strength, and elongation of the additively manufactured sample were comparable to the feeding filler metal used (represented by the dash lines in Figure 41), indicating the successful production of the alloy with low defects through the WAAM process [85].

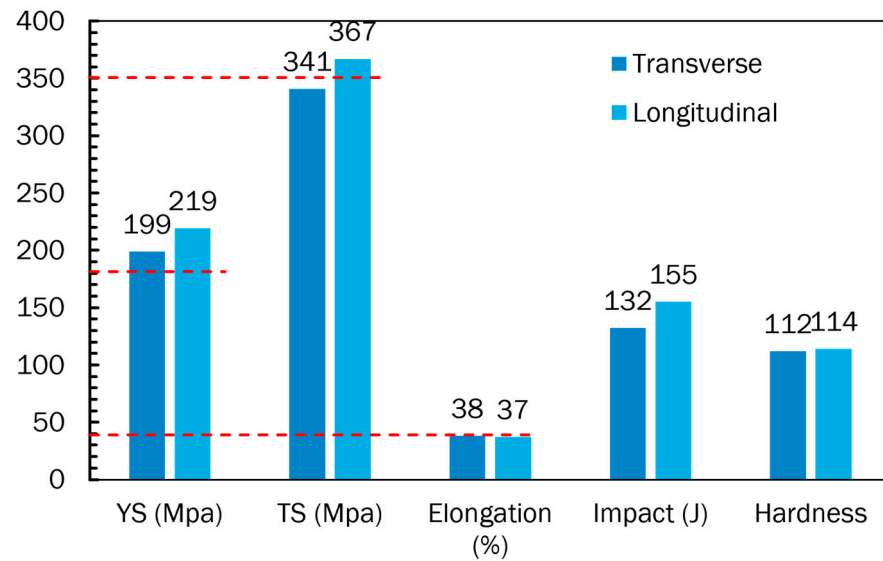


Figure 41. Mechanical properties of Cu–Ni alloy fabricated by the WAAM process (the composition of filler: Cu–Si(0.082), Mn(0.89), S(0.01), P(0.04), Fe(0.64), Ti(0.25), and Ni(30.13) (wt.%) [85].

Karnati et al. [92] reported that increasing the copper content enhances the strength and ductility of the L-DED-fabricated Cu–Ni alloy (Figure 42). The ultimate tensile strength values were reported to vary due to the anisotropy caused by the directional solidification occurring during thin-wall fabrication. The study also found that the variation in strength and ductility is influenced by changes in scan speed, with slower scan speeds leading to decreased strength and ductility.



Figure 42. Mechanical properties of miniature tensile Cu–Ni alloy samples manufactured by the L-DED process using various blends of copper–nickel powders listed in Table 5 (Reprinted with permission from [92]).

To evaluate the effect of transition length on the mechanical properties, Karnati et al. [93] performed hardness and tensile testing on samples produced with various sets of power and duty cycles. Figure 43 shows that the hardness value gradually varied for the longest transition length, while the shortest transition length depicted a relatively sharp change in hardness. The increase in copper content in the microstructure resulted in a decrease in the hardness value. Moreover, the samples with a lower copper content (Cu-Ni on Delero-22) provided a higher yield strength (Figure 44).

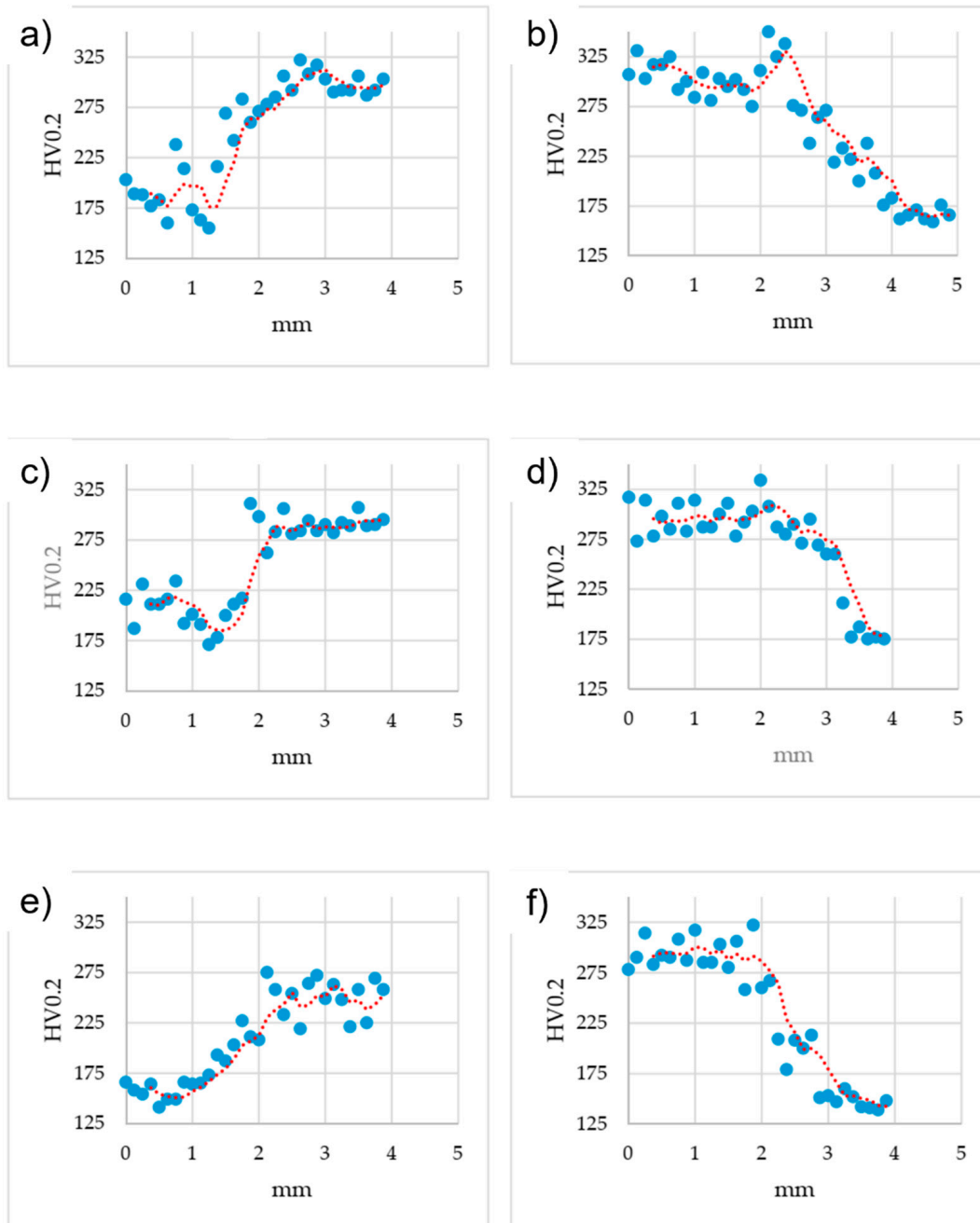


Figure 43. Variation in Vickers hardness values ($HV_{0.2}$) along the height of the L-DED-deposited copper-nickel-graded material. (a,c,e): Hardness plots on set 1, set 2, and set 3 deposits of 100/0 (Ni/Cu) on 30/70 (Ni/Cu), respectively. (b,d,f): Hardness plots of set 1, set 2, and set 3 deposits of 30/70 (Ni/Cu) on 100/0 (Ni/Cu) (solid circles are the spot measurement, and the red dotted line is the moving average trend line with four measurements as the period) (Reprinted with permission from [93]).

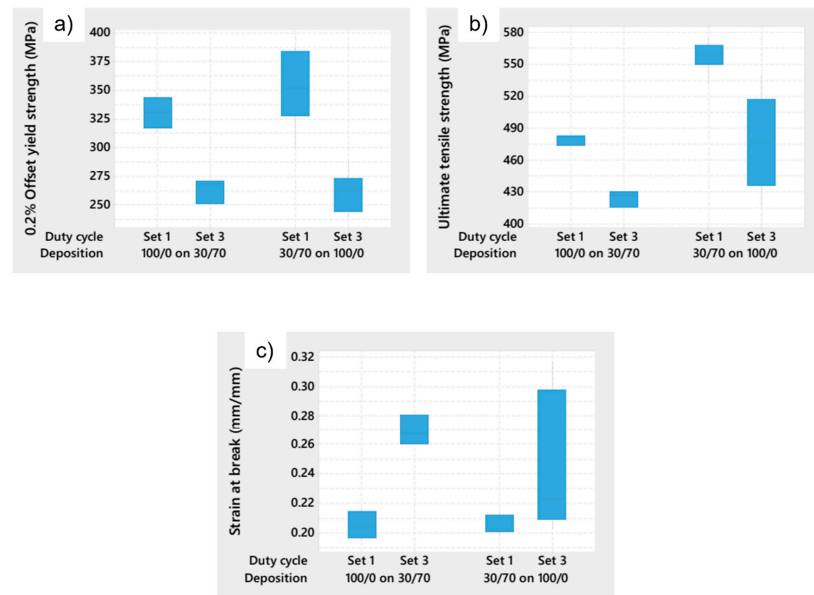


Figure 44. (a) It represents 0.2% offset yield strength, (b) ultimate tensile strength, and (c) strain to break for the miniature tensile Cu-Ni alloy samples manufactured by L-DED using different sets of power and duty cycles (Reprinted with permission from [93]).

3.2.3. Thermal/Electrical Conductivity of DED-Fabricated Cu-Ni Alloys

Li et al. [94] compared the thermal and electrical conductivity of an L-DED-fabricated Cu-Ni alloy in the x, y, and z directions (Figure 45a,b), which revealed an anisotropic behavior in various directions. Assessing the influence of L-DED parameters on the electrical and thermal conductivities of the samples (Figure 45c,d) showed that the sample with the lowest density (the B1S1 sample in Table 6) offers the lowest thermal and electrical conductivities. On the other hand, reducing the stepover distance and depositing the tracks closer together resulted in a complete melting between adjacent tracks and thus the highest electrical and thermal conductivities, as seen for the B1S2 sample (see Table 6).

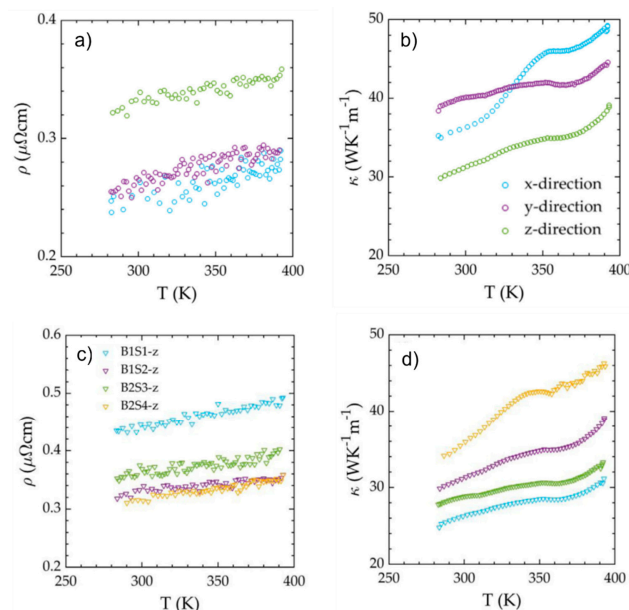


Figure 45. Resistivity and thermal conductivity along (a,b) x, y (in-plane), and z (cross-plane) directions from the same block of the L-DED-fabricated Cu-Ni sample (B1S2 in Table 6), and (c,d) in the cross-plane direction measured for different blocks of the L-DED samples listed in Table 6 (Reprinted with permission from [94]).

3.2.4. Corrosion Behavior of DED-Fabricated Cu-Ni Alloys

Guo et al. [85] conducted polarization and electrochemical impedance spectroscopy (PDP and EIS) measurements on the WAAM-fabricated Cu-Ni alloy (see Figure 46). The PDP results indicated the formation of a passive layer on the surface of the sample, as evidenced by the stabilization of the anodic current over a wide range of potentials. A sudden increase in the current density was observed at a certain polarization potential, indicating a breakdown in the passive film, which is known as pitting corrosion [85]. Their EIS results also indicated the formation of a high-impedance passive film on the surface, confirming the excellent corrosion resistance of the Cu-Ni alloy fabricated using WAAM [85]. However, the authors did not compare the corrosion test results with a reference sample.

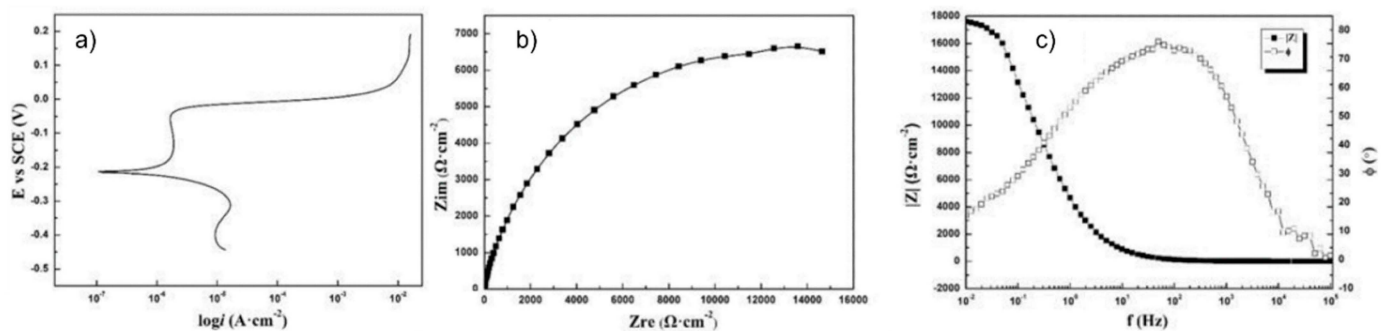


Figure 46. (a) PDP and (b,c) EIS results for the Cu-Ni alloy fabricated by WAAM process (Reprinted with permission from [85]).

4. AM of Tin-Bronzes

Of the various AM methods, L-PBF has emerged as the most common technique for 3D-printing tin-bronzes. Therefore, this section focuses primarily on a comprehensive review of L-PBF-fabricated tin-bronzes. A brief overview is also provided for the limited attempts at 3D-printing tin-bronzes using other AM techniques.

4.1. Microstructure and Mechanical Properties of L-PBF-Fabricated Tin-Bronzes versus the Cast Counterparts

Cu-10Sn bronze is considered one of the most suitable copper alloys for L-PBF fabrication since its as-solidified microstructure meets the expected mechanical properties requirements for widespread use in bearing products and thus does not require any post-printing heat treatment [103]. It has been shown that the dominant micro-constituents formed during casting and L-PBF of Cu-10Sn alloy are nearly identical to one another, that is, α -Cu(Sn) and δ -Cu₄₁Sn₁₁ in both cases, with the only exception being a minor fraction of the ϵ -Cu₃Sn phase, which only forms in the case of the additively manufactured part (see Figure 47a for the corresponding XRD patterns) [104]. However, microstructural characterizations by SEM analysis revealed different morphologies and sizes of the formed phases, which are illustrated in Figure 47b–e [104]. According to Figure 47b,c, the L-PBF counterpart exhibited α -Cu in a cored dendritic morphology, with a higher Sn concentration at the edges of the dendrites as compared to the centers. Additionally, eutectoid α + δ formed in the interdendritic regions, along with the presence of spherical pores with a maximum size of 300 nm, due to shrinkage [104]. It is notable that the equilibrium ϵ -phase normally cannot be detected at room temperature due to its slow formation. Instead, the eutectoid reaction takes place at the edges of the dendrites, which are enriched in Sn (more than 13.5 wt.%) [103]. Moreover, a comparison between SEM images taken from the AM and cast Cu-10Sn bronze at the same magnification (Figure 47d,e) displays the influence of the fabrication process on the size of the micro-constituents formed during the solidification process at different cooling rates. The finer microstructure formed in the L-PBF sample can be attributed to the faster cooling rate associated with the nature of the L-PBF process,

which has a cooling rate range of 10^2 – 10^4 K/s [105], as compared to mold casting, which has a cooling rate of around 10^2 K/s [106].

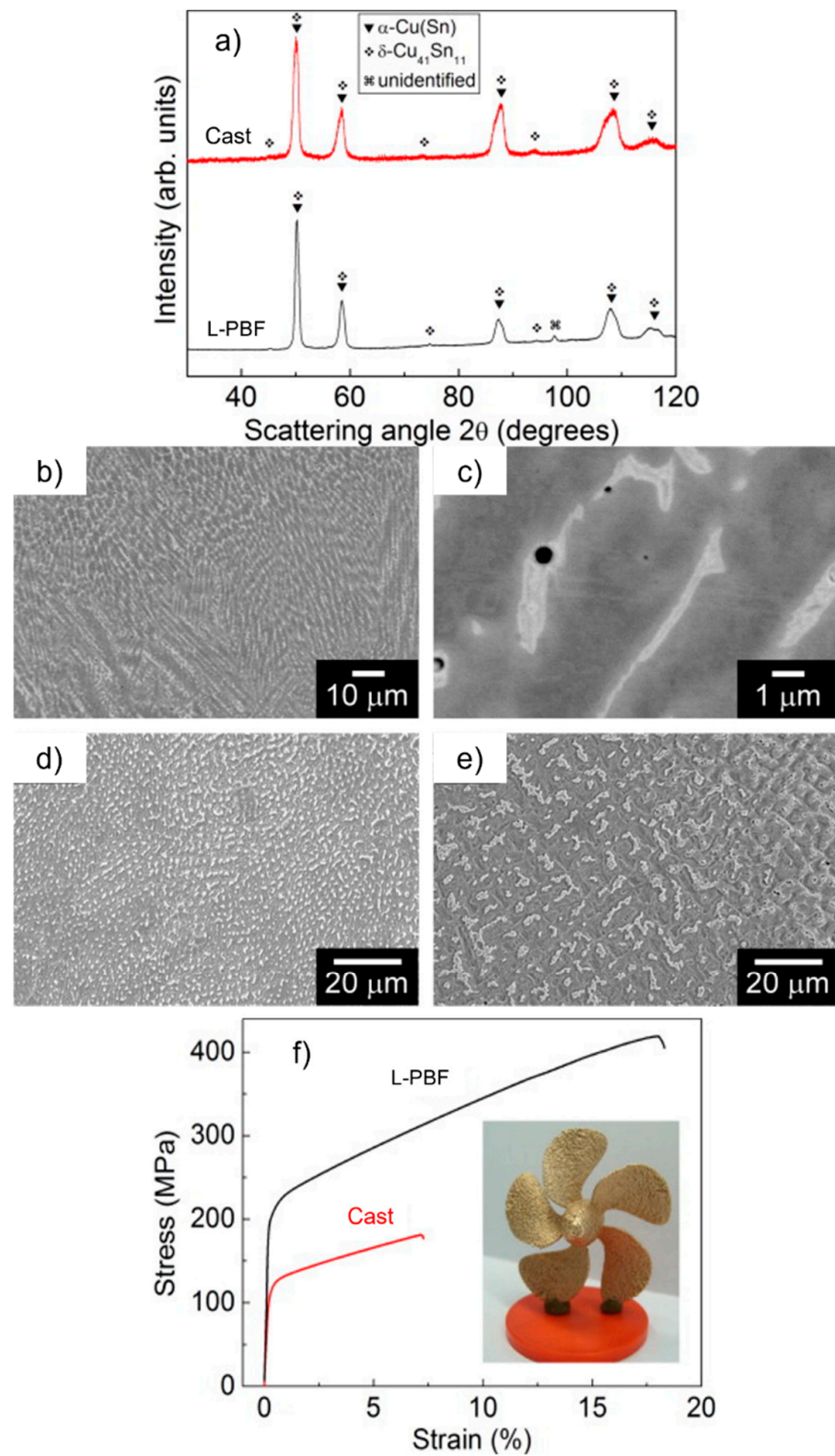


Figure 47. (a) XRD patterns of L-PBF and cast Cu-10Sn alloy, along with the corresponding SEM images taken from the microstructure of (b–d) L-PBF and (e) cast Cu-10Sn alloy, and (f) the corresponding stress–strain curves (Reprinted with permission from [104]).

As can be seen in Figure 47f, the finer microstructure of the L-PBF sample dramatically boosted the mechanical properties of the materials as compared to their cast counterparts [104]. Interestingly, the obtained mechanical properties in the L-PBF Cu–10Sn alloy are comparable to those of the cast Cu–10Sn–2Zn–1.5Fe alloy, which is reinforced by the addition of iron nano-particles [107]. This case study exemplifies an impressive application of AM technology, which improves the mechanical properties of the tin-bronze alloy to a degree that obviates the need for additional nano-particle reinforcement agents to strengthen the material.

The strengthening mechanism in the tin-bronzes can be likened to that of composite materials, in which a soft α -matrix is reinforced by a homogeneously distributed hard ($\alpha+\delta$)-eutectoid phase. This is similar to the AM-processed Al–Si alloys, characterized by a soft Al matrix reinforced by a hard residual Si network continuously distributed along the inter-cellular regions [108]. The superior mechanical properties of the AM-processed Cu–10Sn part can be attributed to its smaller distance between eutectoid particles (λ), which was measured to be approximately 2.3 μm compared to the cast material with a λ value of around 5.3 μm [104]. The effect of λ size on the mechanical properties of the material can be rationalized by the Hall–Petch equation mechanism, where a smaller λ size results in a higher density of boundaries between α -matrix and ($\alpha+\delta$)-reinforcement, which hinders the movement of dislocations [109].

Another microstructural difference between cast and L-PBF tin-bronze alloys was detected through high-magnification and high-resolution TEM images in a recent study by Karthik et al. [110]. They investigated the L-PBF of Cu–13Sn alloy and reported the precipitation of nano-size phases in the as-printed condition, shown in Figure 48a–c [110]. The precipitation of fine intermetallic phases is predictable in some Cu alloys, like Cu–Cr–Nb [111] and Cu–Cr–Zr [112], according to their phase diagrams. However, as mentioned earlier, tin-bronzes have a sluggish behavior in the formation of ϵ -phase (Cu_3Sn) precipitates in the as-solidified condition, unless they are artificially aged at around 300 °C for an extended period of time (~1000 h) [113]. This long aging process is not commercially viable, so the strengthening mechanism of the conventionally fabricated tin-bronzes is limited to modifying the casting process either by the addition of inoculant agents to refine the microstructure or by adjusting the cooling rate to achieve the desired microstructure [110]. The rapid cooling rate associated with AM processes ($\sim 10^4$ – 10^5 °C/s [114]) is also against the formation of precipitates in the as-printed structure due to the decreased atomic diffusion, which results in solute trapping and ultimately the formation of a supersaturated solid solution. However, the incremental melting process frequently reheats the previously deposited layers to 350–500 °C, which is even higher than the aging temperature (280–300 °C). This results in the precipitation of nano-scale Cu-rich secondary phases in the supersaturated α -Cu matrix. This distinct microstructural characteristic can be considered an advantage of the L-PBF process, because it enables precipitation hardening without the need for post-printing aging processes, even in the sluggish system of tin-bronze alloys [110].

In Figure 48f, Karthik et al. [110] compared the mechanical properties of the L-PBF Cu–13Sn alloy (denoted as the present study) to those of other tin-bronzes fabricated by L-PBF or other methods. It is evident that the L-PBF Cu–13Sn alloy has superior strength and ductility compared to other L-PBF or conventionally fabricated Cu alloys, which can be attributed to different factors, including the formation of nano-precipitates in the as-printed structure, among others.

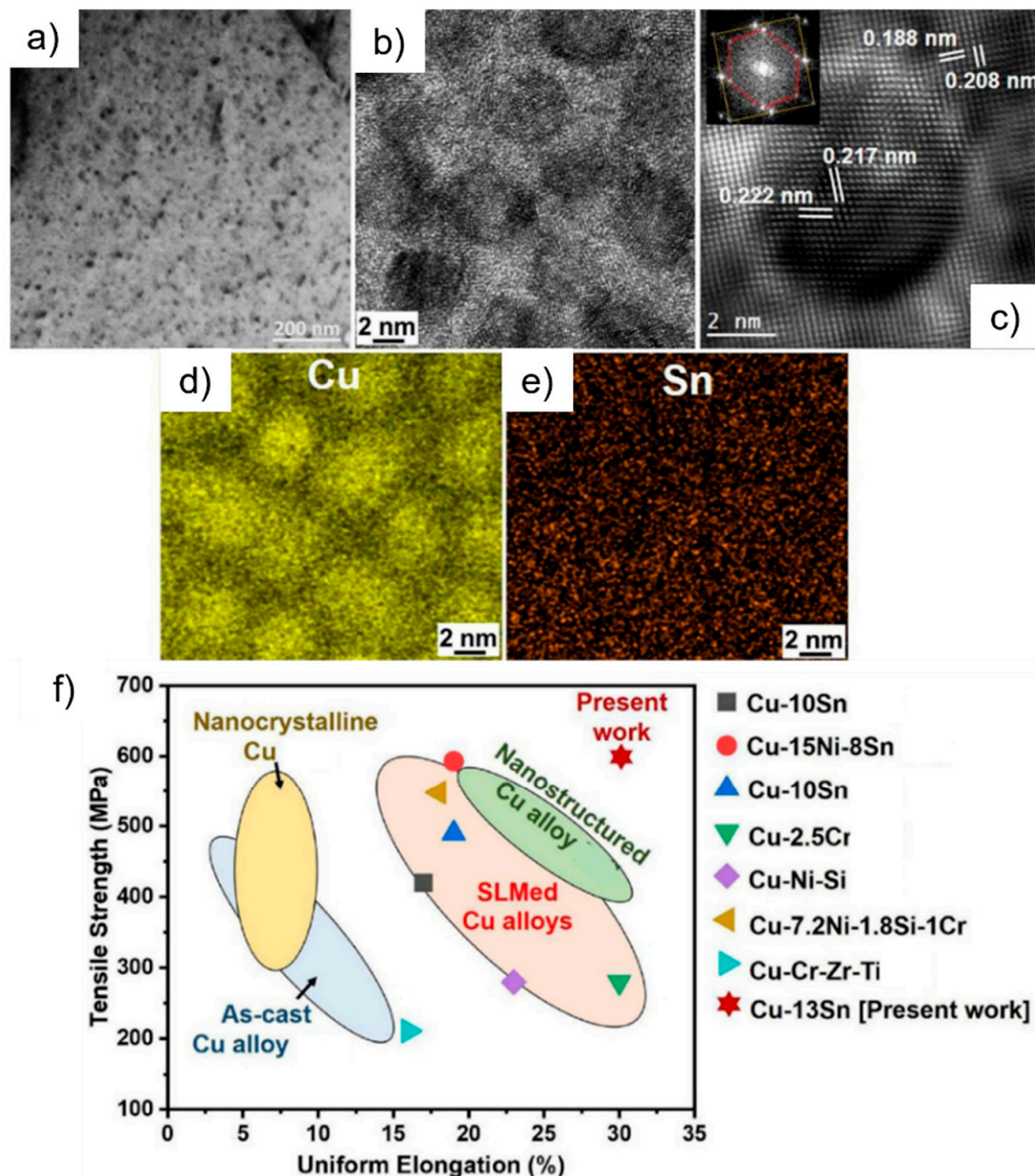


Figure 48. (a,b) Bright-field TEM images, (c) higher resolution TEM image, and (d,e) EDS elemental maps taken from L-PBF-fabricated Cu-13Sn alloy. (f) A comparison between the mechanical properties of the L-PBF Cu-13Sn alloy (denoted as the present study) and other tin-bronzes fabricated by L-PBF or other fabrication methods (Reprinted with permission from [110]).

4.2. Effect of Laser Energy Density on the Microstructure, Relative Density, and Mechanical Properties of L-PBF-Produced Tin-Bronzes

Deng et al. [115] studied the effect of laser energy on the microstructure and mechanical properties of L-PBF Cu-10Sn alloy at different energy density levels, including 210, 220, and 230 J/mm². As depicted in Figure 49, they showed that increasing the energy density up to 220 J/mm² increases the relative density and also mechanical properties, that is, strength, ductility, and hardness of the fabricated parts [115]. In particular, at the energy density of 220 J/mm² with the maximum relative density of 8.9 g/cm³, the best combination of mechanical properties was obtained, which are by far higher than those of the cast counterpart [115].

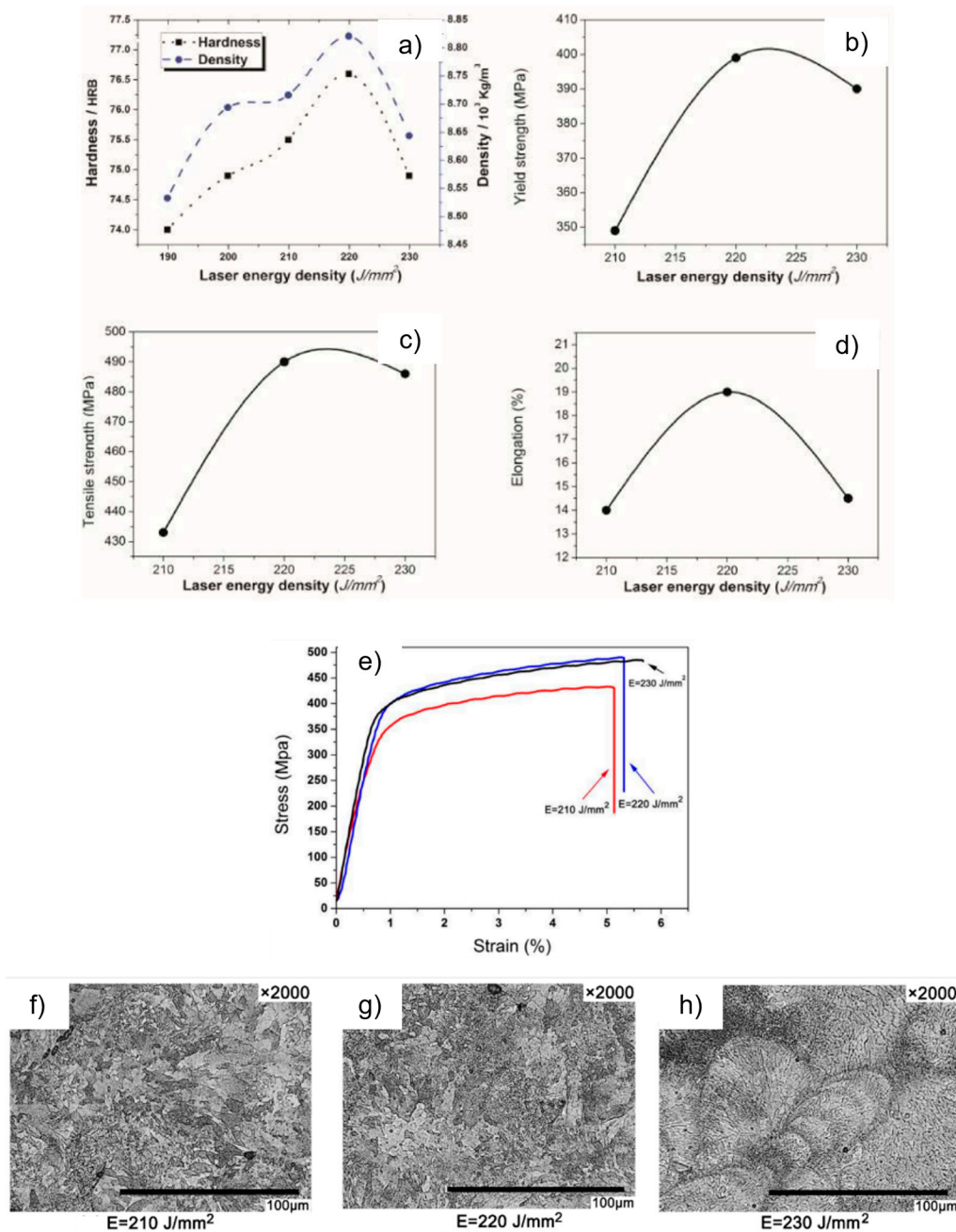


Figure 49. Effect of laser energy density on the (a) hardness and relative density, (b) yield strength, (c) tensile strength, and (d) ductility of L-PBF Cu-10Sn alloy, along with (e) the corresponding stress–strain curves. Microstructure of L-PBF Cu-10Sn parts fabricated at energy densities of (f) 210, (g) 220, and (h) 230 J/mm² (Reprinted with permission from [115]).

The improved mechanical properties achieved at the energy density of 220 J/mm² as compared to 210 J/mm² were correlated to the microstructural refinement obtained as a result of the higher energy density (see Figure 49f–h) [115]. However, the study did not provide a clear explanation for the microstructural refinement at higher energy densities. On the other hand, the reduction in mechanical properties at the highest energy density (230 J/mm²) was attributed to rapid heating, which led to insufficient energy diffusion. This caused the direct vaporization of materials prior to the melting step and also the breakup of molten metal into a row of spheres due to surface tension (known as the balling effect) [115,116].

Zhang et al. [117] also studied the effect of energy density at different laser powers on the relative density and the microstructure of the L-PBF Cu-15Ni-8Sn alloy. As depicted in Figure 50a, they showed that increasing the energy density in all laser powers improves the relative density of the final product [117]. Figure 50b–g illustrates the effect of different energy densities on the microstructure of the L-PBF Cu-15Ni-8Sn alloy [117]. Continuous and elongated overlapping melting tracks are obvious in the case of the highest energy density (142 J/mm^3) (Figure 50b,e), while reducing the energy density to 70 J/mm^3 resulted in shorter melting tracks along with a higher pore content (Figure 50c,f) [117]. A further decrease in the energy density to 35 J/mm^3 also led to disordered melting tracks with an oval morphology, along with unmelted particles and pores with a size of $\sim 20 \text{ }\mu\text{m}$. These incomplete melting characteristics could adversely affect the mechanical properties of the end-product (Figure 50d,g) [117].

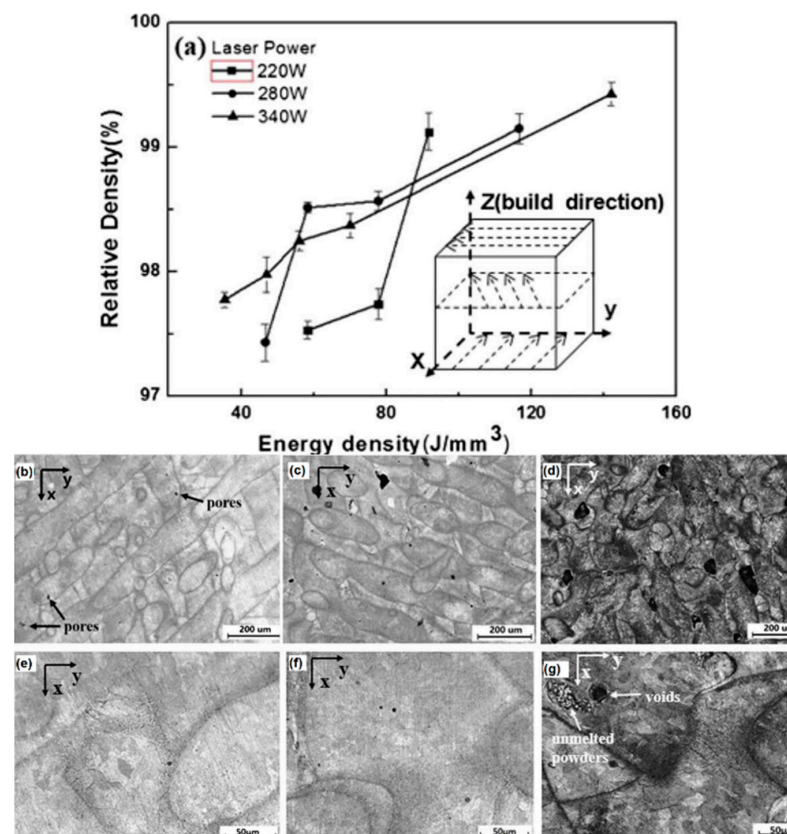


Figure 50. (a) Effect of laser energy density at different laser powers on the relative density of the L-PBF Cu-15Ni-8Sn alloy. SEM images at different magnifications taken from the microstructure of the L-PBF Cu-15Ni-8Sn alloy fabricated with a laser power of 340 W and energy densities of (b,e) 142 J/mm^3 , (c,f) 70 J/mm^3 , and (d,g) 142 J/mm^3 (Reprinted with permission from [117]).

4.3. Solidification Behavior at Different Regions of L-PBF Tin-Bronzes

The sequential melting and solidification processes, along with the effect of overlapping deposited tracks during the L-PBF process, result in different solidification modes at different regions of additively manufactured parts. Figure 51a–d schematically illustrates the forming mechanism of the Cu-15Sn alloy produced by L-PBF [8]. As can be seen in Figure 51a, during the deposition of the initial track in each layer, the heat sink is primarily governed by the substrate/previous layer rather than the surrounding powder since the thermal conductivity of the bulk material is much higher than that of the powder [8]. The resulting significant temperature gradient in the building direction, combined with the influence of constitutional undercooling on crystal growth, leads to rapid dendritic growth along the direction of the temperature gradient [8]. According to Figure 51b, during the

deposition of the adjacent track in the same layer, the overlapping area experiences a greater temperature gradient due to the presence of the adjacent solid track as compared to the molten pool center. This results in a minor degree of supercooling (see Figure 51d for more details), and consequently, a cellular structure will form in the overlapping area [8]. As shown in Figure 51c, during the deposition of the next layer, the laser irradiation remelts a part of the previous layer, which leads to epitaxial growth preferentially oriented along the building direction [8]. Figure 51e–h shows the side view of an L-PBF-fabricated Cu-10Sn alloy showing three distinct regions with different microstructures [118]. Region 1, magnified in Figure 51f, shows the boundary between two adjacent regions, which experienced cellular growth, while region 2, magnified in Figure 51g, is taken from the melt pool center, which has a much coarser dendritic structure [118]. The epitaxial growth can also be observed from one layer to the subsequent layer (region 3), which is shown in Figure 51h at higher magnification [118].

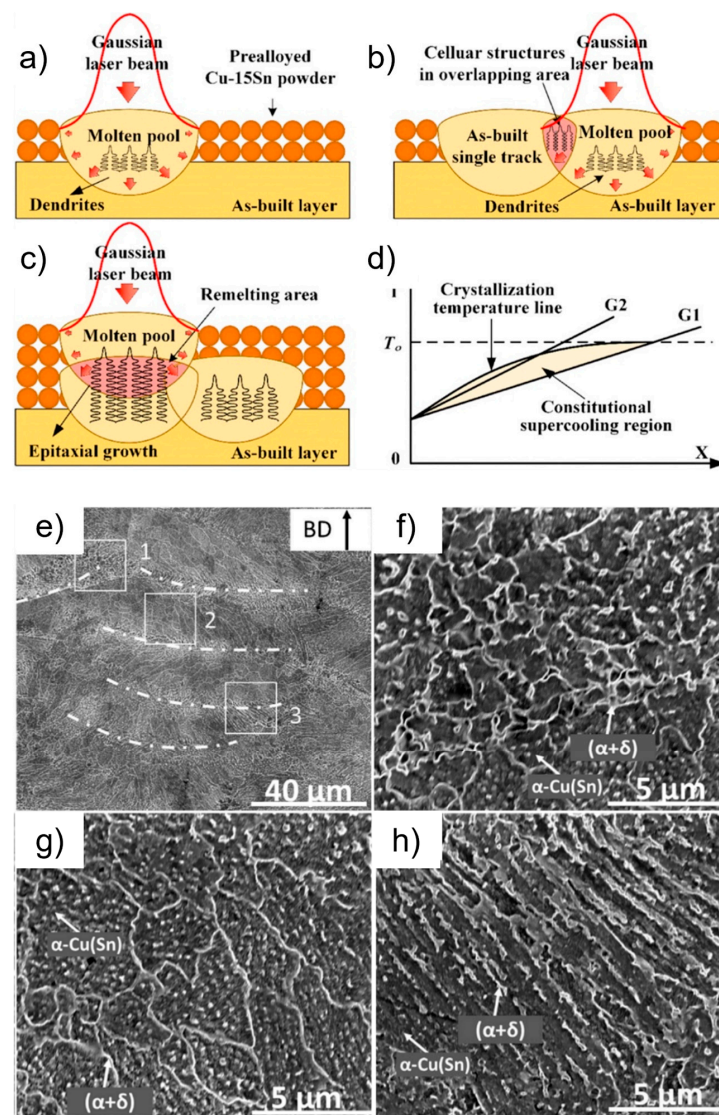


Figure 51. Schematic illustration from the formation sequence of the L-PBF-fabricated Cu-15Sn alloy: (a) the initial deposited track in each layer, (b) the adjacent deposited track in the same layer, (c) the first deposited track in the subsequent layer, and (d) the effect of temperature gradient on the supercooling [8]. SEM images showing the microstructure of an L-PBF fabricated Cu-10Sn alloy at (e) low-magnification side view and high-magnification images from (f) region 1, (g) region 2, and (h) region 3 (Reprinted with permission from [118]).

4.4. Post-Printing Annealing of L-PBF Tin-Bronzes

4.4.1. Effect of Post-Printing Annealing on the Microstructure of L-PBF Tin-Bronzes

The effect of post-printing annealing on Cu-10Sn [118] and Cu-15Sn [8] bronzes has been investigated, and both studies reported similar findings regarding microstructural characteristics and phase transformations. Zeng et al. [118] conducted a study on the phase transformations from the feedstock powder to the L-PBF part and ultimately to the annealed Cu-10Sn alloy using the XRD analysis illustrated in Figure 52. They showed that the feedstock pre-alloyed powder consisted of soft face-centered cubic (FCC) α -Cu(Sn) and hard δ intermetallic phases [118]. The as-printed Cu-10Sn bronze also contained the same phases, but the diffraction peaks of the α phases were shifted to lower angles as compared to the raw powder. For instance, the (111) peak of the α phase was shifted from 43.01° in the feedstock powder to 42.87° in the as-printed part [118], which indicates a higher lattice parameter as a result of further diffusion of Sn (as a solute) into the α phase (as the solvent) during the laser treatment [8,118].

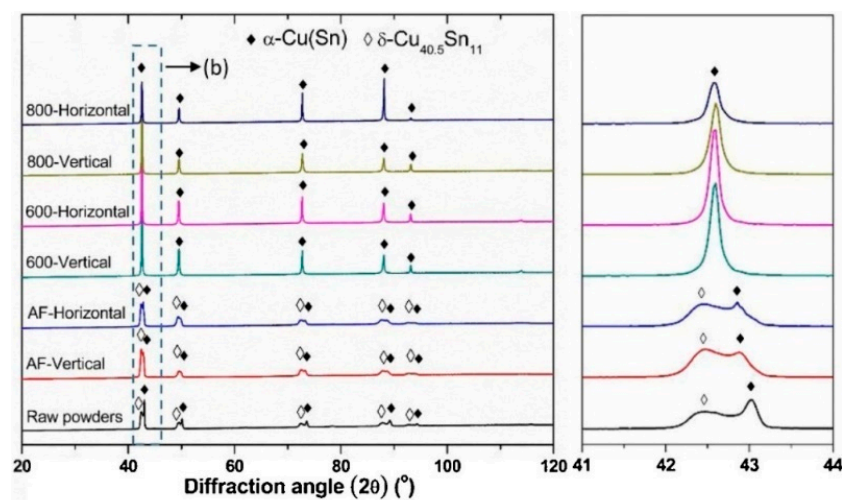


Figure 52. XRD patterns of the raw Cu-10Sn pre-alloyed powders, L-PBF part in the as-fabricated (AF) condition, and annealed samples at 600 and 800 °C in horizontal and vertical directions (Reprinted with permission from [118]).

Mao et al. [8] detected the diffraction peak of CuO at about $2\theta = 38.3^\circ$ in the L-PBF Cu-15Sn (see Figure 53a), indicating the interaction between Cu and oxygen during high energy laser treatment, while the oxygen content remained low during the L-PBF process. In both L-PBF Cu-10Sn [118] and Cu-15Sn [8] alloys, the diffraction peaks of δ were eliminated after annealing treatment (see Figures 52 and 53a). In addition, further shift of the α -Cu(Sn) (111) peak to a smaller angle in the annealed samples confirms additional diffusion and solubility of Sn as substitutional atoms in the crystal structure of Cu atoms, resulting in a further increase in the lattice parameter of the Cu matrix [119]. The narrower peaks of α -Cu(Sn) in the annealed samples also demonstrate considerable grain growth and more compositional homogenization during the post-printing heat treatment [8,118].

The microstructural variations in the as-printed Cu-15Sn bronze and the annealed sample at 600 °C are shown in Figure 53b–g [8]. The low-magnification SEM image in Figure 53b taken from the top view of the as-printed Cu-15Sn samples shows a very fine microstructure, which is attributed to the rapid cooling rates during the laser treatment [8]. Similar to the observations reported by Zeng et al. [118], a cellular structure can be seen in the overlapping regions (see Figure 53c), while the melt pool centers consist of a dendritic structure (see Figure 53e). In addition, the side view of the Cu-15Sn sample depicted in Figure 53d shows the directional epitaxial growth along the building direction, which is also in agreement with observations by Zeng et al. [118] in the case of L-PBF of the Cu-10Sn alloy. The as-printed Cu-15Sn bronze sample (see Figure 53b–e) [8] also exhibits a

dual-phase structure comprising of α -Cu(Sn) and δ -Cu₄₁Sn₁₁. Nevertheless, the annealing process resulted in the decomposition of δ -Cu₄₁Sn₁₁, as evidenced in Figure 53f [8]. The side view of the annealed L-PBF Cu-15Sn bronze illustrated in Figure 53g also shows the coarsening of the elongated grains in this sample [8].

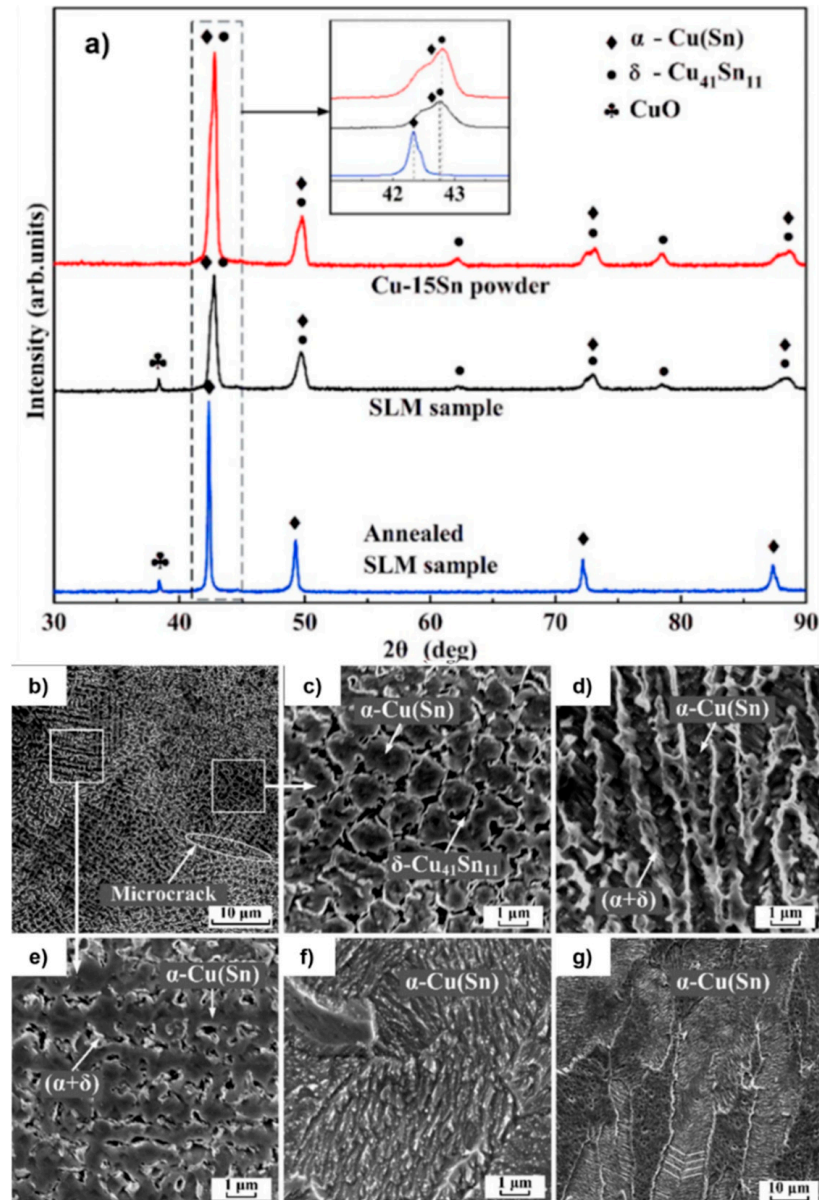


Figure 53. (a) XRD patterns of the raw Cu-15Sn pre-alloyed powders, the L-PBF-fabricated part, and the annealed sample at 600 °C for 4 h, along with the (b–e) microstructure of the as-printed and (f,g) annealed L-PBF Cu-15Sn samples (Reprinted with permission from [8]).

The EBSD analysis of the as-printed and annealed L-PBF Cu-10Sn samples also confirmed the grain coarsening during the post-printing annealing process [118]. Figure 54a,b illustrate a complex grain structure in the as-printed Cu-10Sn samples with a mixture of equiaxed and uniaxial grains having an average grain size of ~ 2 μm. However, a noticeable change in the grain morphology was observed in the annealed samples, characterized by predominantly coarser equiaxed grains with maximum sizes of around 8 μm and ~ 120 μm for annealing temperatures of 600 °C and 800 °C, respectively [118].

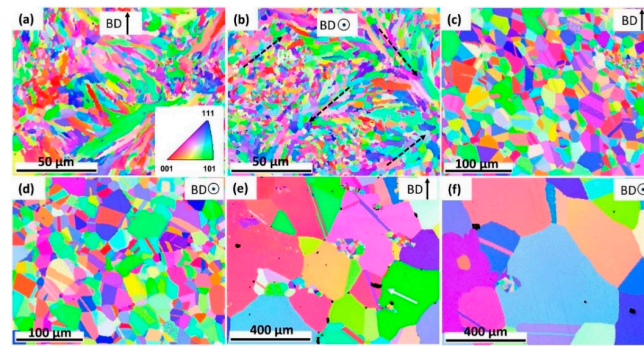


Figure 54. EBSD-IPF maps of L-PBF Cu-10Sn samples: (a) as-printed-horizontal, (b) as-printed-vertical, (c) annealed at 600 °C-horizontal, (d) annealed at 600 °C-vertical, (e) annealed at 800 °C-horizontal, and (f) annealed at 800 °C-vertical (Reprinted with permission from [118]).

4.4.2. Effect of Post-Printing Annealing on the Mechanical Properties of L-PBF Tin-Bronzes

Mao et al. [8] compared the mechanical properties of the as-printed and annealed L-PBF Cu-15Sn samples with the conventionally fabricated QSn15-1-1 bar. Their stress–strain curves and corresponding fractured surfaces are illustrated in Figure 55 [8]. Notably, a significant improvement in both strength and ductility was revealed in the L-PBF sample compared to the conventionally fabricated QSn15-1-1 bar, which is attributed to the fine-grain strengthening mechanism [8,120]. On the other hand, the annealed L-PBF Cu-15Sn samples showed increased ductility at the expense of a reduction in the material's strength [8]. The reduction in strength during annealing treatment was attributed to grain coarsening, the elimination of hard δ -Cu₄₁Sn₁₁ intermetallic phases, and residual stress relief during post-printing annealing treatment [8]. The fractured surface morphologies were in agreement with the results of mechanical testing. Evidence of cleavage steps and the brittle fracture was observed in the as-printed sample (see Figure 55b,c), while dimple-like features and plastic deformation were detected in the case of the annealed sample (see Figure 55d,e) [8].

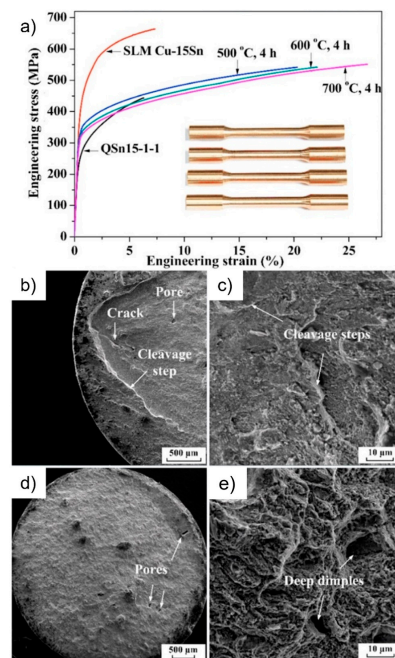
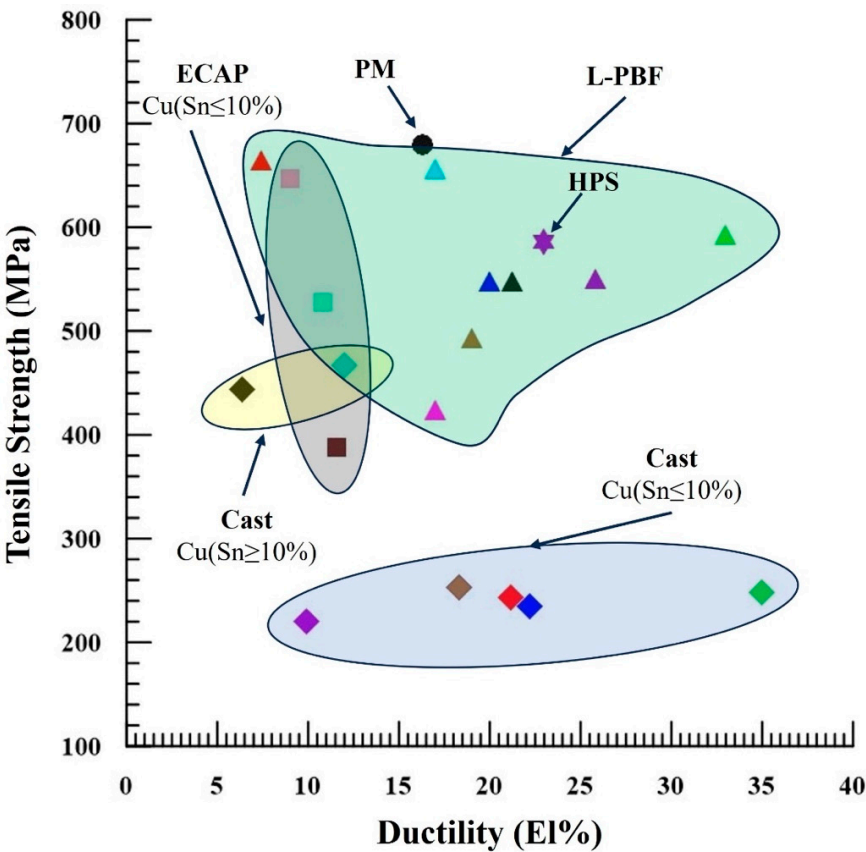


Figure 55. (a) Stress–strain curves of the conventionally fabricated QSn15-1-1 bar, as-printed, and annealed L-PBF Cu-15Sn samples at 500, 600, and 700 °C, along with the fractured surfaces of (b,c) as-printed and (d,e) annealed L-PBF Cu-15Sn samples at 600 °C for 4 h (Reprinted with permission from [8]).

To obtain a comprehensive understanding of the impact of processing and heat treatment on the mechanical properties of Cu-Sn alloys, Figure 56 presents an overview of the mechanical properties across various tin-bronze variations. These properties were derived from diverse manufacturing processes, including casting, L-PBF, LENS (laser engineered net shaping), HPS (hot press sintering), PM (powder metallurgy), and ECAP (equal channel angular pressing).



Method	Alloy	Symbol	Ref.	Method	Alloy	Symbol	Ref.
Cast	Cu-2Sn	◆	[118]	HPS	Cu-10Sn	☆	[118]
Cast	Cu-5Sn	◆	[118]	L-PBF	Cu-10Sn	▲	[104]
Cast	Cu-10Sn	◆	[118]	L-PBF	Cu-10Sn	▲	[115]
Cast	Cu-10Sn	◆	[118]	L-PBF	Cu-13Sn	▲	[110]
Cast	Cu-13Sn	◆	[110]	L-PBF	Cu-15Ni-8Sn	▲	[117]
Cast	Cu-10Sn-2Zn	◆	[107]	L-PBF	Cu-15Sn	▲	[8]
Cast	QSn15-1-1	◆	[8]	LPBF + Anneal 500 °C (4h)	Cu-15Sn	▲	[8]
ECAP	Cu-2Sn	■	[118]	LPBF + Anneal 600 °C (4h)	Cu-15Sn	▲	[8]
ECAP	Cu-5Sn	■	[118]	LPBF + Anneal 700 °C (4h)	Cu-15Sn	▲	[8]
ECAP	Cu-10Sn	■	[118]	Powder Metallurgy	Cu-15Ni-8Sn	●	[117]

Figure 56. Summary of the mechanical properties of various tin-bronzes, produced through different conventional and AM methods.

4.4.3. Effect of Post-Printing Annealing on the Thermal Properties of L-PBF Tin-Bronzes

Figure 57a shows the effect of the annealing process at 600 and 800 °C on the thermal conductivity of the L-PBF Cu-10Sn alloy measured at different temperatures [118]. The thermal conductivity of Cu-10Sn alloys can be affected by their microstructural features and the phases formed during processing. The effect of Sn content and δ phase (wt.%) on the thermal conductivity of tin-bronzes available in the literature for as-cast or annealed alloys is illustrated in Figure 57b,c [118]. The higher δ phase content and lower Sn content in the α phase result in higher thermal conductivity, as shown in Figure 57c [118]. On the other hand, the lower Sn content increases the thermal conductivity in tin-bronzes, according to Figure 57b. Therefore, the higher thermal conductivity of the AF sample compared to the annealed samples can be attributed to the presence of the δ phase and lower Sn content in the α phase, which is in contrast to the annealed samples, which consists of an Sn-rich single α phase [118].

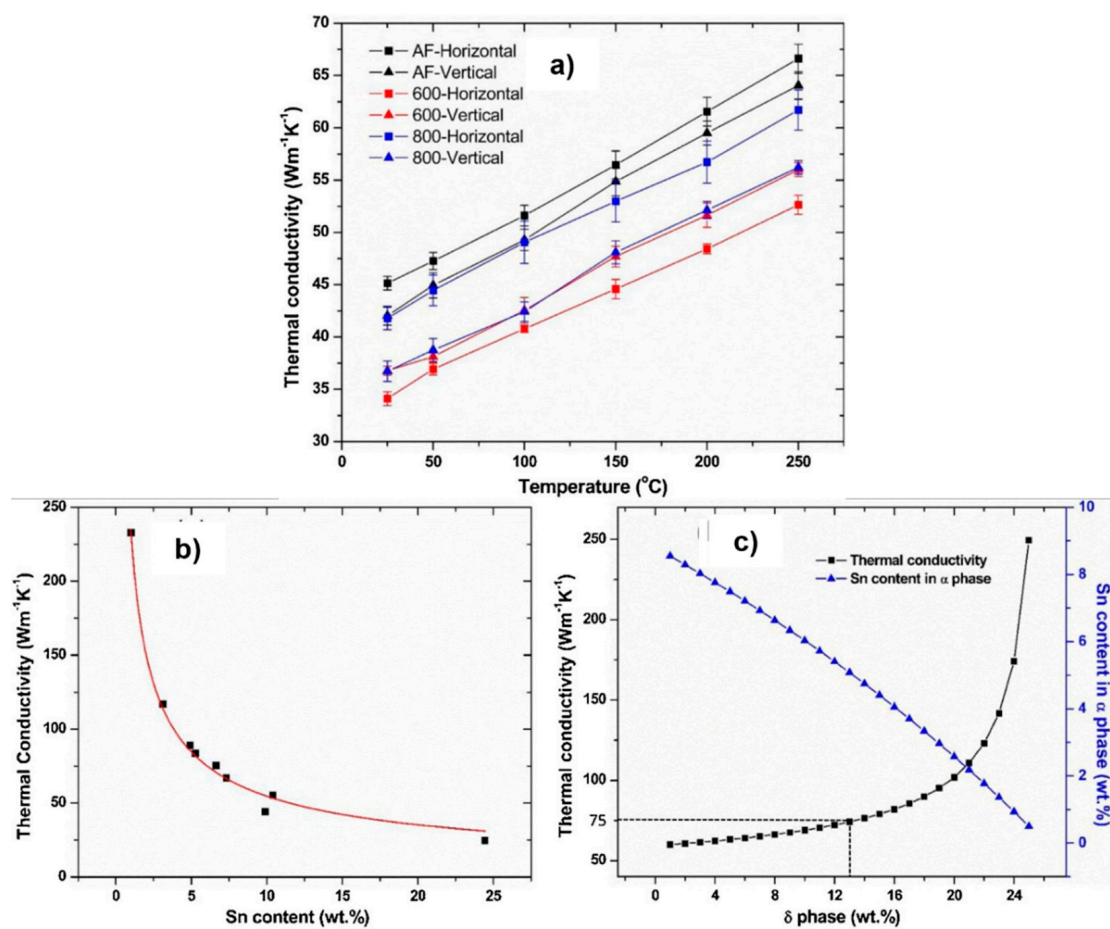


Figure 57. (a) Thermal conductivity of the L-PBF Cu-10Sn alloy in the as-fabricated (AF) and annealed samples at 600 and 800 °C. (b) Effect of Sn content on the thermal conductivity of tin-bronzes and (c) effect of δ phase percentage on the Sn content in the α phase and thermal conductivity of tin-bronzes (Reprinted with permission from [118]).

4.4.4. Effect of Post-Printing Annealing on the Corrosion Properties of L-PBF Tin-Bronzes

Zeng et al. [118] studied the effect of post-process annealing treatment on the corrosion response of the L-PBF Cu-10Sn alloy. According to Figure 58a, the weight loss of the annealed samples was found to be lower than that of the AF sample at all immersion times [118]. The corresponding XRD analysis of corroded surfaces after the immersion test (Figure 58b) revealed the formation of a protective layer of Cu_2O on both the AF and annealed samples [118].

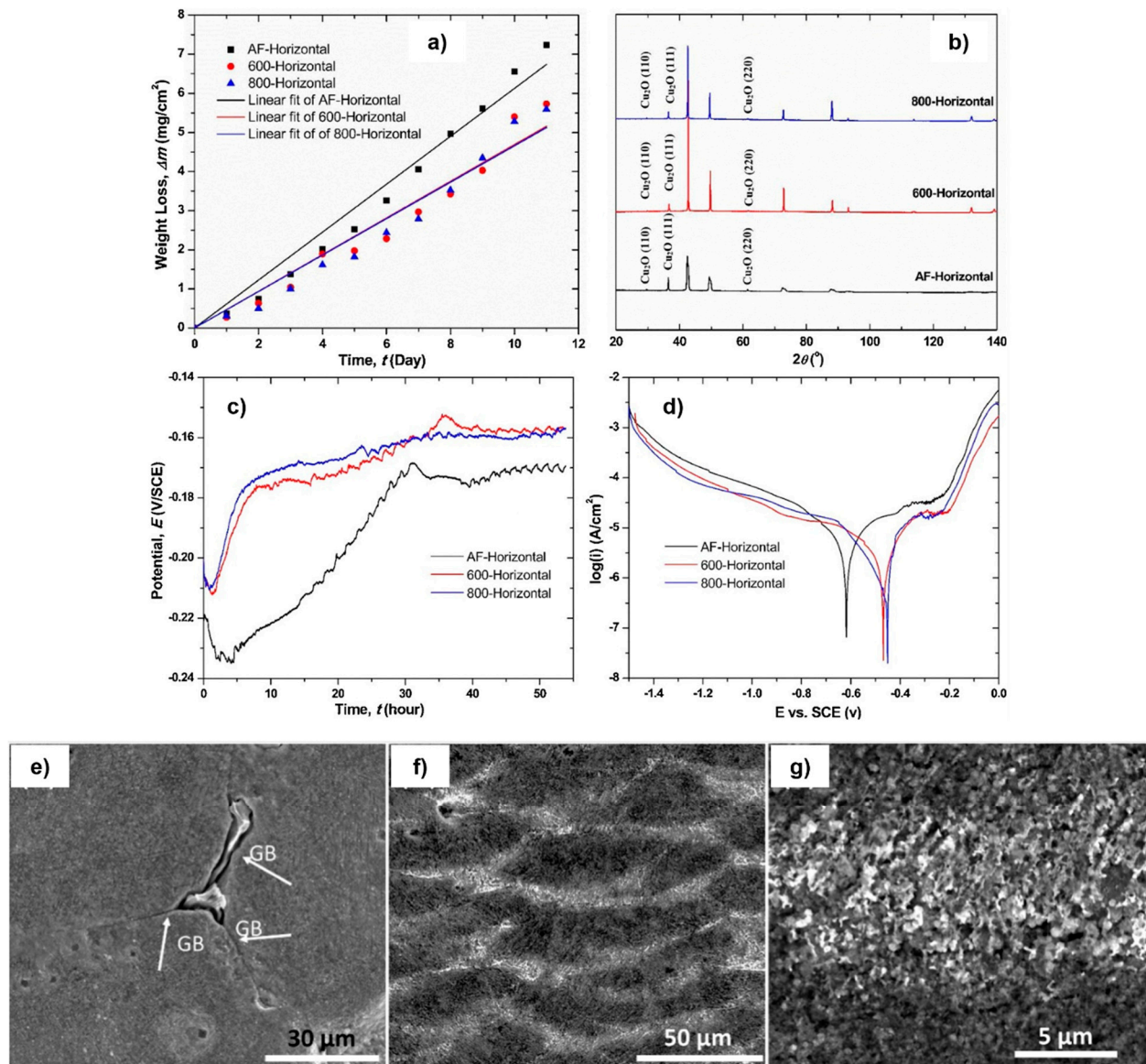


Figure 58. (a) Weight loss versus immersion time curves of AF and annealed L-PBF Cu-10Sn samples at 600 and 800 °C, and (b) XRD results of the corroded surfaces after 11 days of immersion in a 3.5 wt.% NaCl water solution. The results of (c) OCP and (d) PDP tests of the AF and annealed L-PBF Cu-10Sn samples at 600 and 800 °C. SEM images taken from the corroded surfaces of the L-PBF Cu-10Sn alloy after immersion testing of (e) the sample annealed at 800 °C and (f,g) the AF sample (Reprinted with permission from [118]).

The passive region in the potential range between -0.2 and -0.35 V for all samples affirms the formation of a protective oxide layer (Cu_2O) on the surface of the AF and annealed samples, which was confirmed by XRD analysis (Figure 58b) [118]. The results of the OCP and PDP tests (Figure 58c,d) were also in agreement with the weight loss measurements [118]. In particular, the pre-existing compounds on the surface dissolved during the first couple of hours of immersion, resulting in a potential drop, while the formation of the surface oxide layer (Cu_2O) increased the potential to an almost stable value (see Figure 58c) [118]. The PDP curves illustrated in Figure 58d also show higher corrosion current densities and lower corrosion potentials of the AF sample, revealing its lower corrosion resistance as compared to the annealed samples.

Zeng et al. [118] investigated the corrosion mechanism using SEM analysis of corroded surfaces, as depicted in Figure 58e–g. Figure 58e revealed an intergranular corrosion

attack along the grain boundaries (pointed by white arrows) of the annealed sample at 800 °C due to their higher energy compared to the adjacent areas [118], which explains the improved corrosion response of the annealed samples. In particular, the coarser structure formed during annealing decreased the grain boundary density and consequently enhanced the corrosion resistance of the material [121,122]. Micro-galvanic corrosion is another mechanism that dominates the corrosion performance of dual-phase alloys, where different phases act as local anodes and cathodes based on their resistivity [123]. In tin-bronzes, it has been shown that the δ phase exhibits a higher corrosion resistance than the α phase, resulting in micro-galvanic corrosion [29,124]. The decomposition of the δ phase during post-printing annealing of L-PBF tin-bronzes deactivates the micro-galvanic corrosion and subsequently improves the electrochemical stability of the material [118]. The white and dark regions formed on the corroded surface of the AF sample are an indication of micro-galvanic corrosion arising from the presence of α and δ phases in the microstructure of the material, as shown in Figure 58f,g [118].

4.5. AM-Fabricated Bimetal Tin-Bronzes and Dissimilar Metallic Materials

AM offers a unique capability of fabricating multi-material structures with a wide range of applications in different engineering service conditions where distinct properties are required at different positions of a specific component [39,125–127]. Figure 59 summarizes the different AM methods used for producing bimetallic materials, outlining the common advantages and disadvantages associated with each method.

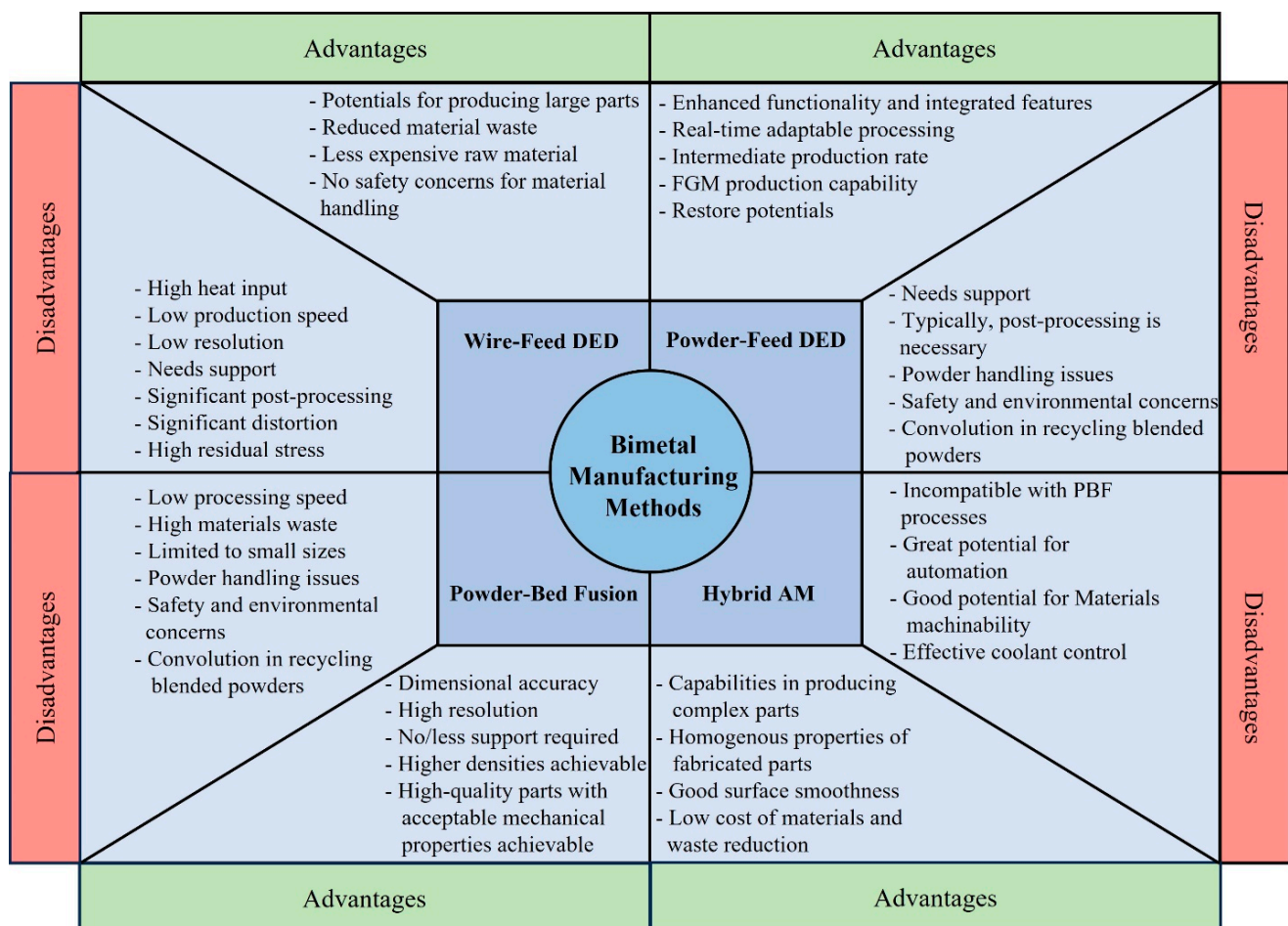


Figure 59. The pros and cons of different AM methods employed in bimetallic material fabrication [39,128–133].

4.5.1. AM of Bimetallic Cu10Sn-Ti6Al4V Structure Using the L-PBF Technique

Titanium alloys have a great combination of properties, including low density, high specific strength, and good corrosion resistance, making them attractive materials for the aerospace industry for the fabrication of engine parts, load-bearing structures, and landing gears [134]. However, the high cost of Ti alloys has led to interest in producing bimetallic components using Ti and other metallic materials, such as stainless steel, Al, and Ni [134]. One challenge in producing bimetallic components of Ti is poor solid solubility and consequent formation of brittle intermetallic phases, such as Fe_2Ti [135], Ni_3Ti [136], and Ti_3Al [137], due to the difference in crystal structure between Ti and other elements. To address this, Cu alloys can be added as an interlayer to prevent the diffusion of Ti and the development of brittle intermetallic phases [138].

Wei et al. [139] studied the bonding mechanisms of Cu-10Sn (CuA) to Ti6Al4V (TiA) during the L-PBF process using different build strategies, including direct bonding, remelting, and the production of an FGM interlayer, which are schematically illustrated in Figure 60a–c. According to the macrostructural analysis of the interface of Cu10Sn-Ti6Al4V (Figure 60), the direct bonding strategy and FGM methods resulted in apparent delamination, while no obvious cracks were formed in the sample processed using the remelting strategy [139].

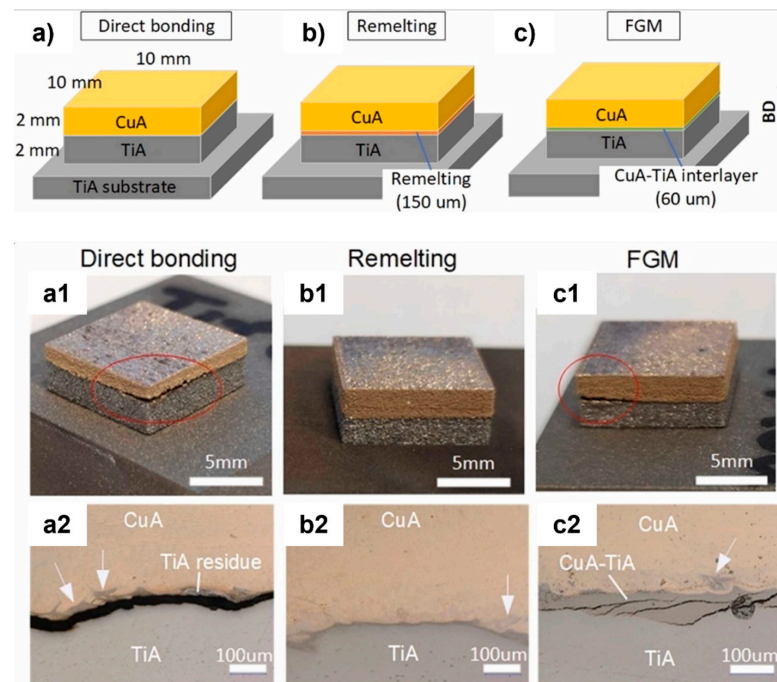


Figure 60. (a–c) Schematic illustration of the L-PBF Cu10Sn-Ti6Al4V bimetallic structure with different interface processing strategies. Cross-section of L-PBF Cu10Sn-Ti6Al4V bimetallic structure fabricated using (a1,a2) direct bonding strategy, (b1,b2) remelting method, and (c1,c2) FGM strategy (Reprinted with permission from [139]).

The Ti6Al4V side was characterized by acicular α' martensite (see Figure 61), and the Cu10Sn side was composed of α and $(\alpha + \delta)$ -eutectoid phases (see Figure 61(b2–b4)) [139]. In the case of direct bonding, a thin reaction zone was formed at the interface with a different morphology from that of the Cu10Sn and Ti6Al4V sides (see Figure 61(c2)) [139]. According to Figure 61(c1,c3), no bonding was observed between the reaction zone and the subsequently deposited Cu layer, while a sound interface was detected between the Ti side and the reaction zone [139]. On the other hand, the remelting technique resulted in a sound interface between the Cu and Ti sides due to the excessive heat generated during the process, which transitioned to keyhole mode and acted as anchors fixing the Cu side

on the Ti side, as shown in Figure 61(d1–d3) [139]. In the case of the FGM technique, some unmelted Ti powders were observed in the interlayer shown by the white arrows in Figure 61(a3,e2) [139]. The direct bonding technique resulted in a narrow Ti-Cu reaction zone with less than 10 μm thickness and the separation of the Cu part from the preprinted Ti layer [139]. The FGM method led to the formation of brittle intermetallic phases between Ti and Cu, such as TiCu , Ti_2Cu_3 , Cu_3Ti , and Cu_4Ti_3 , with a hardness of more than 1000 HV, resulting in cracks and delamination of the Cu side from the Ti side [139]. However, remelting of the interfacial bonding between Ti and Cu parts, along with a few initial layers of the Cu side, resulted in a keyhole mode, leading to more laser absorption, a higher temperature of the HAZ, and better mixing of Ti and Cu atoms, ultimately resulting in defect-free bonding between the two sides of the bimetallic material [139].

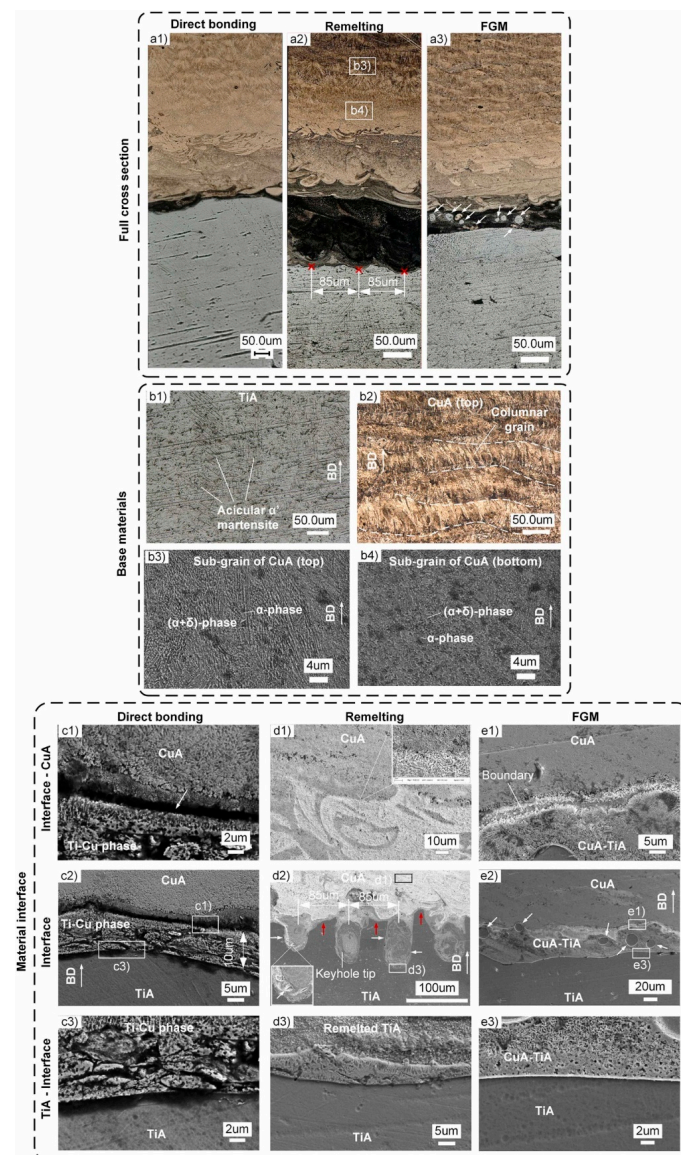


Figure 61. (a1–e3) Microstructural features of the interface between Cu10Sn and Ti6Al4V sides of the bimetallic structure fabricated by L-PBF with direct bonding strategy, remelting method, and FGM techniques (Reprinted with permission from [139]).

4.5.2. AM of Bimetallic Cu10Sn- 316L Structure Using the L-PBF Technique

Stainless steel-bronze bimetallic structures are extensively employed in different industries, such as automobile manufacturing, nuclear power, and power generation.

These structures combine high stiffness, hardness, and strength with good corrosion resistance from stainless steel and excellent heat conduction and wear resistance from bronze [140,141]. Bimetallic components of steel and bronze were traditionally fabricated using diffusion welding [142], laser welding [143], and explosive welding [144]. However, in 2019, Chen et al. [145] investigated the fabrication of the 316L/CuSn10 bimetallic structure using the L-PBF process. Figure 62a,b shows the L-PBF bimetallic 316L/CuSn10 structure along with the schematic illustrations of the interlayer staggered scanning strategy and island scanning strategy [145].

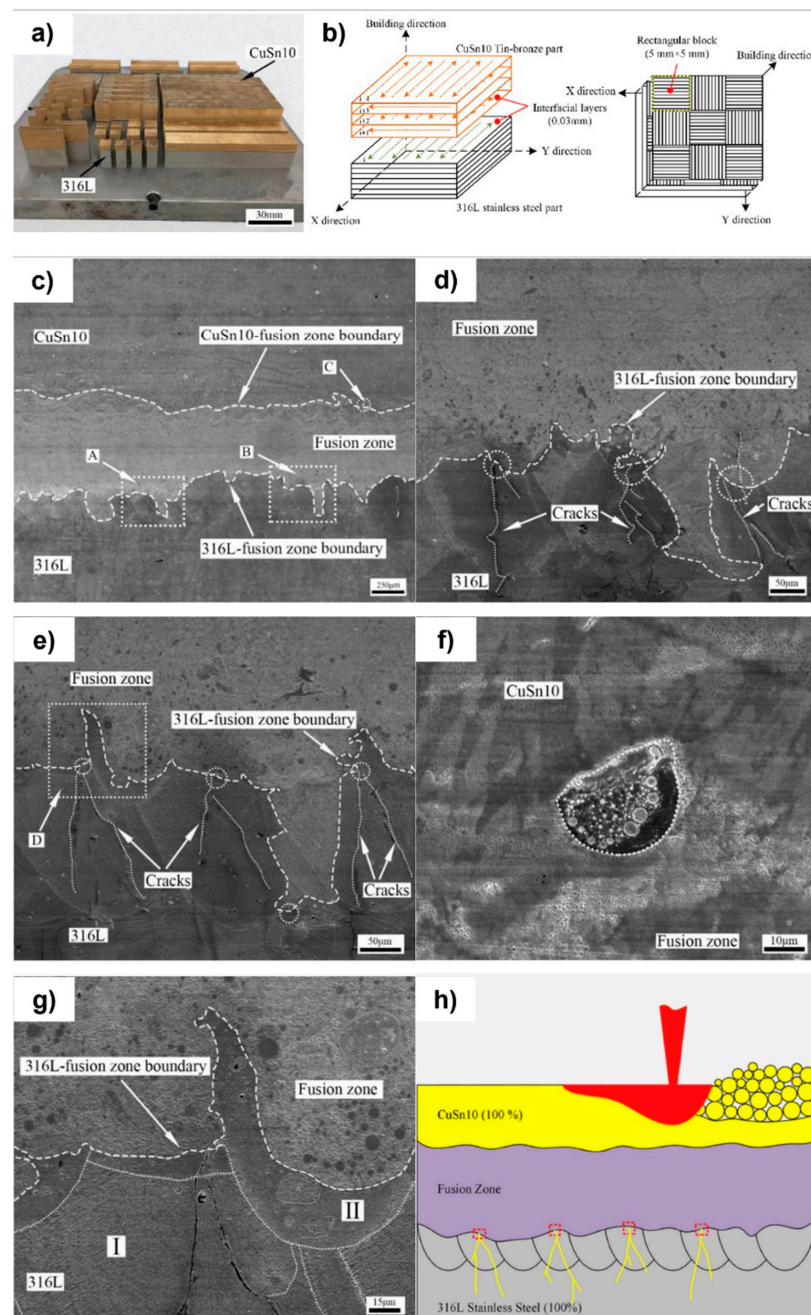


Figure 62. (a) L-PBF bimetallic 316L/CuSn10 structure and (b) the schematic illustrations of the interlayer staggered scanning strategy (left) and island scanning strategy (right). (c) The entire interfacial microstructure of L-PBF bimetallic 316L/CuSn10, (d) magnified area A of (c), (e) magnified area B of (c), (f) magnified area C of (c), (g) magnified area D of (e), and (h) a schematic illustration of the nucleation site and propagation direction of the cracks (Reprinted with permission from [145]).

According to the interfacial microstructure of L-PBF bimetallic 316L/CuSn10 shown in Figure 62c–h, some micro-cracks were formed at the boundary of the fusion zone (bonding region) and 316L side, which are indicated as square regions of A and B in Figure 62c [145]. The propagation of some dendritic cracks towards the 316L side is also observable in the higher magnification images shown in Figure 62d,e,g [145]. Figure 62h schematically shows the nucleation site and propagation direction of the cracks, which are essentially perpendicular to the fusion zone towards the 316L part, attributed to the higher thermal conductivity of copper, causing a considerable heat concentration in the fusion zone, and excessive thermal stresses [145]. Although no crack was formed on the copper side, large unmelted steel powders were observed in the CuSn10 region (see Figure 62f) [145].

The XRD results of each side (CuSn10 and 316L) along with the interface region of the L-PBF bimetallic 316L/CuSn10 structure are shown in Figure 63 [145]. The bronze side was found to consist of Cu(Sn) solid solution and $\text{Cu}_{41}\text{Sn}_{11}$ intermetallic phases, while the 316L side showed high-intensity peaks of γ -Fe (austenite phase) [145]. On the other hand, the XRD pattern of the interface region was characterized by a combination of these peaks, with those associated with bronze having a higher intensity than those of stainless steel due to the considerable residual stress in the 316L region [145]. Interestingly, no Fe/Cu intermetallic phases were formed in the interface region, which is beneficial to the strength of the bonding between the two materials [145,146].

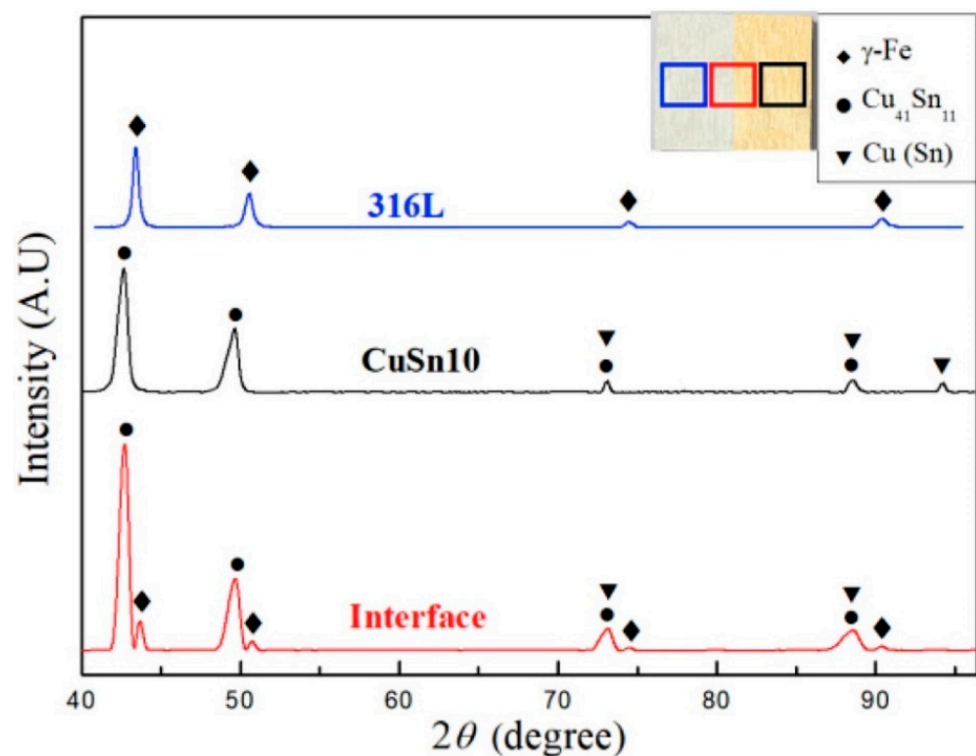


Figure 63. XRD patterns taken from the L-PBF bimetallic 316L/CuSn10 structure in different regions, including the 316L side, CuSn10 side, and interface region (Reprinted with permission from [145]).

The results of the tensile tests showed that both horizontally and vertically combined bimetallic components had lower strength and ductility compared to the single 316L SS and CuSn10 samples (see Figure 64) due to the propagation of the pre-existing dendritic cracks during the uniaxial tensile loading [145]. However, the tensile strength of the L-PBF bimetallic 316L/CuSn10 was found to be higher than the joint strength of conventionally processed steel/copper structures reported in the literature [145,147–149].

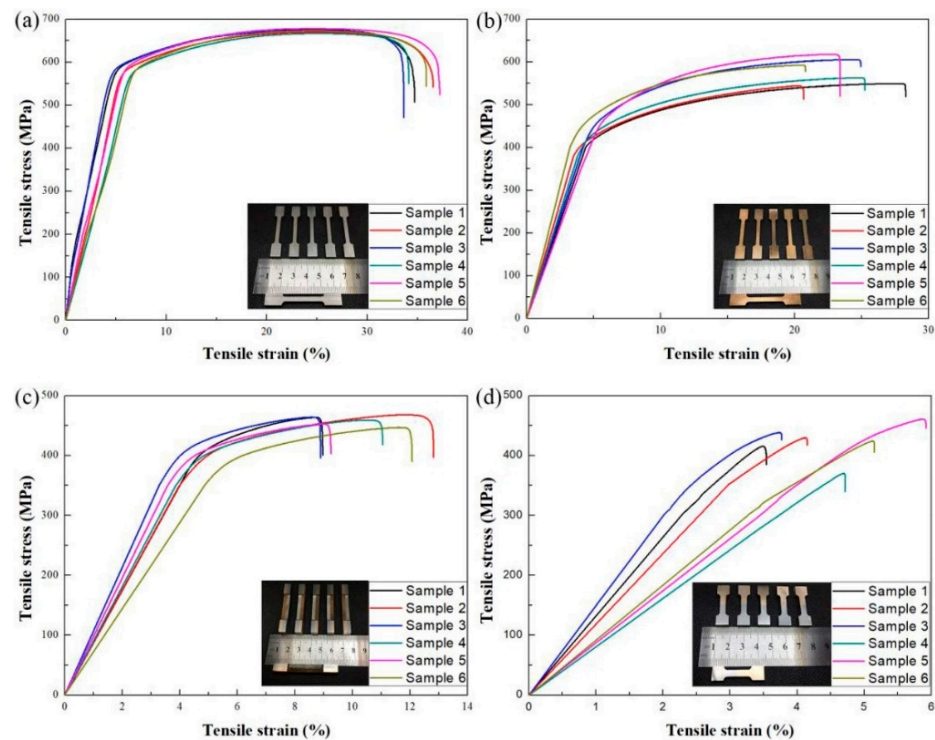


Figure 64. Stress–strain curves of single parts of (a) 316L SS, (b) CuSn10, and (c) horizontally combined and (d) vertically combined 316L/CuSn10 bimetallic materials fabricated by L-PBF (Reprinted with permission from [145]).

4.6. AM of Tin-Bronze Using Alternative Processes

Only one study in the literature has investigated the 3D printing of tin-bronzes using extrusion-based AM (also known as fused deposition modeling or FDM) of CuSn10 parts [150]. In this AM method, metallic powders are mixed with polymeric binders to improve the viscosity of the feedstock material during the printing process [150]. After printing, a post-printing debinding process is required to remove the polymeric binder, followed by a sintering process in an Al_2O_3 crucible to improve density [150]. Figure 65 provides a schematic illustration of the FDM process [150].

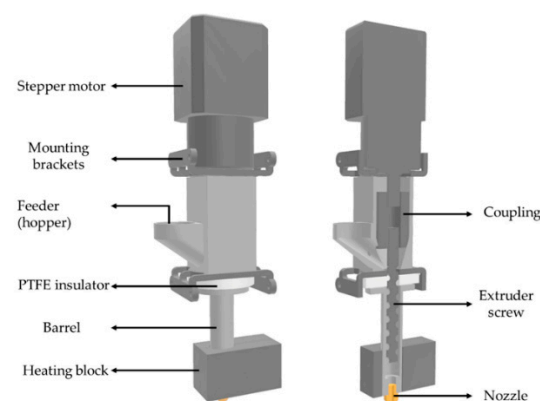


Figure 65. A schematic illustration showing the FDM process (Reprinted with permission from [150]).

The authors of this study investigated the effect of printing speed and layer thickness on the density and mechanical properties of the FDM-produced CuSn10 bronze [150]. It was revealed that reducing the layer thickness eliminated the formation of voids in the as-printed condition, while increasing the print speed led to a slight reduction in the density of the as-printed parts. The authors also noted that reducing the layer thickness enhanced

the density of the FDM-fabricated tin-bronzes, resulting in a more even and seamless transition from one layer to the next [150]. Following the process optimizations, the authors also studied the effect of post-printing sintering on the mechanical response, shape stability, porosity level, and density of the FDM-fabricated parts [150]. It was reported that raising the sintering temperature improved both the density and strength of the material as compared to the as-printed condition [150]. According to Figure 66a–c, an increase in sintering temperature caused the morphology of the pores to change from irregular to rounded shape and the porosity level to decrease from $19.33 \pm 3.91\%$ to $4.45 \pm 2.89\%$ [150]. The results of mechanical testing were also consistent with the microscopy analysis, as higher sintering temperatures improved the combination of strength, ductility, and toughness [150]. Figure 66d depicts the stress–strain curves of the FDM-produced Cu-10Sn bronze sintered at temperatures of 850 °C, 875 °C, and 900 °C [150].

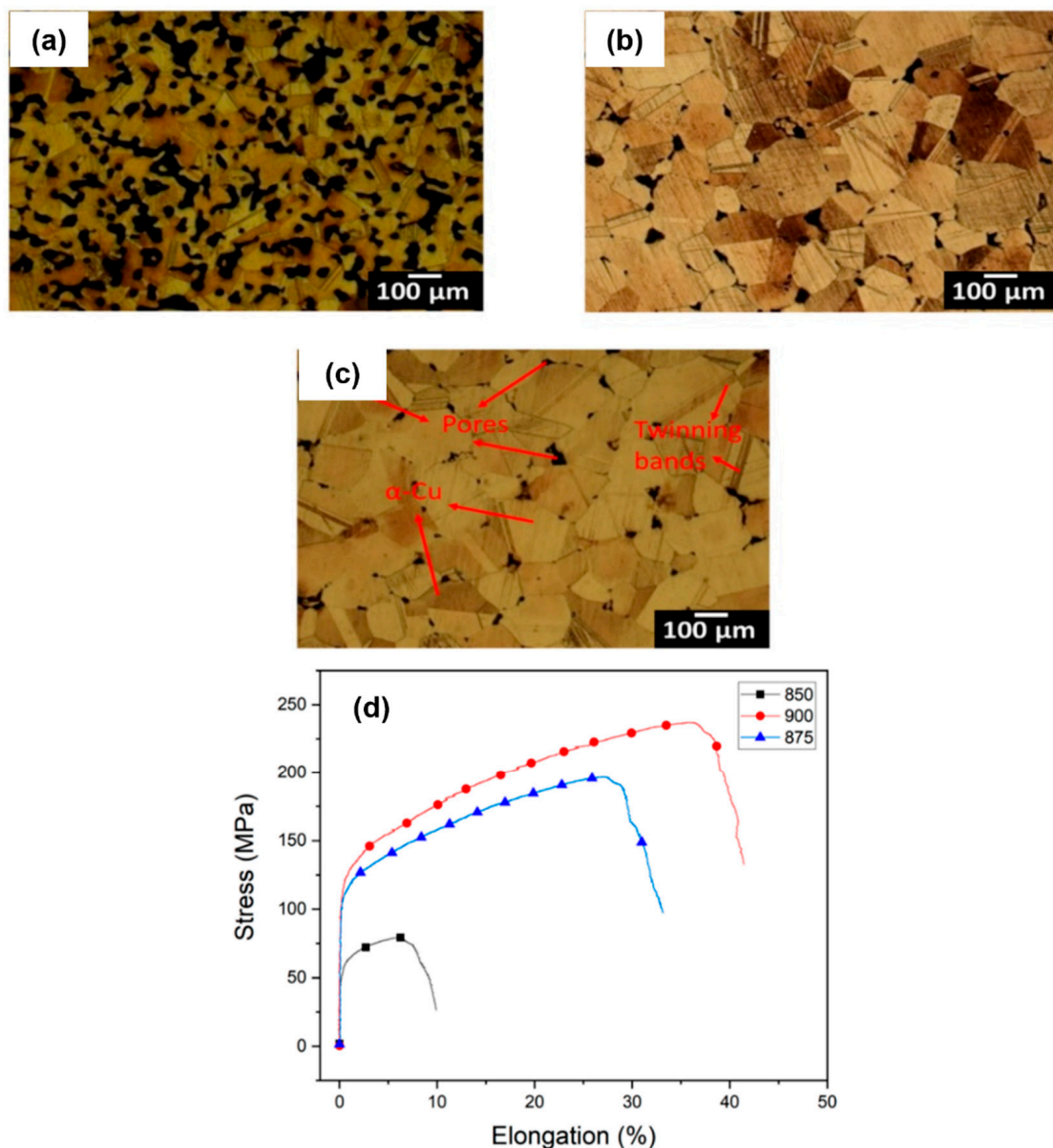


Figure 66. Optical microscopy images showing the porosity distribution in FDM-fabricated Cu-10Sn bronze sintered at temperatures of (a) 850 °C, (b) 875 °C, and (c) 900 °C. (d) Stress–strain curves of the FDM-produced Cu-10Sn bronze sintered at temperatures of 850 °C, 875 °C, and 900 °C (Reprinted with permission from [150]).

5. AM of NAB Alloys

As stated earlier, NAB alloys are primarily used in the marine industry, where most of the parts are large in size. Therefore, the most appropriate AM method for the production of NAB alloys is the WAAM technique, although some research has been conducted on other AM techniques, for example, L-PBF, L-DED, and EBM, for the fabrication of NAB alloys. Table 7 provides an overview of all the existing literature on the AM of NAB alloys. Moreover, Figures 67 and 68 provide a summary of the microstructural characteristics and mechanical properties of NAB alloys manufactured through different conventional and AM methods. These visuals enable a quick comparison of the diverse impacts of AM techniques on the microstructure and mechanical properties of the NAB alloys.

Table 7. A summary of all the available studies on the AM of NAB alloys.

AM Process	Alloy	Pre/Post/In-Situ Treatments	Ref.
WAAM (CMT)	AWS 5.1 ERCuNiAl, Cu-5.2Ni-8.8Al-3.3Fe		[22]
WAAM	AWS A5.7 ERCuNiAl Cu-9Al-4Ni-4Fe-1Mn (C95800)		[151]
WAAM	Cu-9Al-4Fe-4Ni-1Mn		[152]
WAAM	Cu-9Al-4.5Ni-3.5Fe-1.3 Mn	- Post-process homogenization at 900 °C for 2 h, followed by water quenching, and then tempering at 450, 550, 650, and 750 °C for 6 h	[153]
WAAM	Cu-9Al-4Fe-4Ni-1 Mn	- Post-heating at 350 °C for 2 h, 550 °C for 4 h, and 675 °C for 6 h	[154]
WAAM	Cu-9Al-4Ni-4Fe-1Mn	- Post-heating at 350 °C for 2 h, 550 °C for 4 h, and 675 °C for 6 h	[155]
WAAM	Cu-8Al-2Ni-2Fe-2Mn		[156]
WAAM	Cu-8Al-2Ni-2Fe-2Mn	- In-situ UVA treatment and two interpass temperatures of 100 and 400 °C	[157]
WAAM (CMT)	CuAl8Ni2Fe2M2 (SCu6327) and CuAl9Ni5 (SCu6328)		[158]
WAAM	Cu-9Al-3.5Fe-4.5Ni-1.3Mn	Post-process: - Homogenization at 900 °C for 2 h, followed by water quenching - Homogenization at 900 °C for 2 h, followed by water quenching, and then tempering at 675 °C for 6 h - Direct tempering at 675 °C for 6 h	[159]
WAAM	Bimetal: A5.7 ERCuNiAl solid NAB wire on a 316L stainless steel		[160]
WAAM	Bimetal: A5.7 ERCuNiAl solid NAB wire on a 316L stainless steel		[161]

Table 7. Cont.

AM Process	Alloy	Pre/Post/In-Situ Treatments	Ref.
WAAM	Bimetal: A5.7 ERCuNiAl solid NAB wire on a 316L stainless steel		[162]
L-PBF	NAB alloys C63000 (Cu-10.2Al-4.8Fe-5.0Ni-0.2Si) and C95800 (Cu-9.0Al-4.0Fe-4.6Ni-1.9Mn)	- Post-heating at 675 °C for 6 h	[163]
L-PBF	Cu-9Al-4Fe-3Ni	Post-heating at: - 600 °C for 1 h, followed by air cooling - 700 °C for 2 h, followed by air cooling - 850 °C for 1 h, followed by water quenching, and then heating at 720 °C for 5 h, followed by air cooling - 930 °C for 30 min, followed by furnace cooling - 980 °C for 2 h, followed by furnace cooling - 980 °C for 2 h, followed by furnace cooling to 600 °C, followed by air cooling	[164]
L-PBF	C95800 NAB alloy (Cu-9.8Al-5.2Ni-4.6Fe-0.3 Mn)	- Post-heating at 600, 700, 800, and 900 °C for 1 h	[165]
EBM	C63000 NAB alloy (Cu-9.5Al-4.2Ni-4Fe-1.2 Mn)		[166]
EBM	(Fe, Ni)Al-reinforced NAB alloy (81.1Cu- 9.5Al-4.2Ni-4.0Fe-1.2Mn)		[167]
L-DED	Bimetal: NAB on 15-5 PH stainless steel		[168]
L-DED	Bimetal: CuNi2SiCr alloy layered on a cast AlBC3 NAB alloy		[169]
L-DED	Bimetal: CuNi2SiCr alloy layered on a cast AlBC3 NAB alloy		[170]
L-DED	Cu-9Al-5Fe-5Ni		[171]

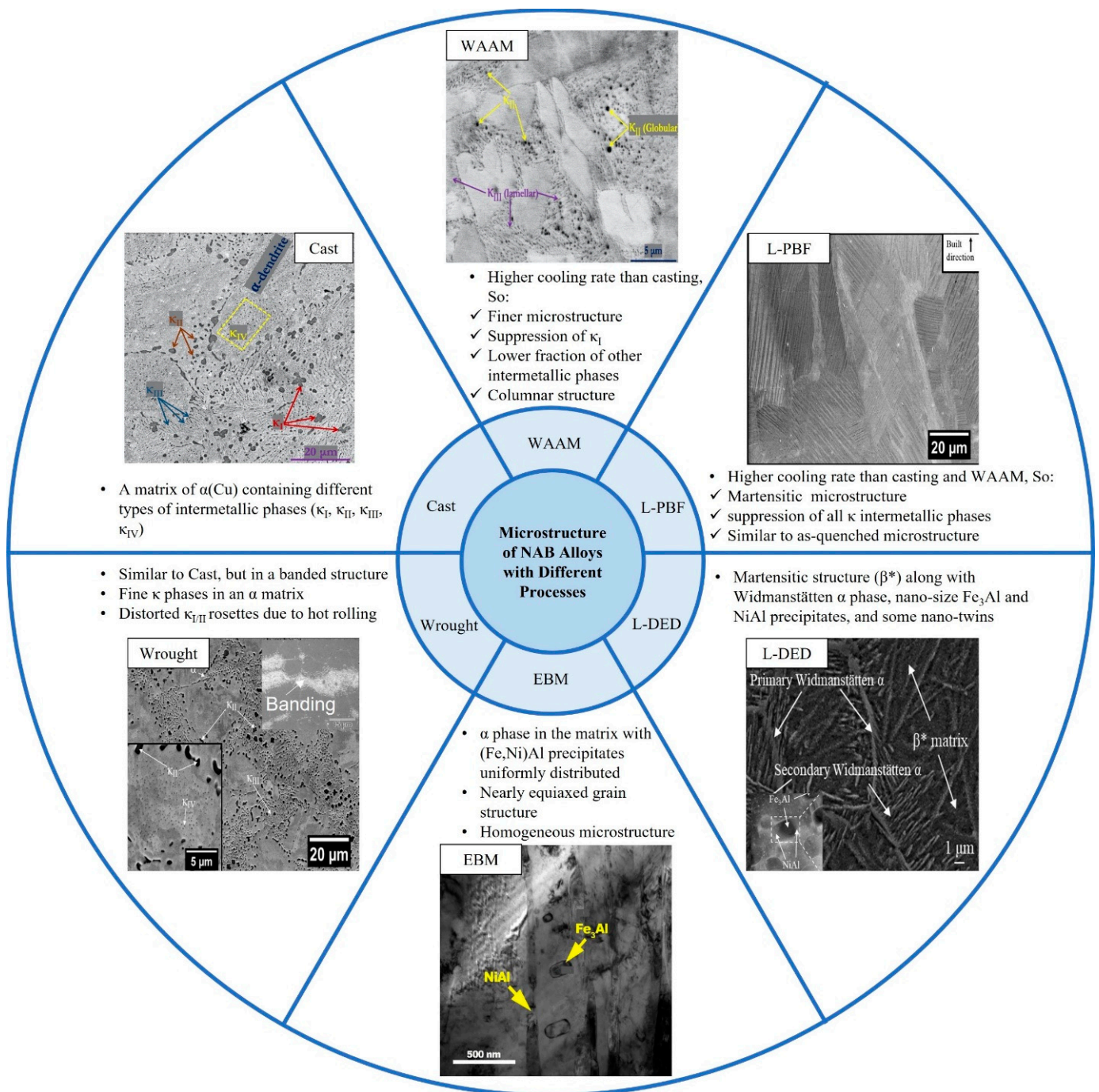
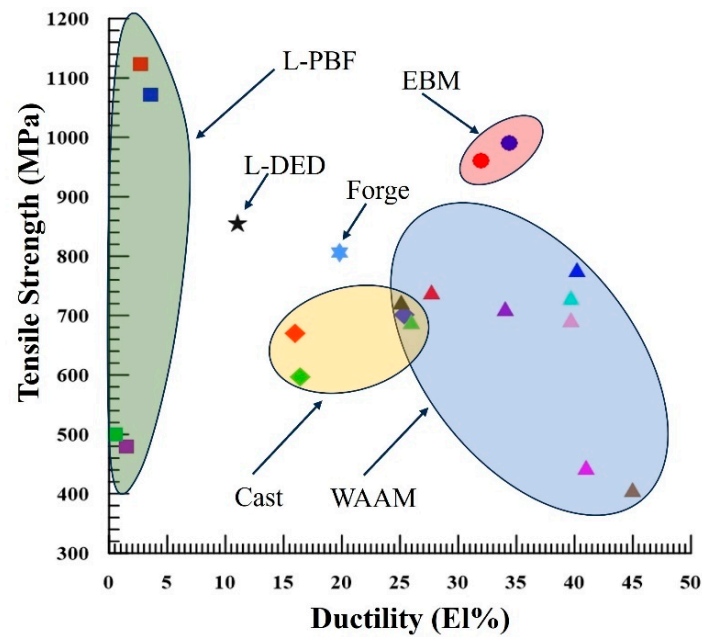


Figure 67. A summary of microstructural features observed in NAB alloys fabricated using different conventional and AM methods [19,155,165,167,171].



Method	Alloy	Direction	Symbol	Ref.	Method	Alloy	Direction	Symbol	Ref.
WAAM	Cu-5.2Ni-8.8Al-3.3Fe (AWS 5.1)	DD	▲	[22]	Cast	Cu-4.28Ni-9.11Al-3.3Fe(C63000)		◆	[22]
WAAM	Cu-5.2Ni-8.8Al-3.3Fe (AWS 5.1)	BD	▲	[22]	Cast	Cu-9Al-4Fe-4Ni-1Mn		◆	[152]
WAAM	Cu-9Al-4Fe-4Ni-1Mn	BD	▲	[152]	Cast	Cu-8.8Al-4.4Fe-5.2Ni-1.1Mn		◆	[163]
WAAM	Cu-9Al-4.5Ni-3.5Fe-1.3 Mn	DD	▲	[153]	L-PBF	Cu-10.2Al-4.8Fe-5.0Ni-0.2Si (C63000)	BD	■	[163]
WAAM	Cu-9Al-4.5Ni-3.5Fe-1.3 Mn	BD	▲	[153]	L-PBF	Cu-9.0Al-4.0Fe-4.6Ni-1.9Mn (C95800)	BD	■	[163]
WAAM	Cu-9Al-4Fe-4Ni-1 Mn	BD	▲	[154]	L-PBF	Cu-9Al-4Fe-3Ni		■	[164]
WAAM	Cu-8Al-2Ni-2Fe-2Mn	DD	▲	[156]	L-PBF	Cu-9.8Al-5.2Ni-4.6Fe-0.3 Mn (C95800)	BD	■	[165]
WAAM	Cu-8Al-2Ni-2Fe-2Mn	BD	▲	[156]	EBM	Cu-9.5Al-4.2Ni-4Fe-1.2 Mn (C63000)	BD	●	[166]
WAAM	Cu-9Al-3.5Fe-4.5Ni-1.3Mn	DD	▲	[159]	EBM	Cu-9.5Al-4.2Ni-4Fe-1.2 Mn (C63000)	DD	●	[166]
L-DED	Cu-9Al-5Fe-5Ni	DD	★	[171]	Forged	Cu-(9.5-11)Al-(4.5-5.5)Fe-(4.5-5.5)Ni-(0-0.3)Mn		★	[163]

BD = Building Direction, DD = Deposition Direction

Figure 68. An overview of the mechanical properties exhibited by NAB alloys fabricated by diverse conventional and AM methods.

5.1. WAAM of NAB Alloys

5.1.1. Microstructure of WAAM-Produced NAB Alloys

The microstructure of NAB alloys at room temperature typically includes three primary phases, that is, (i) α , a Cu-rich phase with an FCC crystal structure, (ii) β' , a martensitic phase with a $D0_3$ or B2 crystal structure, and (iii) different intermetallic phases, such as κ_I , κ_{II} , κ_{III} , and κ_{IV} , which are identified according to their chemical compositions, shapes and morphologies, distributions, and locations of formation [165].

Dharmendraa et al. [152] investigated the microstructural characteristics of a WAAM-fabricated NAB alloy (Cu-9Al-4Fe-4Ni-1Mn) and compared it with its cast counterpart. They reported that the microstructure of the cast NAB alloy consisted of an α -Cu matrix with four different types of intermetallic phases (κ_I , κ_{II} , κ_{III} , and κ_{IV}) (see Figure 69a,b), while the WAAM part exhibited a finer microstructure, suppression of κ_I , and a lower fraction of other intermetallic phases due to a high cooling rate as compared to the cast counterpart (see Figure 69c–e) [152]. However, they reported that the cooling rate during

the WAAM process was not fast enough to produce a martensitic transformation. Their further microstructural analysis using TEM and SAED (shown in Figure 70) identified the intermetallic phases as globular Fe_3Al (κ_{II}), lamellar NiAl (κ_{III}), and Fe-rich (κ_{IV}) phases.

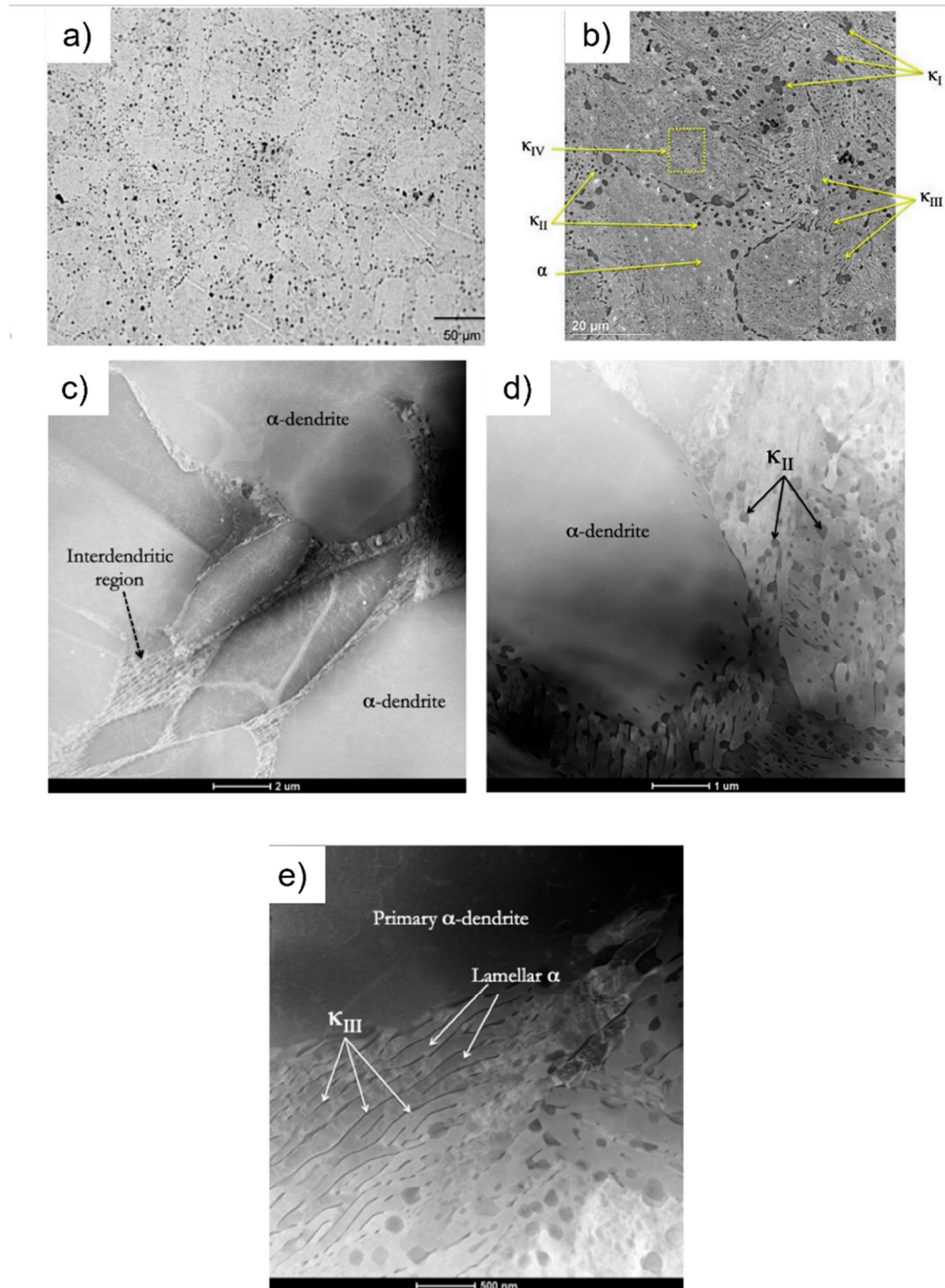


Figure 69. Microstructure of the cast NAB using (a) optical and (b) SEM images. TEM images taken from the microstructure of WAAM-fabricated NAB alloy: (c) low-magnification image showing the general microstructure, and (d,e) high-magnification images showing the intermetallic phases (Reprinted with permission from [152]).

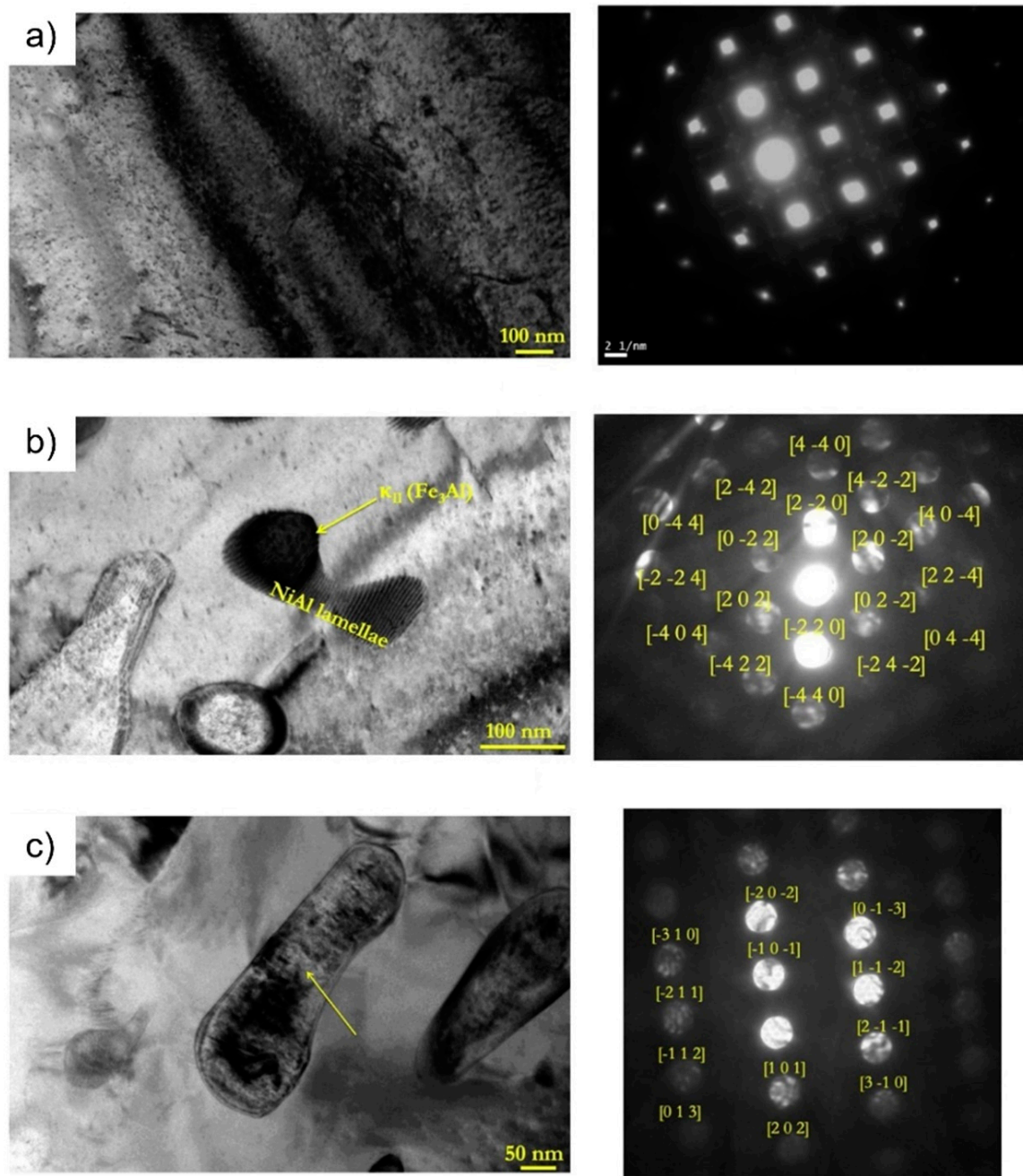


Figure 70. Bright-field TEM images indicating (a) Cu matrix along with the corresponding SAED pattern confirming the presence of α phase and κ_{IV} intermetallic, (b) globular κ_{II} phases characterized as Fe₃Al, and (c) lamellar κ_{III} phases characterized as NiAl (Reprinted with permission from [152]).

In later studies, Dharmendraa et al. [154,155] also conducted post-printing heat treatments, including 350 °C for 2 h (HT-1), 550 °C for 4 h (HT-2), and 675 °C for 6 h (HT-3). According to Figure 71, they found that HT-1 resulted in no significant microstructural alteration, while higher temperatures and longer times (HT-2 and HT-3) significantly affected the size, morphology, and distribution of precipitates. In particular, HT-2 led to the coarsening of κ_{II} , the formation of a new phase (κ_V) with a needle-like morphology, partial spheroidizing of κ_{III} , and a reduction in the volume fraction of κ_{IV} . Meanwhile, HT-3 resulted in the coarsening of κ_{II} and κ_V phases, full spheroidization of lamellar κ_{III} , and a drastic reduction in the volume fraction of κ_{IV} .

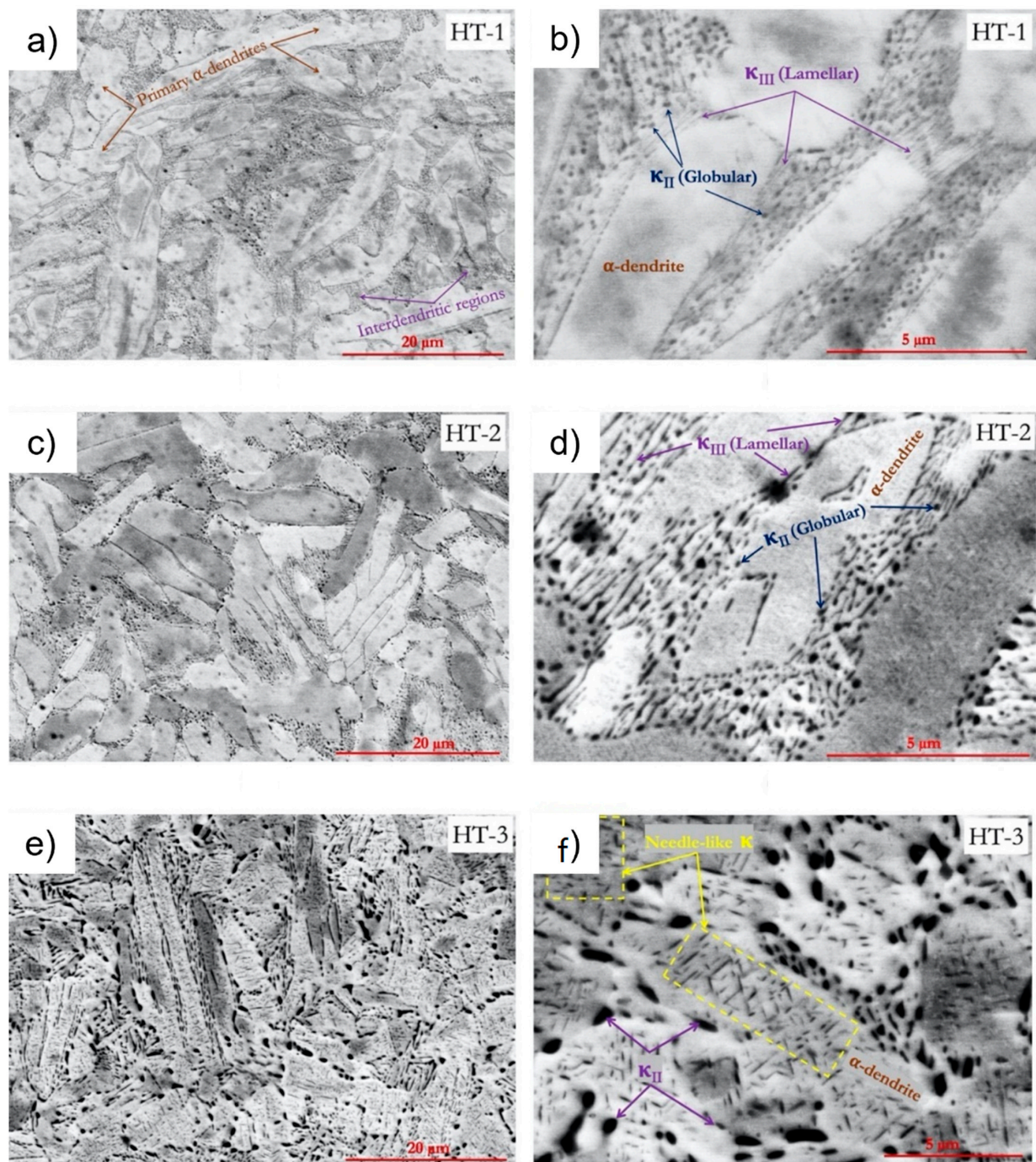


Figure 71. Microstructure of heat-treated WAAM-produced NAB in three different conditions: (a,b) 350 °C for 2 h (HT-1), (c,d) 550 °C for 4 h (HT-2), and (e,f) 675 °C for 6 h (HT-3) (Reprinted with permission from [154]).

In a complementary study, Dharmendraa et al. [151] investigated the volume fraction, morphology, distribution, and size of κ -precipitates at the bottom, middle, and top areas of square bars of WAAM-fabricated NAB alloy (~16 cm in height) using a combination of transmission Kikuchi diffraction and atom probe tomography techniques. Although they reported that the average size of the κ_{IV} precipitates was slightly larger in the middle area, it was concluded that a nearly uniform precipitate distribution in a homogenous microstructure was formed in the WAAM-fabricated NAB alloy. This indicates that the WAAM process is feasible for the fabrication of NAB parts [151]. In a similar study, Chen et al. [156]

investigated the effect of height on the microstructure of a WAAM-fabricated Cu-8Al-2Ni-2Fe-2Mn alloy. They observed dendritic and cellular grains at the bottom region, followed by epitaxial growth of columnar dendrites at the middle region and equiaxed dendrites at the top regions of the deposited wall (see Figure 72). The microstructural variation along the building direction was found to be correlated to the dynamics of G/R and $G \times R$ values, which are influenced by the complex thermal history during the WAAM process. They also reported that the dendrite arm spacing and grain size successively increased in the middle and top regions due to heat accumulation (see Figure 73).

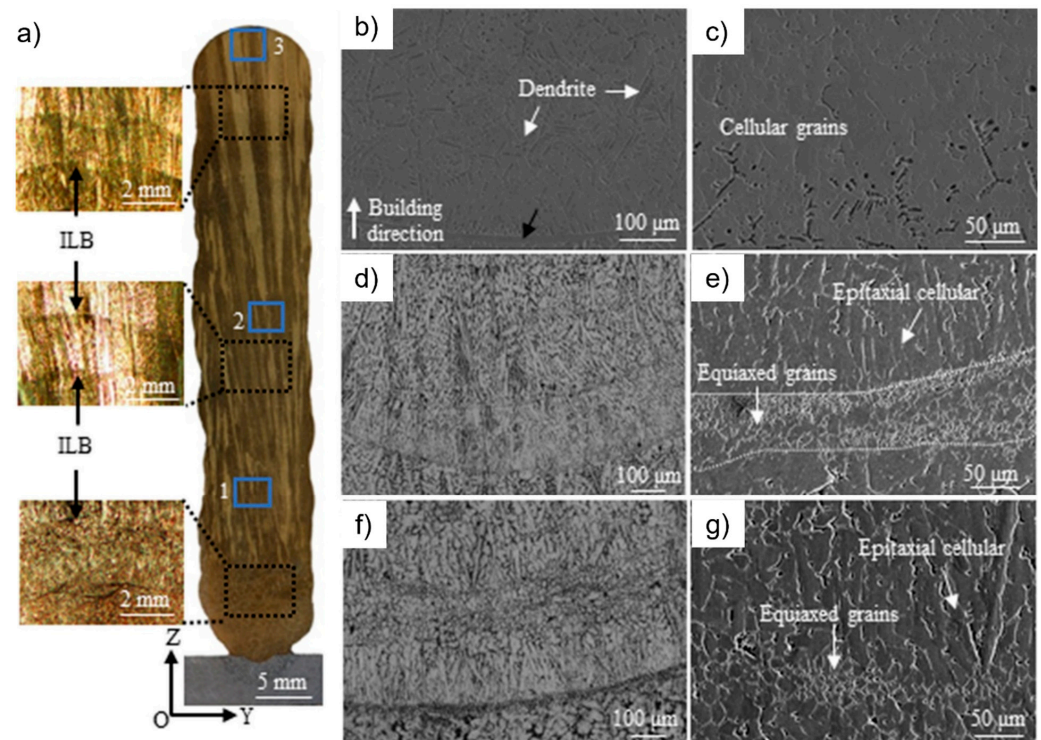


Figure 72. (a) Macrostructure of WAAM-fabricated NAB alloy (Cu-8Al-2Ni-2Fe-2Mn), microstructural features at (b) the bottom area of the first deposited layer, (c) transition from dendritic structure to cellular grains in the first deposited layer, (d,e) low- and high-magnification micrographs taken from the first interlayer band area, and (f,g) low- and high-magnification micrographs taken from the second interlayer band area (Reprinted with permission from [156]).

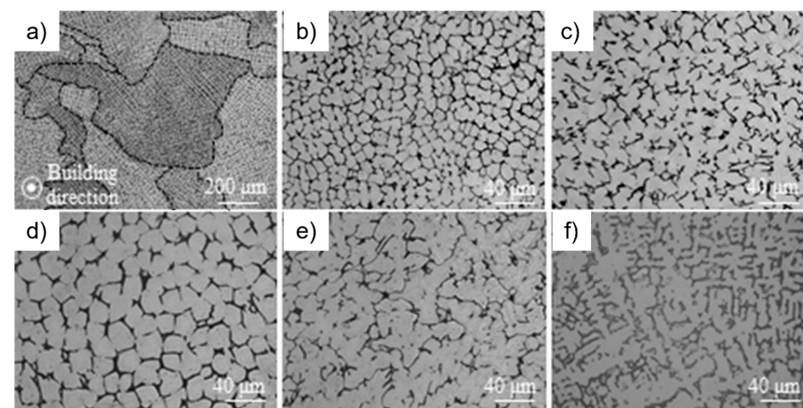


Figure 73. Top view of the microstructure of WAAM-fabricated NAB alloy (Cu-8Al-2Ni-2Fe-2Mn) taken from different locations of (a–c) bottom area, (d,e) top area, and (f) the very last deposited layer, confirming the microstructural coarsening from the bottom to the top regions (Reprinted with permission from [156]).

In a noteworthy attempt by Chen et al. [157], they utilized a novel ultrasonic vibration-assisted (UVA) WAAM system to eliminate the columnar structure of the WAAM-NAB alloy (Cu-8Al-2Ni-2Fe-2Mn), minimize the anisotropic properties, and also improve the mechanical performance of the as-built NAB part. They also investigated the effect of interpass temperature and reported that a combination of UVA treatment and utilization of an interpass temperature lower than 400 °C results in the breakage of coarse columnar dendritic structure, mainly due to the acoustic streaming effect. Figure 74 compares the macrostructure of the WAAM NAB with and without ultrasonic vibration, confirming the removal of the columnar structure [157].

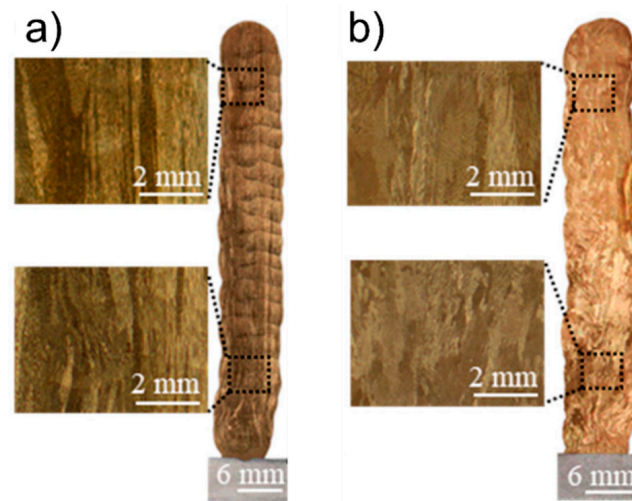


Figure 74. Effect of ultrasonic vibration on the columnar structure of WAAM NAB, (a) without ultrasonic vibration and (b) with ultrasonic vibration (Reprinted with permission from [157]).

In a recent study, Queguineur et al. [158] attempted to increase the deposition rate and improve the economics of WAAM fabrication of NABs using the tandem method, which involves replacing the single CMT torch with the CMT Twin strategy, as shown in Figure 75. They concluded that the CMT Twin strategy resulted in a wider bed fusion and improved the deposition rate but also led to excessive heat accumulation, resulting in longer cooling times between the layers, which diminished the advantages of employing the tandem method [158]. Therefore, they suggested using the CMT Twin method for large parts where each deposited layer is long enough to allow the fabricated part to cool down sufficiently before the next layer is deposited [158].

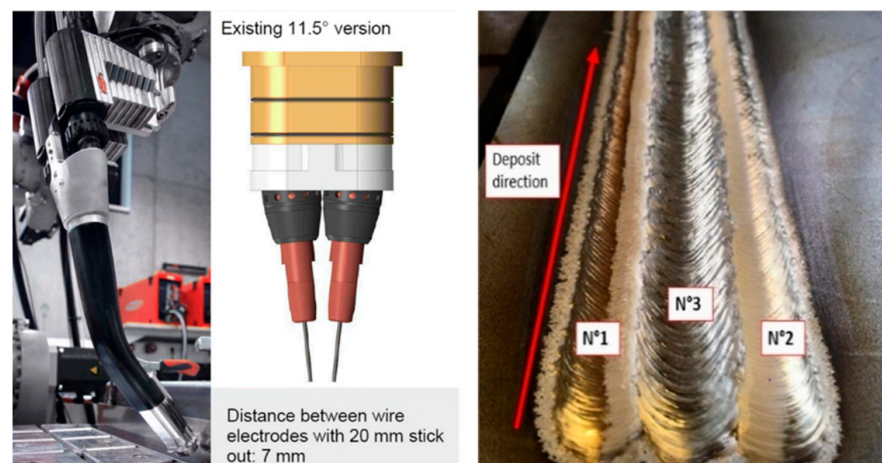


Figure 75. CMT Twin torch along with the first deposited layer of NAB using a CMT Twin torch (Reprinted with permission from [158]).

5.1.2. Mechanical Properties of WAAM-Fabricated NAB Alloys

According to the results of the uniaxial tensile testing conducted by Dharmendraa et al. [152] (see Figure 76a), the WAAM-fabricated NAB exhibited significantly elevated yield strength and ductility due to its finer microstructure, the absence of κ_I as a detrimental phase to ductility, and the formation of finer κ_{IV} precipitates [152]. They also reported that post-printing heat treatment above 550 °C improves the tensile strength but decreases the ductility of the WAAM-fabricated NAB alloy, primarily due to the formation of new κ_V precipitates (see Figure 76b) [154].

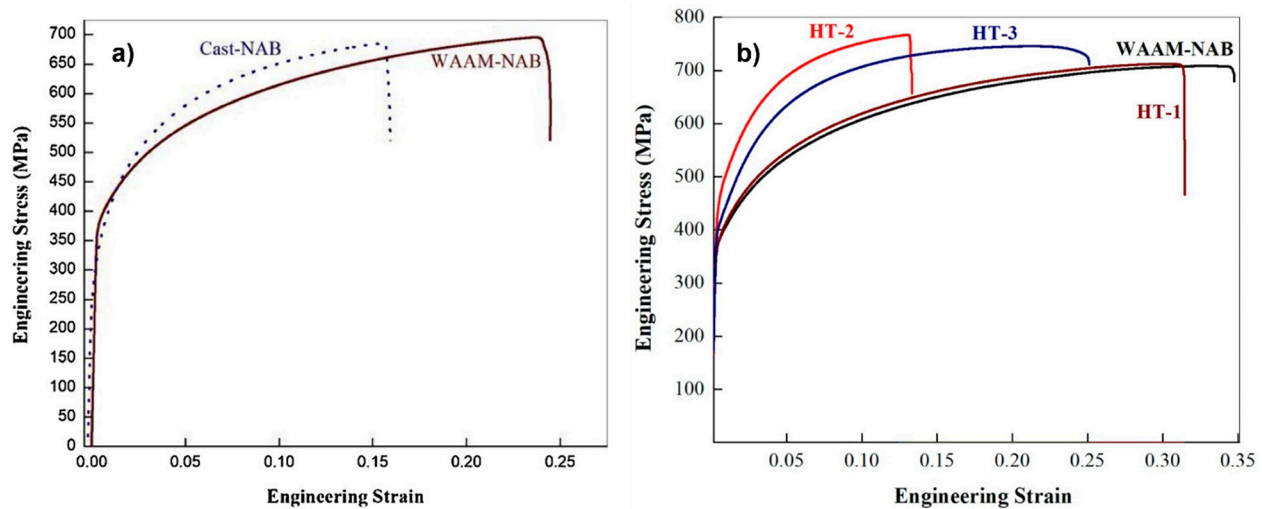


Figure 76. (a) Engineering stress–strain curves of the cast and WAAM-NABs (Reprinted with permission from [152]). (b) Stress–strain curves of the WAAM NAB in as-built and heat-treated conditions of HT-1 (350 °C for 2 h), HT-2 (550 °C for 4 h), and HT-3 (675 °C for 6 h) (Reprinted with permission from [154]).

However, Dharmendraa et al. [152] did not investigate the mechanical properties of the WAAM-fabricated NAB in different directions to investigate the potential anisotropy, which is a limitation of their study. In contrast, Kim et al. [22] studied the mechanical properties of the WAAM NAB part in longitudinal and transverse directions, revealing anisotropic mechanical properties in the as-printed condition with higher tensile strength, hardness, and shock absorption in the longitudinal direction. They also reported that the additively manufactured component showed better wear performance compared to the cast counterpart [22]. Figure 77a,b compares the wear properties of WAAM and cast NABs, showing a higher indentation depth and weight loss in the case of the cast NAB [22]. The uniaxial tensile testing also showed significantly better performance in WAAM NAB as compared to the cast alloy, that is, 50% higher tensile strength, 20% higher average yield strength, and 60% higher average elongation [22]. The microhardness improvement from the cast substrate to the WAAM-fabricated sample is evident in the microhardness profile shown in Figure 77c [22]. However, Kim et al. [22] did not provide microstructural analysis to support their findings.

In a different study, Chen et al. [156] investigated the correlation between the mechanical properties and microstructure of a WAAM-fabricated NAB alloy (Cu-8Al-2Ni-2Fe-2Mn). They concluded that the higher strength and hardness at the bottom region of the WAAM-fabricated NAB alloy were correlated to its fine cellular grain structure, while the larger primary dendrite arm spacing at the top regions decreased the mechanical properties of the as-printed part (see Figures 72 and 73 for microstructural details). They also correlated the higher UTS of the horizontal samples versus the vertical samples to the anisotropic microstructure of the WAAM-fabricated NAB part.

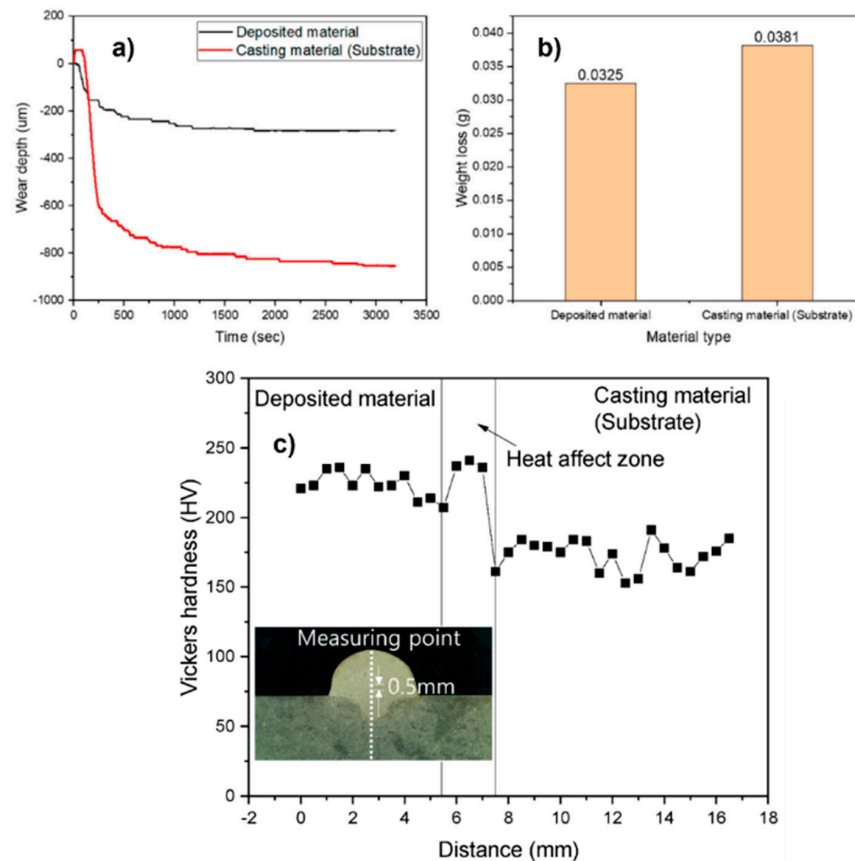


Figure 77. (a) Wear depth and (b) weight loss of the WAAM and cast NABs during wear testing. (c) Microhardness profile showing the transition from the cast substrate to WAAM-fabricated NAB (Reprinted with permission from [22]).

Ultrasonic vibration-assisted (UVA) treatment during the fabrication process has been shown to minimize the anisotropic mechanical properties of WAAM-fabricated NAB parts by eliminating the coarse columnar grain structure along the building direction [157]. This is confirmed by the stress–strain curves of the cast counterpart (C95220 alloys) and the WAAM-fabricated NAB alloy under different conditions (U2 and U3 are with ultrasonic vibration, and C3 is without ultrasonic vibration), as shown in Figure 78. The UVA treatment results in a significant reduction in anisotropy in both the vertical (V) and horizontal (H) directions [157].

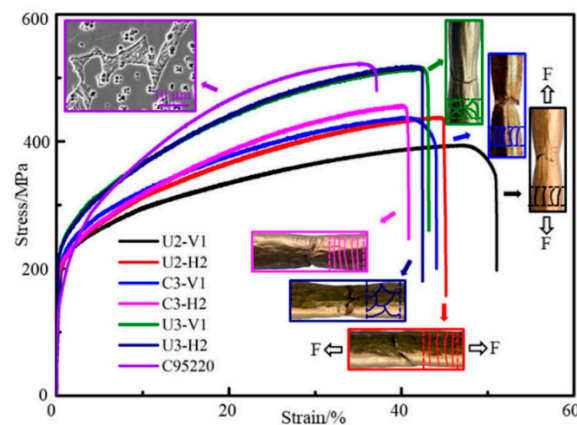


Figure 78. Stress–strain curves of the cast NAB counterpart (C95220 alloys), and the WAAM NAB samples under different conditions (U2 and U3 are with ultrasonic vibration, and C3 is without ultrasonic vibration) (Reprinted with permission from [157]).

Several researchers have investigated the impact of post-fabrication heat treatment on the anisotropic mechanical properties of additively manufactured NAB alloys. For instance, Shen et al. [153] reported that post-printing heat treatment could modify the layer-wise morphologies of the WAAM-fabricated NAB and improve the material's strength through two main mechanisms: grain refinement and precipitate solutions. Additionally, the observed anisotropy in the WAAM NAB alloy's strength was successfully mitigated by implementing quenching and tempering processes, and the ductility was considerably improved in the heat-treated sample at the optimized temperature. According to Figure 79, the as-fabricated WAAM NAB part exhibited superior tensile strength in the transverse and longitudinal orientations compared to the normal direction, while the anisotropic mechanical properties were reduced in the quenched and tempered samples [153].

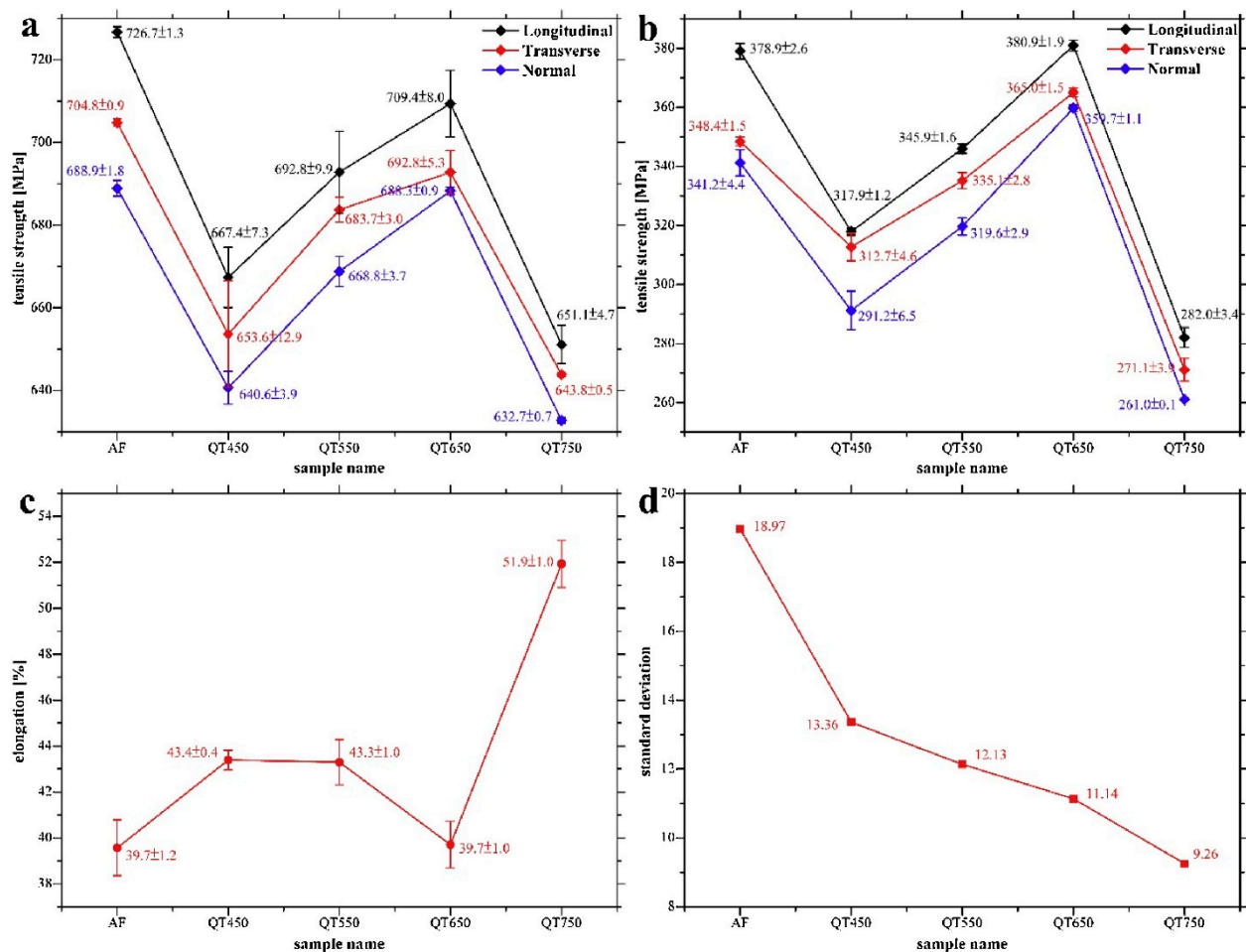


Figure 79. Mechanical properties of a WAAM-fabricated NAB alloy, including (a) tensile strength, (b) yield strength, (c) elongation, and (d) the standard deviation of tensile strength values. (Note: QT = quenching and tempering, and AF = as-fabricated.) (Reprinted with permission from [153]).

In a later study, Shen et al. [159] investigated the effect of different post-printing heat treatments (quenching: Q, quenching and tempering: QT, and direct tempering: T) on the anisotropic mechanical properties of WAAM-fabricated NAB alloys from a crystallographic and texture perspective using EBSD analysis. They concluded that post-printing heat treatment can modify the preferential texture ($\{011\} \langle 211 \rangle$, $\{111\} \langle 110 \rangle$) in the as-fabricated part to $\{111\}$ in the heat-treated samples. Interestingly, they also reported that the minimum anisotropy was achieved in the case of the direct tempering process, while annealing textures intensified when prior homogenization and quenching processes were implemented. Specifically, the pole figures (PFs) of the as-fabricated (AF) and heat-treated

samples (Figure 80) showed that the $\{111\} \langle 110 \rangle$ texture in the AF sample was transformed to a strong $\{111\}$ annealing texture in the Q and QT samples, while a fairly isotropic lattice plane distribution was observed in the case of the T sample with some weak residual $\{111\} \langle 110 \rangle$ inherited from the AF sample [159].

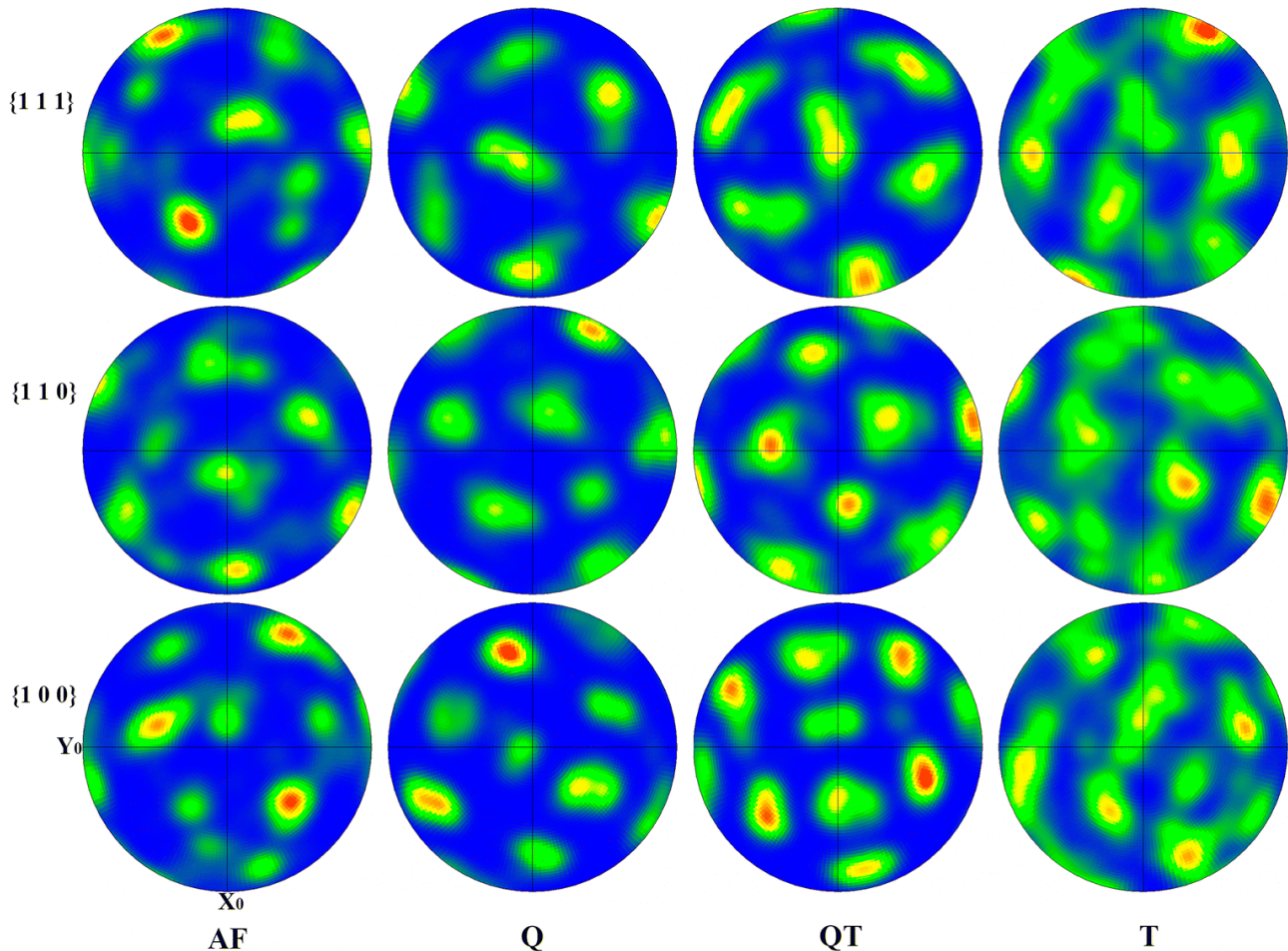


Figure 80. PFs of the WAAM-fabricated NAB alloy in different conditions of As-fabricated (AF), quenched (Q), quenched and tempered (QT), and directly tempered (T) (Reprinted with permission from [159]).

5.2. L-PBF of NAB Alloys

There are a few studies in the literature on the L-PBF of NAB alloys, focusing on the investigation of their microstructure, mechanical properties, corrosion performance, and the effects of post-fabrication heat treatments.

In a recent study, Murray et al. [165] used Cu-9.8Al-5.2Ni-4.6Fe-0.3 Mn (wt.%) powder to fabricate dense NAB parts using the L-PBF process. Unlike the WAAM-fabricated and conventionally processed NAB parts, such as cast and wrought, the higher cooling rate associated with the L-PBF process resulted in a twin-related martensitic structure with no κ phases in the as-printed sample, similar to an as-quenched structure. Figure 81 compares the microstructure of the cast, wrought, and L-PBF-fabricated NAB counterparts.

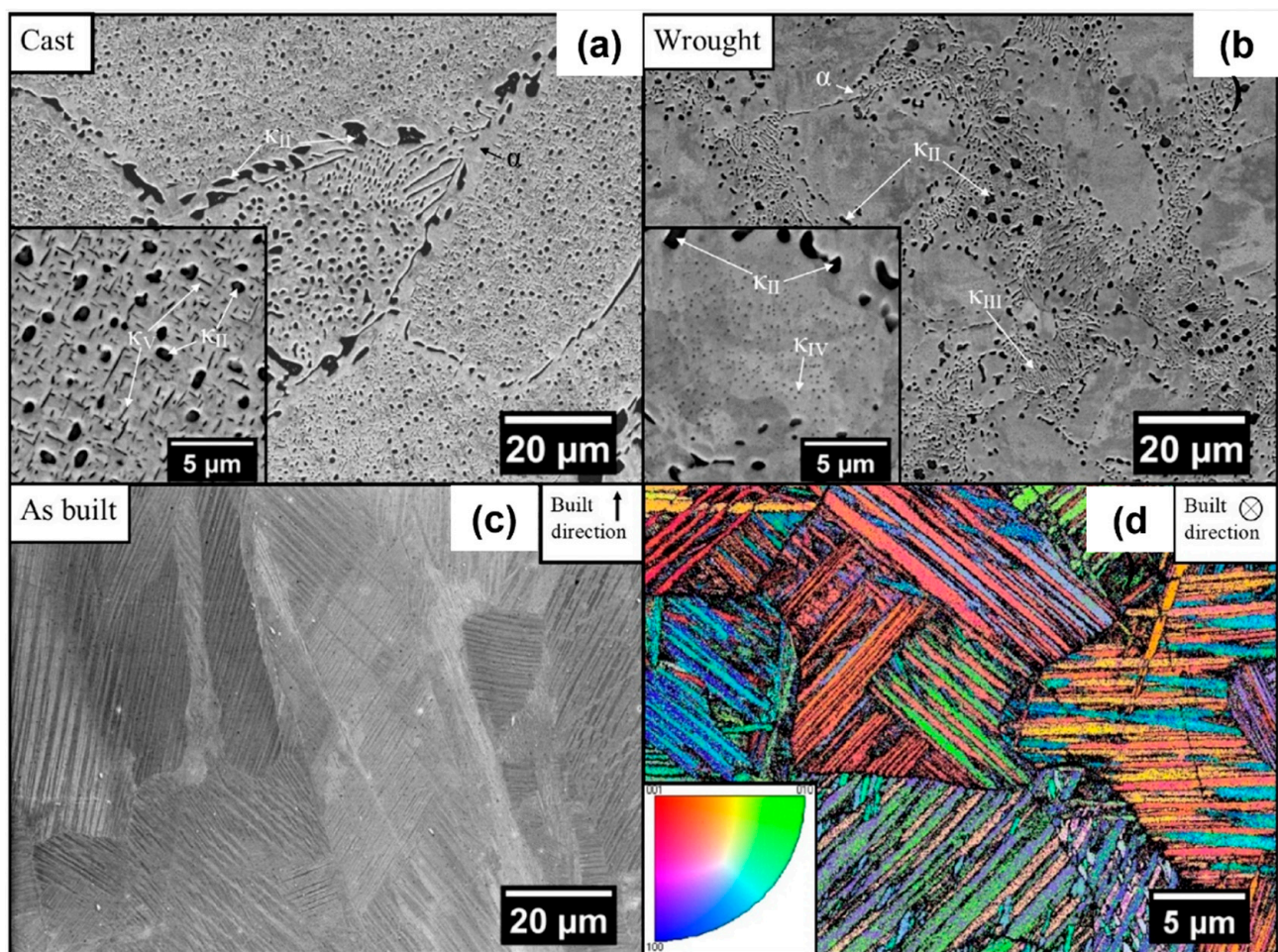


Figure 81. Microstructure of the (a) cast, (b) wrought, and (c,d) L-PBF-fabricated NAB counterparts (Reprinted with permission from [165]).

Nevertheless, subjecting the as-printed sample to a post-printing heat treatment process at 600–700 °C for 1 h led to the formation of traditional NAB alloys' microstructure, where α phase and κ spherical phases were formed along the prior β grain boundaries and martensite lath boundaries [165]. On the other hand, performing higher temperature heat treatments at 800 and 900 °C resulted in the formation of coarser and globular κ phases, along with the appearance of β_1 and γ_1' phases as a result of quenching the β phases formed at high temperatures (800 and 900 °C). Figure 82 shows the microstructure of the heat-treated samples at different magnifications.

The mechanical testing revealed that the as-printed sample with a martensitic structure displayed brittle behavior, while post-printing heat treatment improved the mechanical properties to the point where its ultimate tensile strength and yield strength surpassed those of the conventional cast and wrought NAB alloys. Figure 83a shows the stress–strain curves of the as-printed and heat-treated L-PBF NAB samples, while Figure 83b compares the mechanical properties of the L-PBF NAB alloy with their cast and wrought counterparts. The results of mass loss measurements after 3 and 6 months of seawater immersion exposure showed that the as-printed sample with a uniform martensitic microstructure exhibited mass loss levels one order of magnitude lower than those of the cast and wrought counterparts with a dual phase (α and κ) microstructure (see Figure 83c). Murray et al. [165] correlated this observation to the micro-galvanic coupling formed in a dual phase microstructure, which is α and κ phases in the case of cast and wrought NAB alloys.

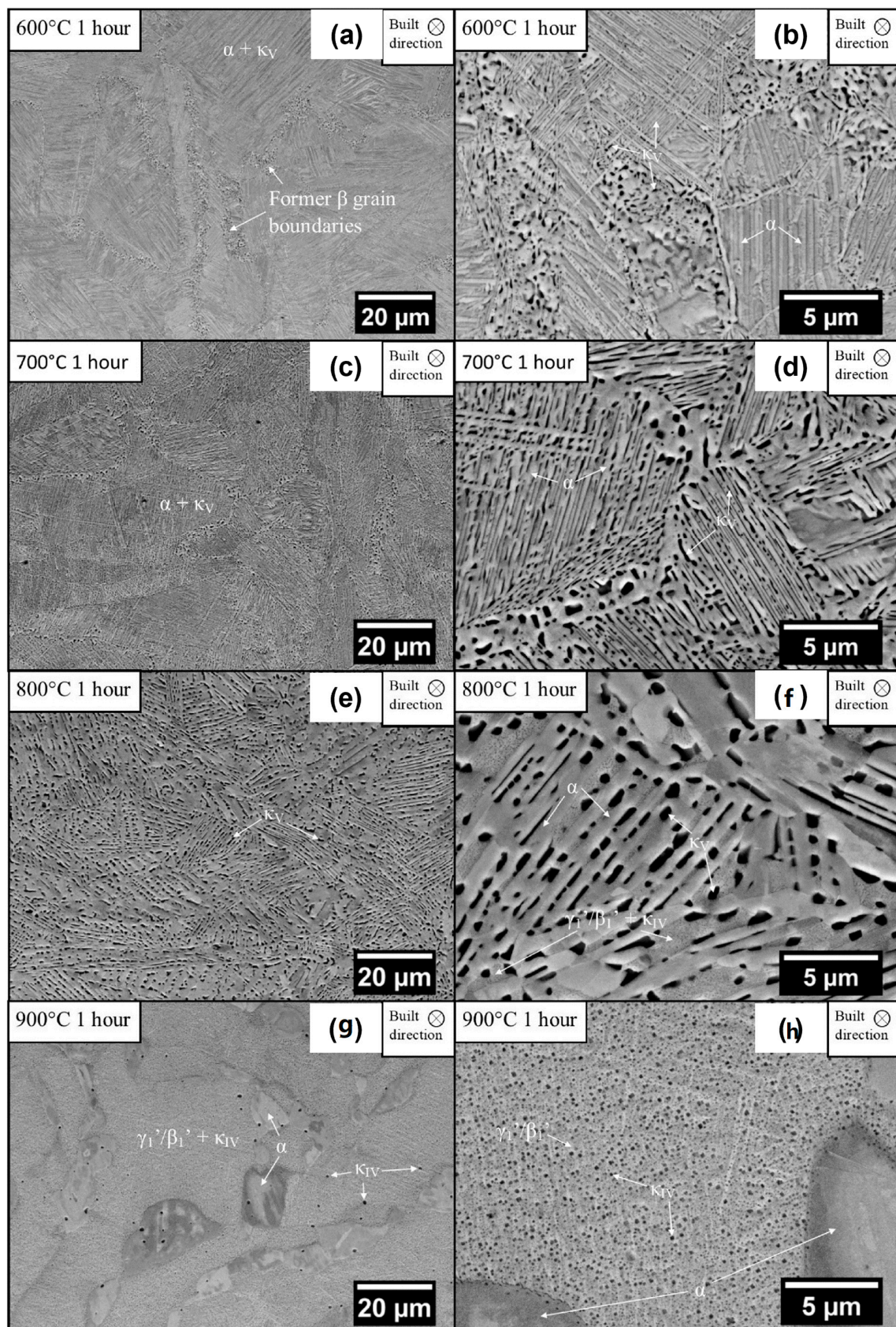


Figure 82. Microstructure of the L-PBF-fabricated NAB samples after different post-printing heat treatment cycles, including (a,b) 600 °C for 1 hour, (c,d) 700 °C for 1 h, (e,f) 800 °C for 1 h, (g,h) 900 °C for 1 hour (Reprinted with permission from [165]).

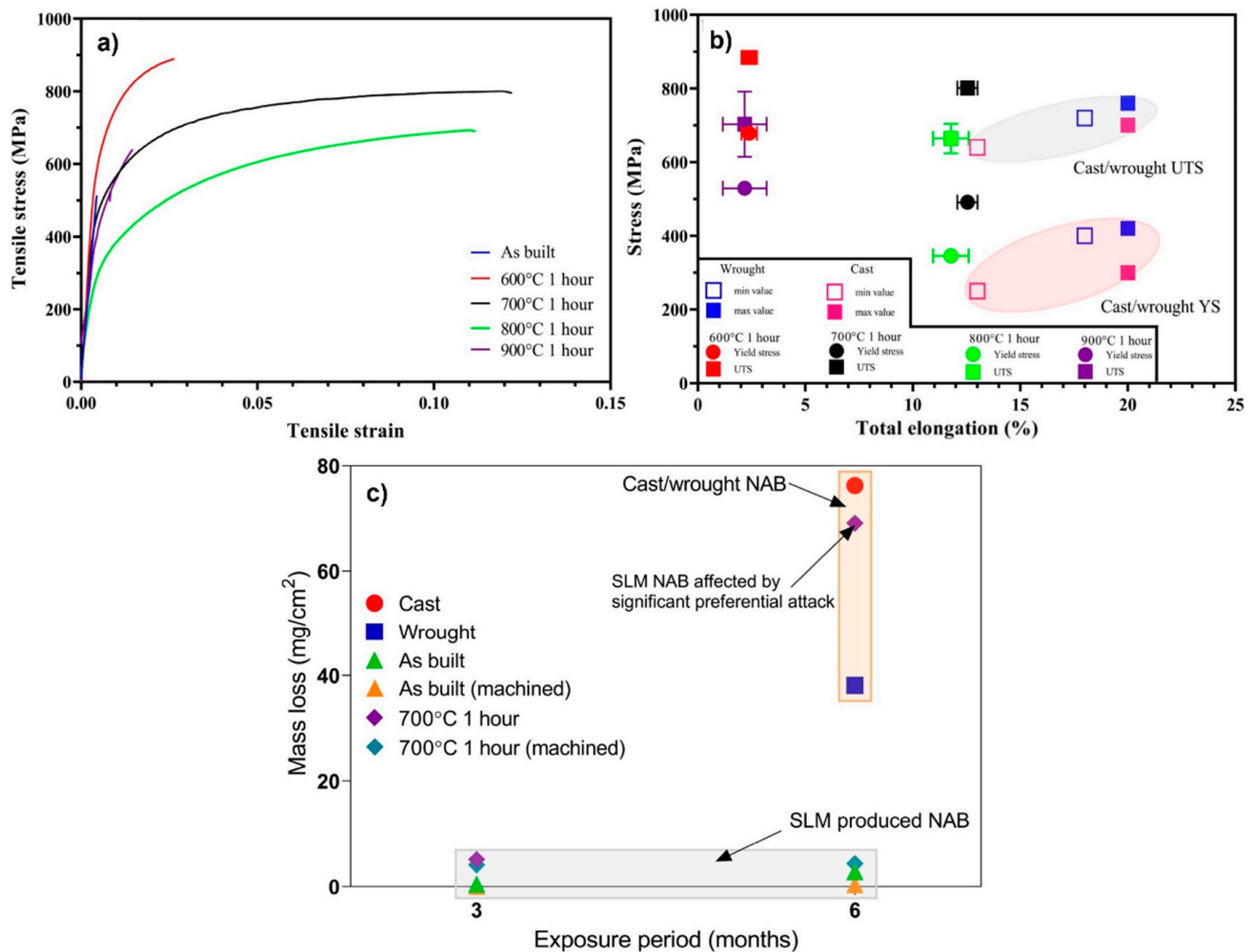


Figure 83. (a) Stress–strain curves of the as-printed and heat-treated L-PBF NAB samples, and (b) a comparison with the mechanical properties of cast and wrought counterparts. (c) Mass loss measurements after seawater exposure for 3 and 6 months in the as-printed and heat-treated L-PBF NAB alloy compared with the cast and wrought counterparts (Reprinted with permission from [165]).

In addition, Alkelae et al. [164] reported that post-printing heat treatment improved the mechanical properties of L-PBF-fabricated NAB alloy (Cu₉Al₄Fe₃Ni) but had a negative impact on its tribological properties. They proposed that the lower wear resistance of the heat-treated samples could be associated with their higher fraction of hard κ precipitates, which might detach from the matrix, resulting in three-body abrasive wear.

In another study, Barr et al. [163] investigated the effect of the chemical composition of the feedstock powder on the tensile and corrosion properties of L-PBF-fabricated NAB alloys. They used C63000 (Cu-10.2Al-4.8Fe-5.0Ni-0.2Si wt.%) and C95800 (Cu-9.0Al-4.0Fe-4.6Ni-1.9Mn wt.%) feedstocks to investigate their processability, mechanical properties, and corrosion resistance in the as-printed and heat-treated conditions. They reported that the lower percentage of aluminum in C95800 resulted in the precipitation of continuous α phases along the β' grain boundaries, while C63000 displayed a uniform β' phase in its microstructure (see Figure 84a,c). The fully β' microstructure of C63000 resulted in high tensile strength (~1120 MPa) but very low ductility (3% strain). On the other hand, the C95800 sample exhibited slightly lower tensile strength and higher ductility due to the presence of continuous bands of α phase (see Figure 84e).

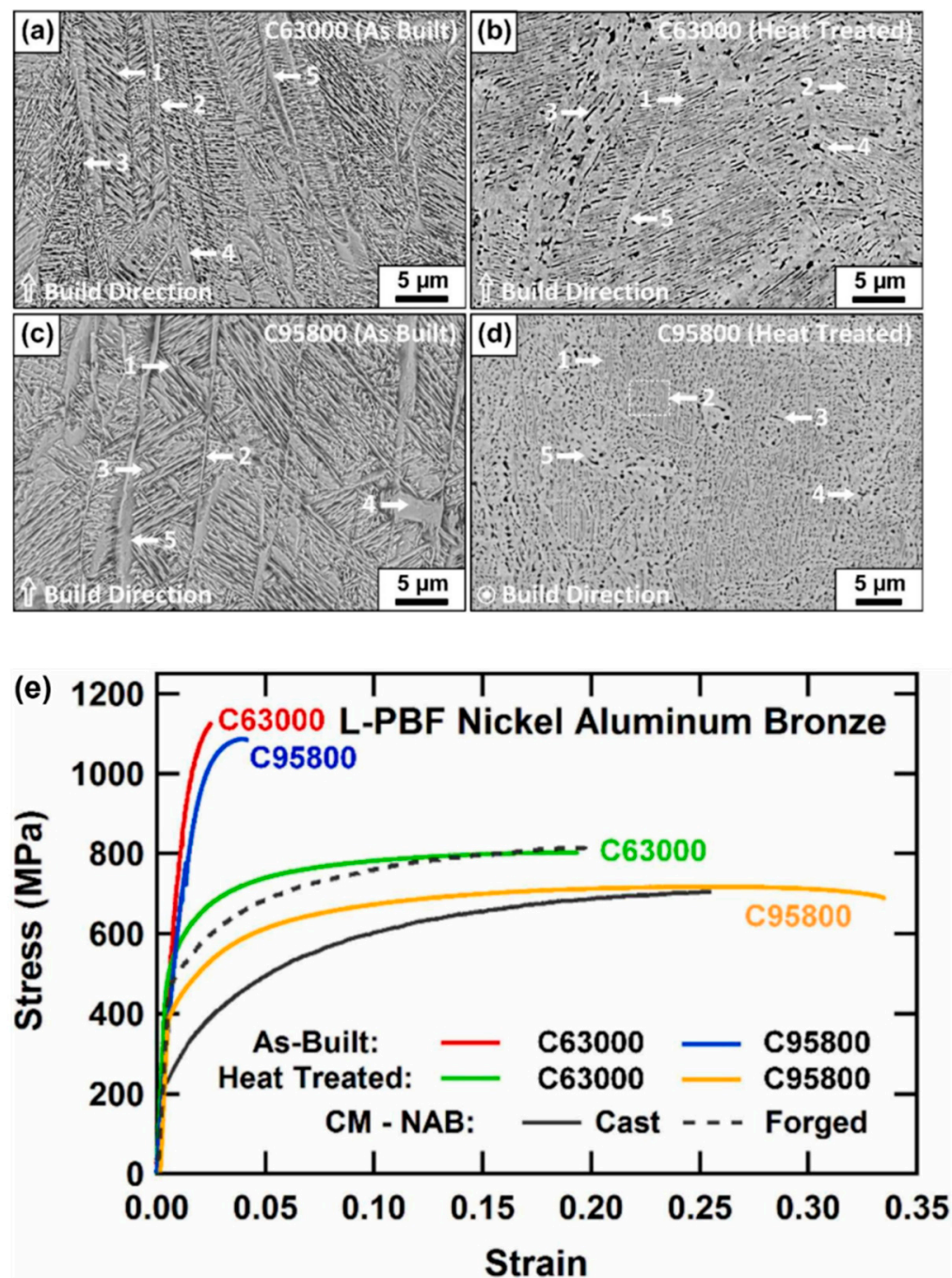


Figure 84. Microstructure of as-built and heat-treated L-PBF NAB alloys using different feedstocks, including (a,b) C63000 and (c,d) C95800. (e) Stress–strain curves of L-PBF-fabricated NAB alloys using two feedstocks of C63000 and C95800 in the as-built and heat-treated conditions, respectively, along with the cast and forged counterparts (Reprinted with permission from [163]).

In the heat-treated condition, the β' phases in C63000 transformed into α and κ_{III} , while the lower content of iron and nickel in C95800 led to the formation of a lower volume fraction of κ precipitates (see Figure 84b,d). The corrosion performance of the heat-treated C63000 and C95800 samples was found to be very similar to the wrought NAB counterpart with a comparable microstructure that contains α and κ phases (see Figure 85).

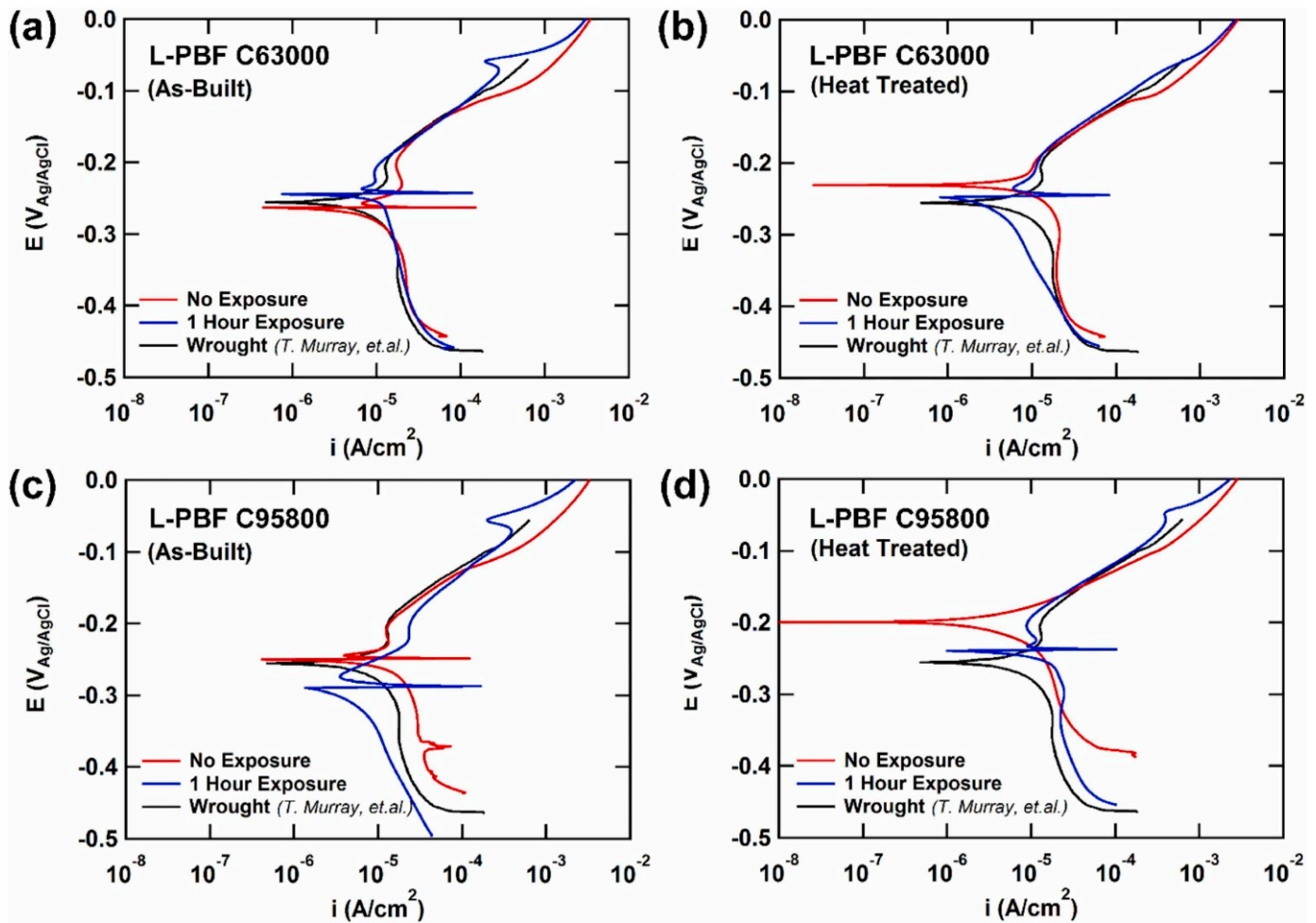


Figure 85. PDP curves of the as-built and heat-treated L-PBF NAB alloys, using different feedstocks of (a,b) C63000 and (c,d) C95800 (Reprinted with permission from [163]).

5.3. EBM of NAB Alloys

There are only two studies in the literature on the EBM of NAB alloys, in which very similar results were reported.

Lu et al. [166] investigated the microstructure and mechanical properties of an EBM-fabricated NAB part using commercial spherical C63000 powders (Cu-9.5Al-4.2Ni-4Fe-1.2Mn). They reported a relatively homogeneous microstructure with a nearly equiaxed grain structure with no sign of columnar grains along the building direction, containing α phase, a high-volume fraction of B2-NiAl, and D03 Fe₃Al precipitates (see Figure 86). They correlated the formation of the equiaxed grain structure to two synergistic reasons: (i) the fairly uniform heating cycle during the EBM process as compared to the L-PBF technique, which minimizes thermal gradients resulting in the nucleation of equiaxed grains rather than columnar grains, and (ii) the formation of a large number of precipitates that could serve as nucleation sites and grain refiners [166].

Similarly, Zhai et al. [167] studied the EBM fabrication of a NAB alloy (81.1Cu-9.5Al-4.2Ni-4.0Fe-1.2Mn) and found similar results to those reported by Lu et al. [166]. They also reported the formation of a high-density part (>99%) containing a homogeneous microstructure with equiaxed grains and uniformly distributed (Fe,Ni)Al precipitates, which collectively resulted in isotropic mechanical properties.

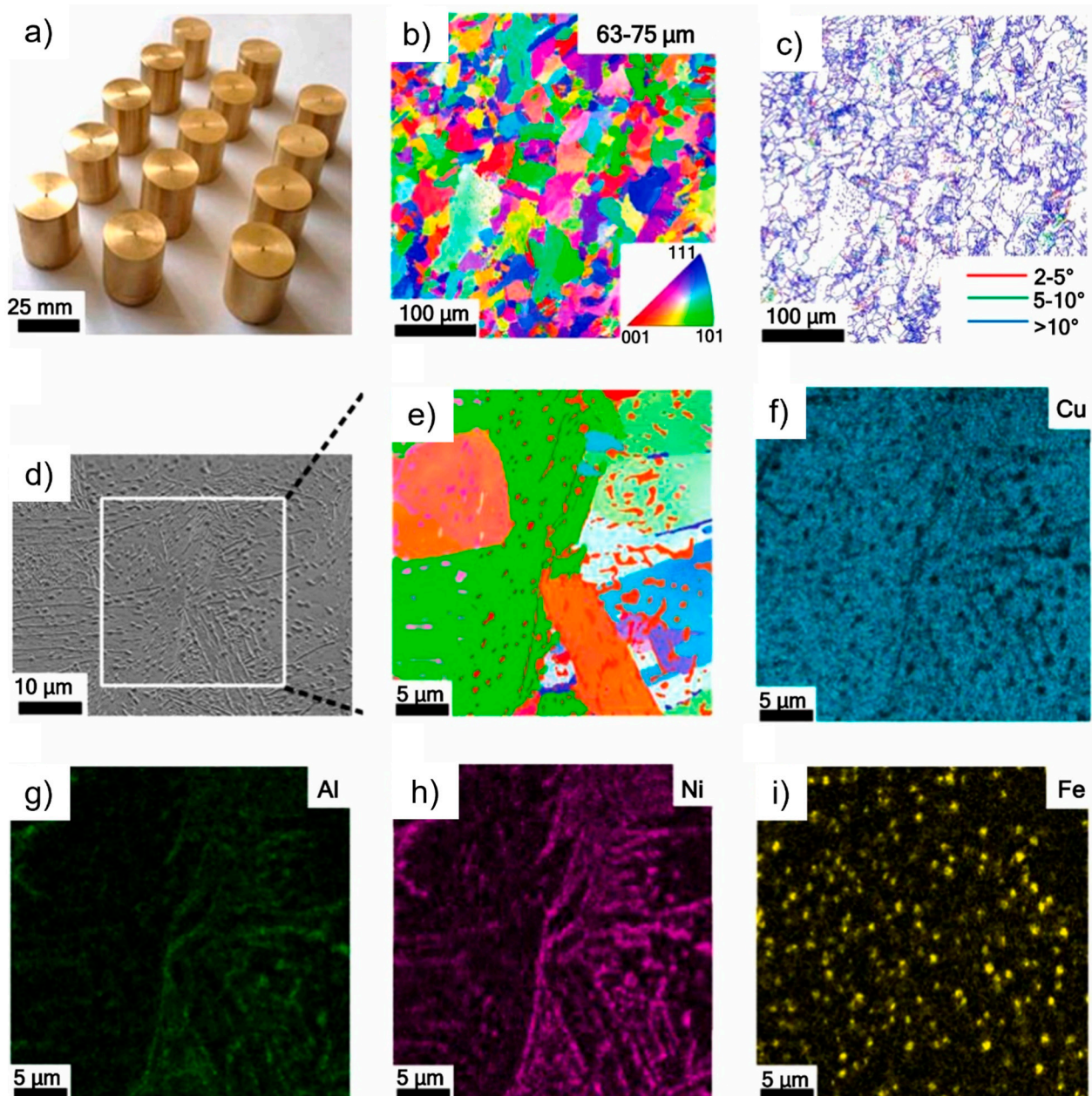


Figure 86. (a) As-fabricated EBM NAB cylindrical parts with a diameter of 25 mm, (b) IPF map of the as-fabricated sample, (c) the corresponding grain boundary map, (d) SEM image showing uniform distribution of precipitates, (e) the IPF map taken from the white square selected areas showing the formation of precipitates on both intergranular and intragranular areas, and (f–i) the corresponding EDS elemental maps of Cu, Al, Ni, and Fe (Reprinted with permission from [166]).

5.4. L-DED of NAB Alloys

There is only one study in the literature on the L-DED of NAB alloys, in which Li et al. [171] investigated the microstructural features and mechanical properties of a NAB alloy (Cu–9Al–5Fe–5Ni) fabricated by laser metal deposition. According to their microstructural characterizations, the as-printed part revealed a martensitic structure (β^*) along with Widmanstätten α phase, nano-size Fe_3Al and NiAl precipitates, and some nano-twins. Figure 87 illustrates the microstructural details of the L-DED-fabricated NAB sample. The formation of a martensitic structure with a plate width of ~ 250 nm can be observed in Figure 87a, with (111) interplanar spacing of $2.19 \text{ \AA}$, as revealed by the SAED

patterns shown in Figure 87b. The EDS elemental maps also confirmed the formation of Fe-rich and Ni-rich precipitates in the β^* phase (Figure 87d–g).

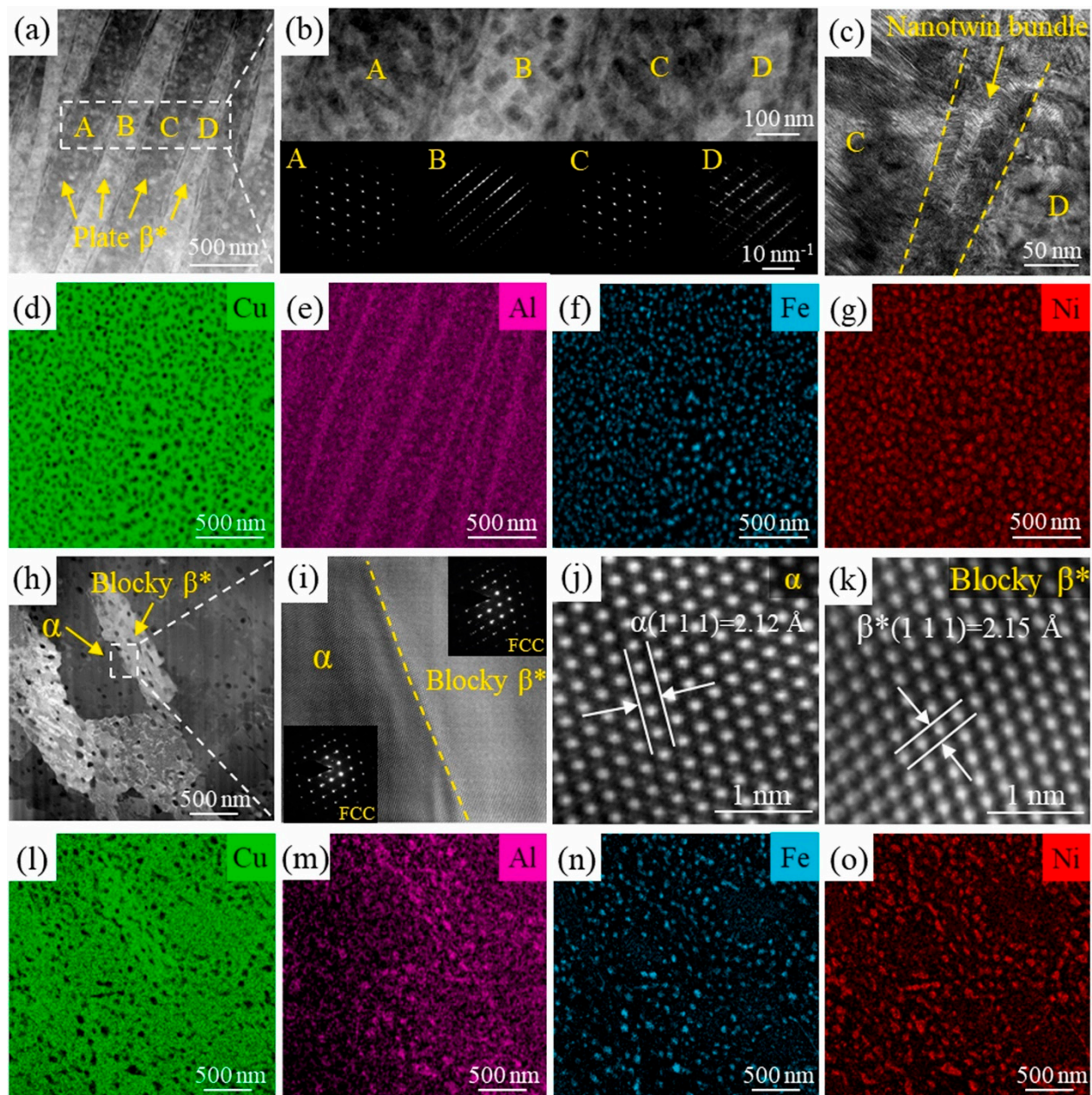


Figure 87. (a–c) TEM images at different magnifications and the corresponding SAED patterns taken from the melt pool center of the L-DED NAB part; (d–g) the corresponding EDS elemental maps of Cu, Al, Fe, and Ni; (h,i) TEM images and the corresponding SAED patterns of α and β^* taken from the melt pool boundary; (j) HRTEM image taken from α ; (k) HRTEM image taken from β^* ; and (l–o) EDS elemental maps taken from the inset in (h) (Reprinted with permission from [171]).

According to the stress–strain curves of the samples fabricated with different process parameters (S1–S8), the mechanical properties of the L-DED NAB part were characterized by a yield strength of 593–713 MPa, an ultimate tensile strength of 769–949 MPa, and an elongation of 10–12% (see Figure 88a,b). These properties were found to be higher than those of the cast and WAAM counterparts. The obtained mechanical properties for the L-DED NAB part were compared with counterparts fabricated by other manufacturing processes, including WAAM, L-PBF, and cast before and after heat treatment, as shown in

Figure 88c. The results of Li et al. [171] proved the feasibility of using the L-DED process to fabricate NAB alloys, such as Cu–9Al–5Fe–5Ni alloy, for marine and offshore applications.

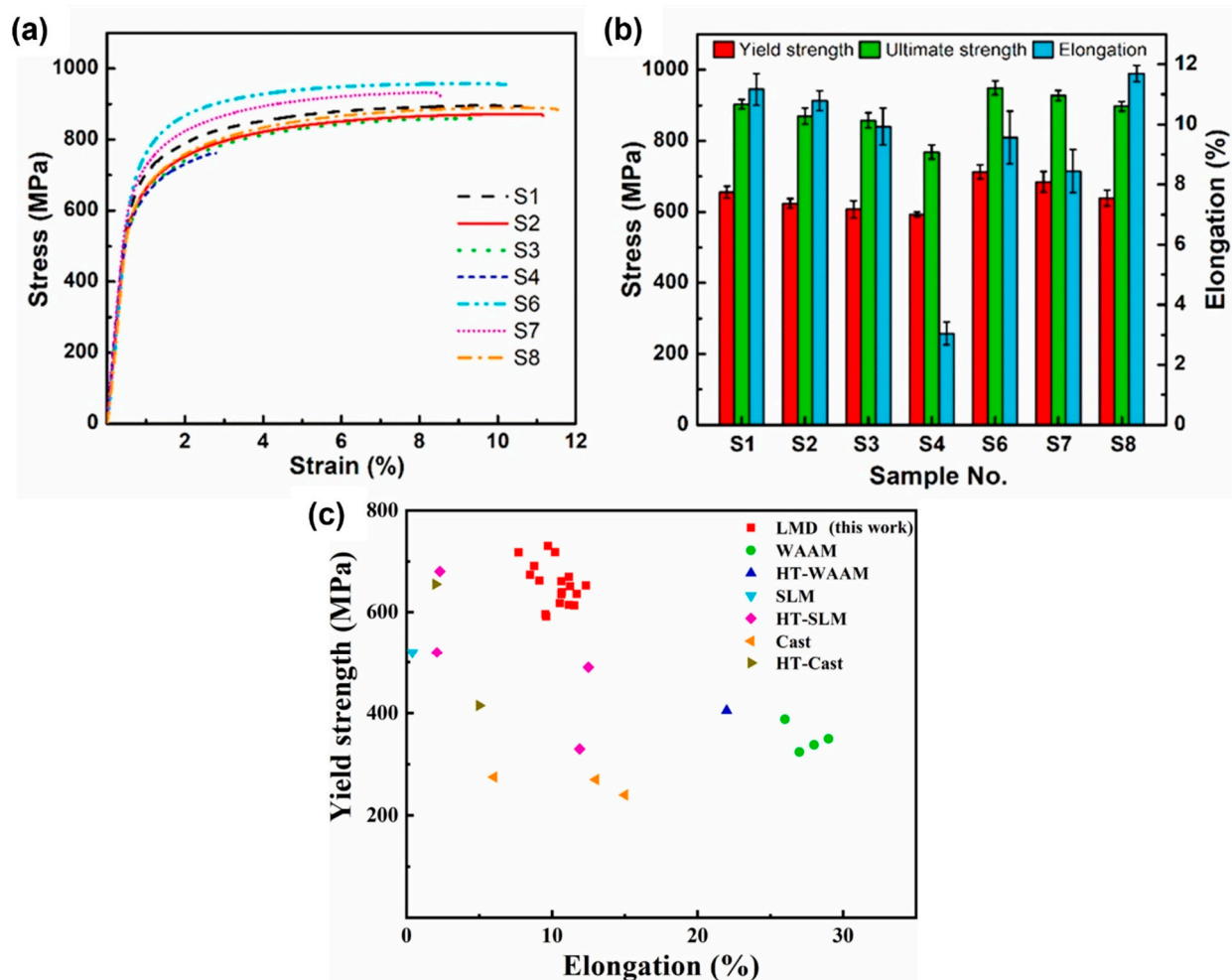


Figure 88. (a) Stress–strain curve of the L-DED NAB part fabricated with different process parameters (S1–S8) and (b) summary of the obtained mechanical properties. (c) A comparison between the mechanical properties of the L-DED NAB part and the counterparts fabricated by other manufacturing processes, including WAAM, L-PBF, and cast before and after heat treatment (Reprinted with permission from [171]).

5.5. AM of Bimetallic NAB Alloys and Dissimilar Metal Combinations

In two complementary studies, Dharmendra et al. [160,162] successfully fabricated a hybrid part of WAAM NAB alloy (9Al–4Ni–4Fe–1Mn) on the 316L stainless steel (SS) plate and investigated the deposition feasibility and cracking tendency for industrial repair and maintenance. While a sound and non-textured inter-diffusion region, including Fe_3Al intermetallic at the NAB/SS interface with a hardness value between that of NAB and 316L SS [160], was reported, some intergranular liquation cracks were observed in the HAZ propagating towards the 316L SS substrate [160]. Figure 89 shows the NAB/316L SS hybrid part and the interface region, including occasional cracks in the HAZ of the SS side. The formation of these cracks was correlated to the differences in physical properties between copper and stainless steel, resulting in the penetration of liquid copper into the intergranular regions of the SS side during the deposition of the very first track [160]. To reduce the liquation cracking susceptibility of the interface, they suggested three strategies, including (i) employing a 316L SS substrate with a finer grain structure, (ii) applying a buffer layer such as Inconel 625 having good metallurgical compatibility with both ferrous

and copper alloys, or (iii) laser cladding of a thin layer of NAB before the deposition by the WAAM process [160].

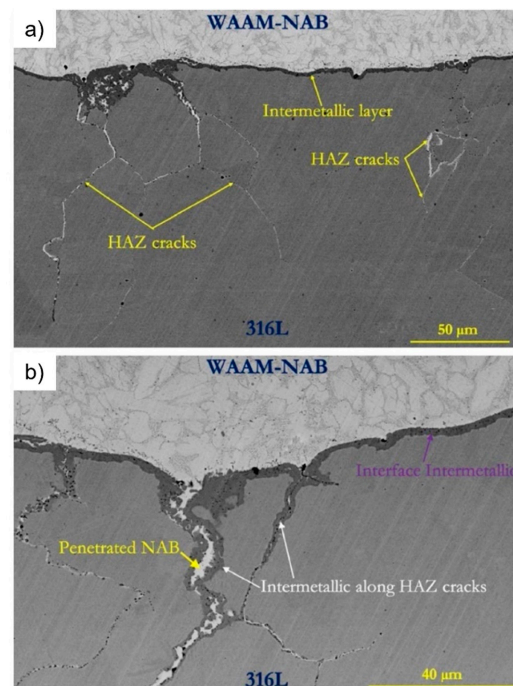


Figure 89. (a) SEM image taken from the interface between WAAM NAB and the 316L SS substrate, showing the formation of cracks in the HAZ of the SS side, and (b) higher magnification SEM image, showing the penetration of liquid NAB into the intergranular regions of the SS side (Reprinted with permission from [160]).

Cai et al. [161] conducted a similar study on the WAAM fabrication of a bimetallic structure of NAB/316L SS. They did not observe any penetration cracks at the interface, as shown in Figure 90. They correlated this observation to the lower current (60 A) and lower line energy (48.9 J/cm) used in their fabrication process compared to the higher values (114 A and 170 J/mm) used by Dharmendra et al. [160]. Although no further discussion was provided by Cai et al. [161], it can be assumed that their use of lower heat input resulted in lower fluidity for the NAB molten metal. As a result, less liquid penetrated through the intergranular regions of the SS side, leading to sound and crack-free interfacial bonding.

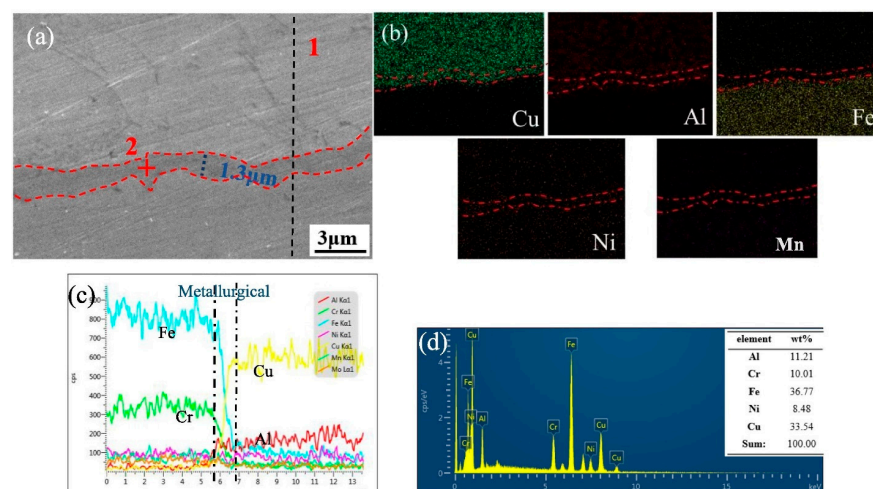


Figure 90. (a) Interface of the WAAM-fabricated NAB/316L bimetal, and (b–d) the corresponding EDS elemental analysis (Reprinted with permission from [161]).

In a recent study, Yao et al. [169] investigated the microstructural features and mechanical properties of a L-DED-fabricated CuNi2SiCr/NAB bimetal. The aim of the study was to evaluate the feasibility of using this technique to repair NAB marine propellers by depositing copper alloy powder (CuNi2SiCr). However, they concluded that repairing damaged NAB propellers using L-DED deposition of CuNi2SiCr powders is not advisable due to the porous structure and absence of reinforcing phases in the microstructure of the deposited layers. This results in lower hardness, strength, and wear resistance of the deposited layers. Specifically, the deposited layers were characterized by a single-phase α microstructure with high toughness and low hardness. On the other hand, the NAB substrate contains the α phase as well as the hard and brittle β and κ phases, resulting in higher hardness, tensile strength, and wear resistance. Figure 91 shows the microstructural features of the interface and each side of the L-DED-fabricated CuNi2SiCr/NAB bimetal part.

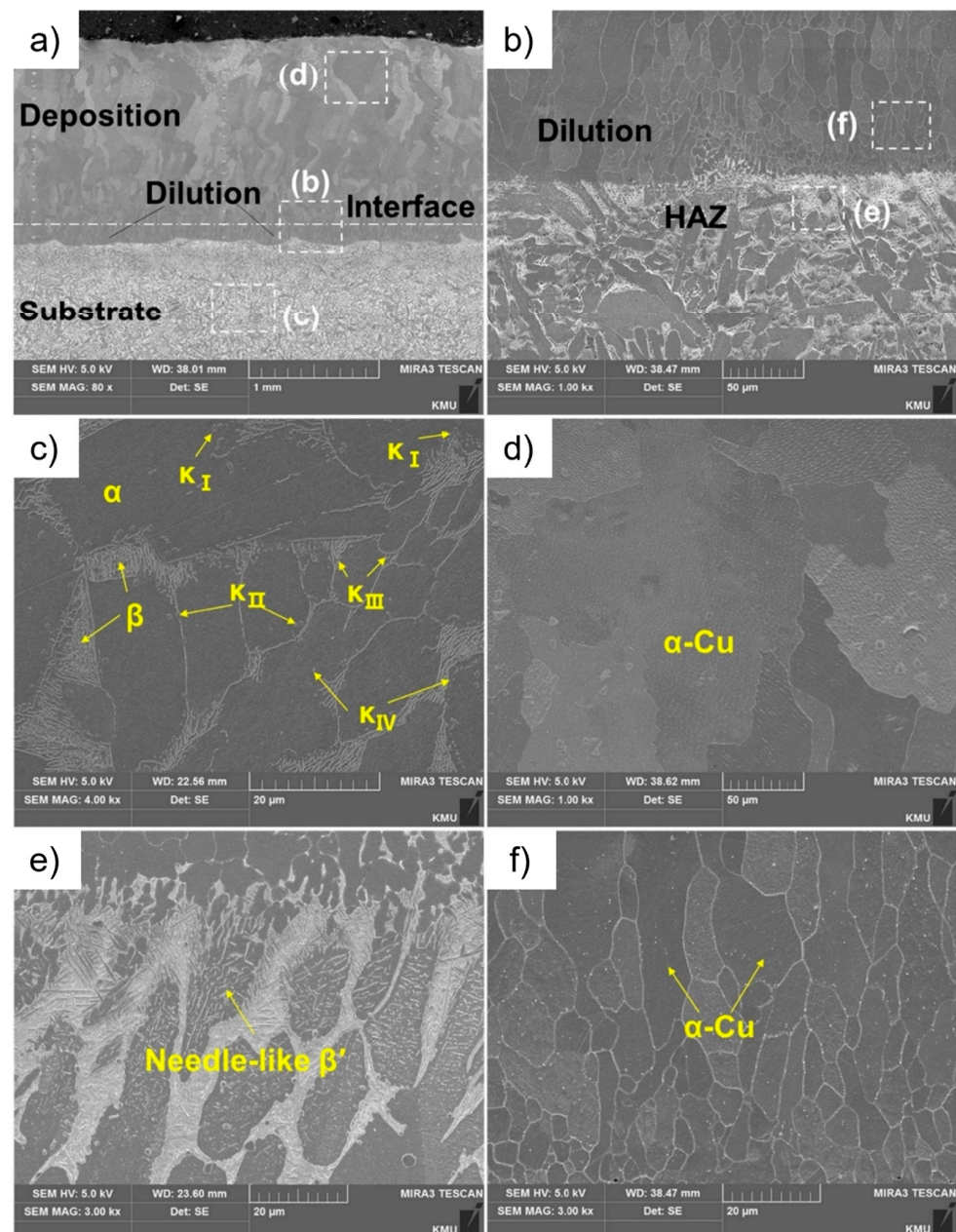


Figure 91. Microstructural features of (a,b) interfacial region of the L-DED-fabricated CuNi2SiCr/NAB bimetal part, (c) NAB substrate, (d) CuNi2SiCr-deposited layers, (e) HAZ region, and (f) diluted region (Reprinted with permission from [169]).

In a complementary study, Yao et al. [170] investigated the corrosion behavior of the L-DED-fabricated CuNi2SiCr/NAB bimetal part and reported that the CuNi2SiCr-deposited layers were characterized by slightly higher electrochemical corrosion stability and lower corrosion current density due to their single-phase (α) microstructure, which eliminates micro-galvanic coupling and selective corrosion between phases compared to the multiple-phase microstructure of the NAB substrate. However, the results of the immersion tests revealed that the corrosion resistance of the NAB substrate was significantly greater than that of the CuNi2SiCr-deposited layers due to the formation of a dense oxide layer (Al_2O_3) on the NAB substrate surface as a result of the presence of Al in its composition. Figure 92 illustrates the surface morphology of the NAB substrate and deposited layers after immersion corrosion tests at different time intervals. Overall, the researchers emphasized that the corrosion resistance of the CuNi2SiCr-deposited layers was lower than that of the NAB substrate. Hence, they recommended against the use of L-DED deposition of CuNi2SiCr powders for repairing NAB propellers unless additional post-treatments such as heat treatment, further alloying, or surface treatments were employed.

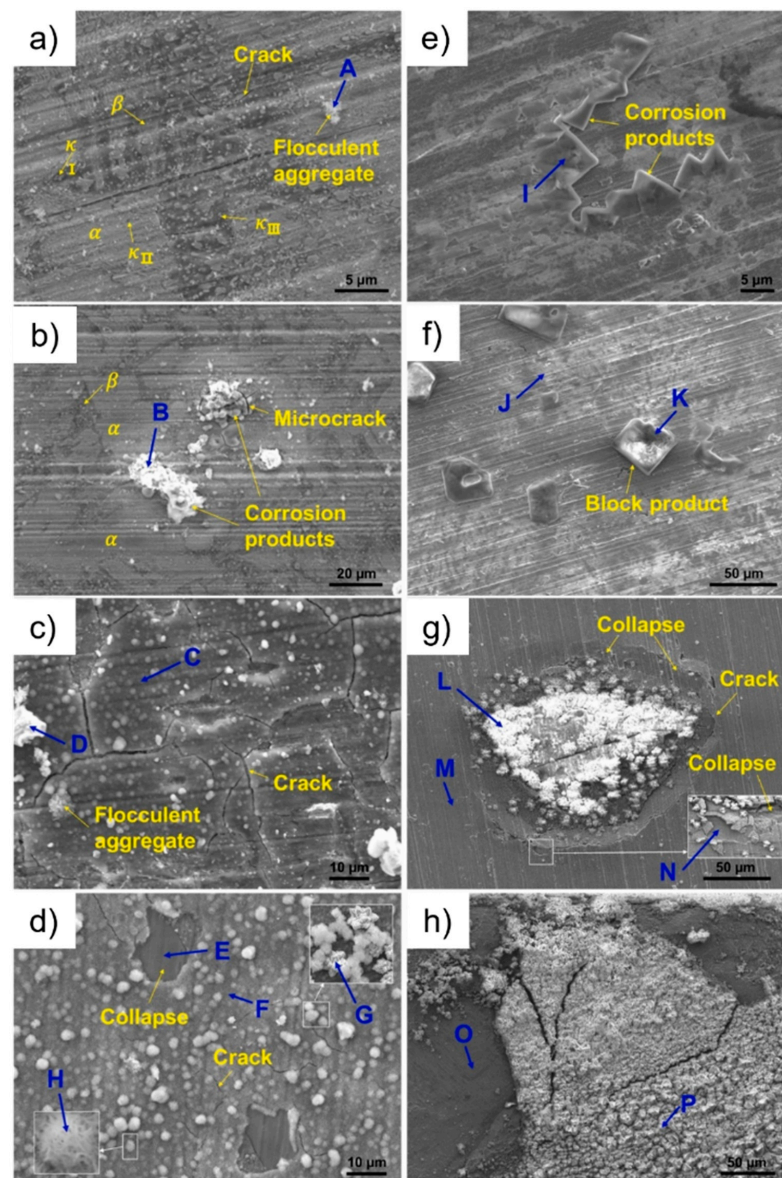


Figure 92. After-immersion surface morphology of the (a–d) NAB substrate and (e–h) deposited layers at different immersion times: (a,e) 1 day, (b,f) 5 days, (c,g) 14 days, and (d,h) 28 days (Reprinted with permission from [170]).

In another study, Li et al. [168] investigated the interface formation in a L-DED-fabricated NAB/15-5 PH stainless steel bimetal part (see Figure 93a–c). They reported the formation of a crack-free interface with no lack of fusion containing Fe_xAl dendrites, which can be seen in Figure 93d–h.

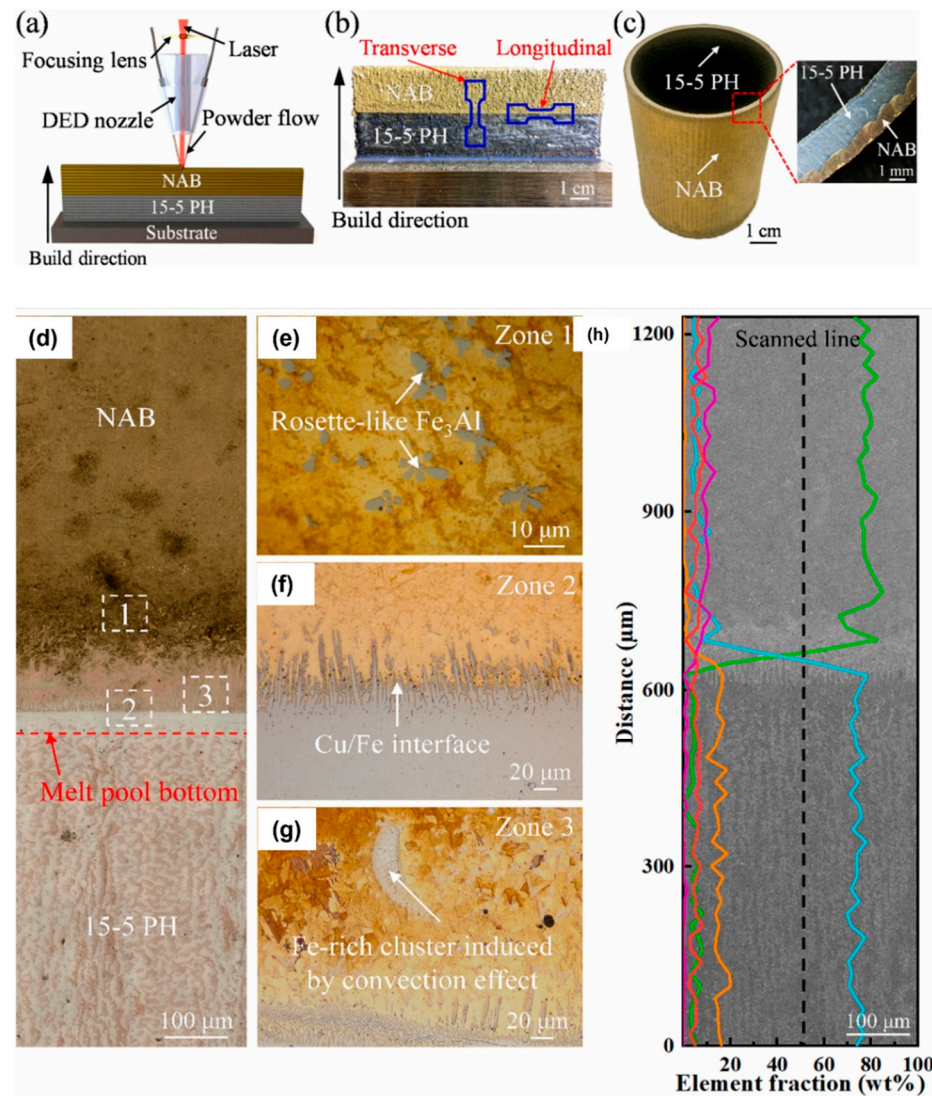


Figure 93. (a) Schematic illustration showing the L-DED fabrication process of NAB/15-5 PH bimetal samples; (b) a representative of the as-fabricated part showing the tensile sample preparation; (c) a prototype of a bimetal NAB/15-5 PH part; (d) low-magnification confocal image, covering the last layer of 15-5 PH side, interface, and the first layer of NAB side; (e–g) higher magnification images taken from zones 1, 2, and 3 of (d), respectively; and (h) EDS elemental line scan covering NAB side, interface, and 15-5 PH side (Reprinted with permission from [168]).

The mechanical testing on the interface region at different orientations (see Figure 93b for sample preparation orientation) revealed that the deformation occurred through different mechanisms in the transverse and longitudinal directions. When tensile loading was applied in the transverse direction, the contribution of the NAB side was found to be more dominant, resulting in better ductility. However, in the longitudinal direction, premature failure was observed due to the brittle Fe_xAl phases constraining the deformation process. The crystal incoherency between Fe_xAl and Cu caused stress concentration and led to cracking at the interface of the Fe_xAl and Cu phases in the bimetal part, as schematically illustrated in Figure 94.

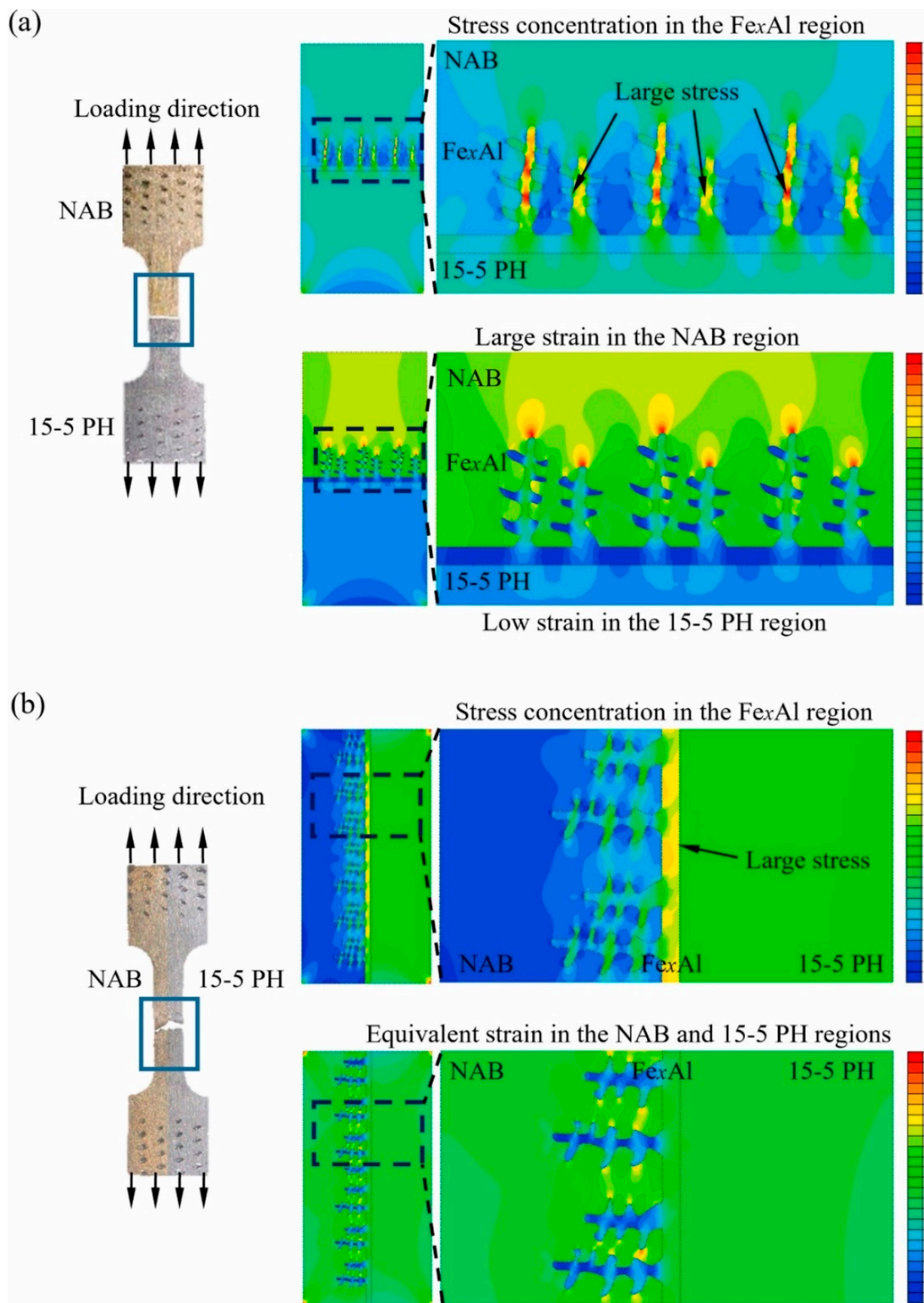


Figure 94. Schematic illustration of stress concentration at the tips of Fe_xAl dendrites during tensile loading in (a) longitudinal and (b) transverse directions in the L-DED-fabricated NAB/15-5 PH bimetal part (Reprinted with permission from [168]).

The results of electrochemical and immersion testing in 3.5 wt.% NaCl electrolyte also revealed that the deposition of NAB on the surface of 15-5 PH increased the corrosion resistance and service lifetime of the bimetal part in the seawater atmosphere. The NAB alloy exhibited higher pitting resistance compared to the SS side (see Figure 95).

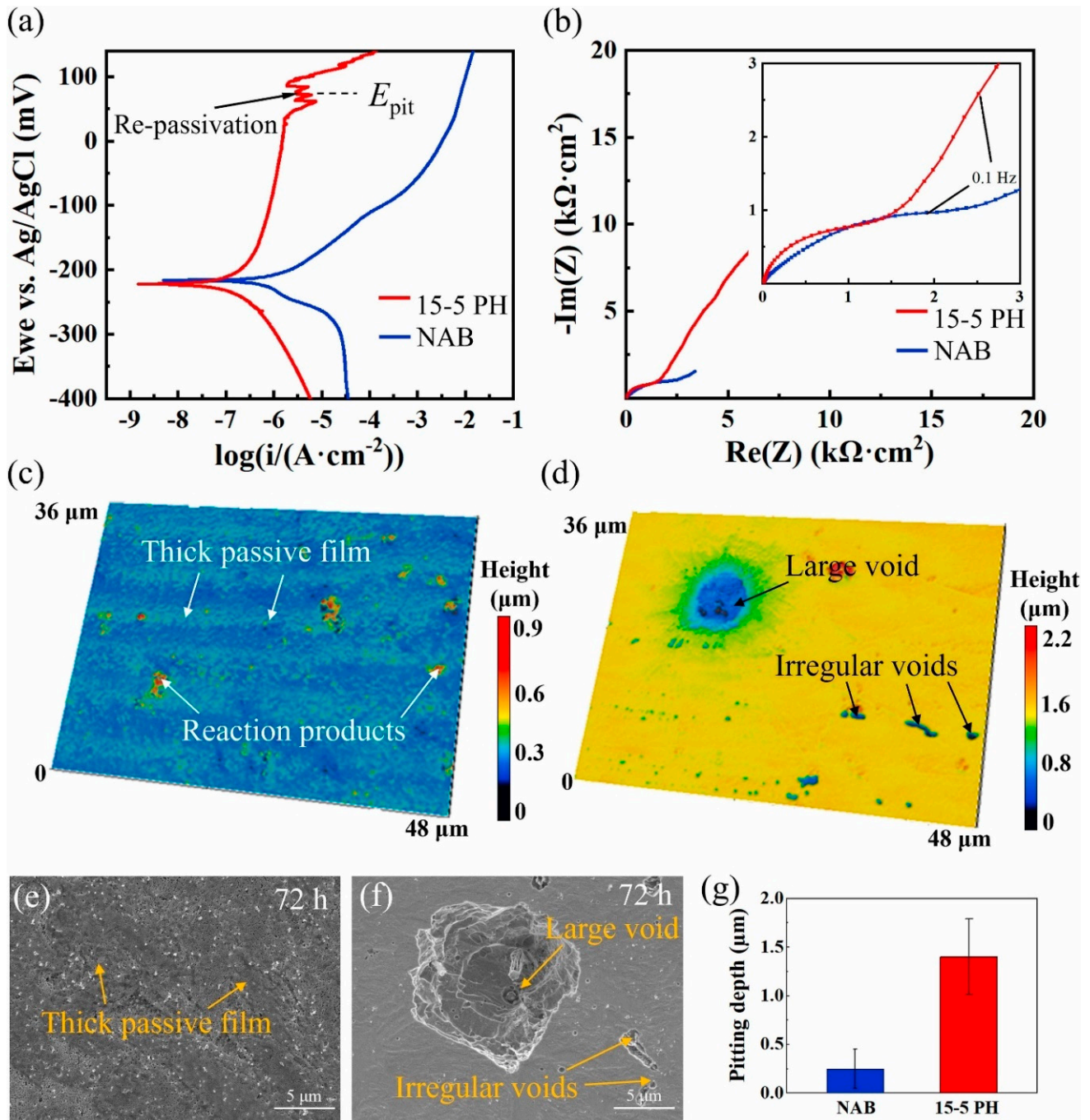


Figure 95. Corrosion properties of the L-DED bimetal NAB/15-5 PH part: (a) PDP curves, and (b) Nyquist plots resulted from EIS testing. Surface profiles of (c) NAB and (d) 15-5 PH after 72 h of immersion. SEM images taken from the corroded surfaces of (e) NAB and (f) 15-5 PH after 72 h of immersion. (g) The depth of the corrosion pits in the NAB and 15-5 PH (Reprinted with permission from [168]).

6. AM of Reinforced Copper Composites

As discussed in the introduction section, AM of pure copper presents challenges due to its low laser absorption, especially in laser powder bed fusion AM [55], resulting in printed parts with insufficient density and low mechanical properties [50,172]. While adding alloying elements to pure copper can improve its mechanical properties, it may compromise the electrical and thermal conductivities of the printed parts. Therefore, researchers have explored the development of copper-based metal matrix composites (MMCs) using AM techniques. The primary goal for the fabrication of these MMCs is to mobilize the Orowan strengthening mechanism in the alloy without negatively impacting its crystallographic structure, electrical conductivity, and thermal conductivity [173].

The addition of different reinforcements to copper matrices produced by AM has been studied in a variety of ways over the past few years. Many studies have focused on the use of carbon allotropes as reinforcements, including diamond, graphene derivatives, and carbon nano-particles. Diamond can provide exceptional thermal conductivity, which is beneficial in producing MMCs suitable for tooling and thermal management applications [174,175]. Graphene, with its unique 2D-structure and excellent properties, can improve the mechanical response of AM-fabricated copper parts without significantly compromising their electrical conductivity [176]. Moreover, the addition of carbon nano-particles to the surface of copper powders has been proposed as a way to improve the laser absorptivity of copper powder particles [177].

Despite the significant benefits gained from using carbon allotropes as reinforcing agents in copper, the segregation of carbon, defects along the grain boundaries, and graphitization during the AM process remain significant drawbacks of copper-carbon MMCs. To address this issue, ceramic reinforcements can be used during AM of copper due to their high stability at higher temperatures [178]. For example, the in-situ formation of ZrB_2 ceramic particles during the AM processing has been found to be effective in improving mechanical properties [178,179]. Differently, copper-alumina composites have shown considerable phase segregation due to their different melting points, leading to the separation and agglomerations of dispersed particles and a consequent loss of dispersion strengthening effect [180]. An alternative approach involves coating the feedstock copper powder particles with low-melting point metals, such as Sn. This method has been found to facilitate easier surface melting of the powders, better necking between the powders, and improved density of the AM-fabricated copper parts [181].

In the upcoming sections, all the available research on the additive manufacturing of copper-based MMCs by incorporating different reinforcing particles into the copper matrix are reviewed. Table 8 presents a summary of the processing parameters and measured properties of additively manufactured reinforced copper composites.

Table 8. Summary of all the processing parameters and properties of additively manufactured reinforced copper composites.

AM Process	Matrix	Reinforcement	Maximum Relative Density (%)	Process Parameters	Reflectance (%)	Maximum Thermal Conductivity (W/m·K)	IACS (%)	Maximum Tensile Strength (MPa)	Maximum Vickers Hardness (HV)	Ref.
DED	Pure Cu	Diamond (5 vol%)	96	Proper scan speed: 12.7 mm/s Hatch spacing: 0.3 mm Proper laser power: 900 W Layer thickness: 0.2 mm	-	330	-	-	-	[175]
DED	Cu-13.96wt.%Ni-10.41wt.%ZrO ₂ -3.04wt.%Al-2.59wt.%Ni-B ₄ C	ZrB ₂	-	Proper scan speed: 3 mm/s Proper laser power: 1800 W	-	-	-	535.24	-	[178]
BJT	Pure Cu	Diamond (10 and 50 vol%)	45.05	Traverse speed: 30 mm/s Rotational speed: 500 rpm Sintering process: 2h 800 °C and 900 °C	-	-	-	-	-	[182]
L-PBF	Pure copper	GO (0.1 wt.%)	90.8 (83.1 for pure Cu)	Proper scan speed: 600 mm/s Hatch spacing: 0.06 mm Proper laser power: 175 W	57.1 (84.1 for pure Cu)	267.93	63.83	164.37	-	[23]
L-PBF	Pure copper	CNPs (0.1 wt.%)	98	Proper scan speed: 400 mm/s Hatch spacing: 0.12 mm Proper laser power: 725 W Layer thickness: 0.03 mm	33 (71 for pure copper)	164.2 *	39.2	125	-	[177]
L-PBF	CuCr0.3	CNPs (0.05 wt.%)	98.6	Proper scan speed: 300 mm/s Hatch spacing: 0.09 mm Proper laser power: 600 W Layer thickness: 0.03 mm	44 (58 for pure CuCr0.3)	326 *	78	271	-	[63]
L-PBF	Pure copper	CNTs (0.5 wt.%)	~85	Proper scan speed: 47 mm/s Hatch spacing: 0.10 mm Proper laser power: 93 W	-	-	-	-	~112	[183]
L-PBF	Cu-14.4wt.%Sn-10.2wt.%Ti-1.5wt.%Zr	Diamond (10 and 20 vol%)	98.5	Hatch spacing: 0.08 mm Proper laser power: 100 W Layer thickness: 0.03 mm	-	-	-	-	-	[184]
SLS	Pure copper	Graphene nanoplatelets (1.9g Cu:0.1g C)	-	Proper scan speed: 2 mm/s Step size: 0.25 mm Proper laser power: 70 W Frequency: 50000 Hz	-	-	-	135	-	[176]

Table 8. Cont.

AM Process	Matrix	Reinforcement	Maximum Relative Density (%)	Process Parameters	Reflectance (%)	Maximum Thermal Conductivity (W/m·K)	IACS (%)	Maximum Tensile Strength (MPa)	Maximum Vickers Hardness (HV)	Ref.
SLS	Cu-4.1wt.%Zr-1.1wt.%B	ZrB ₂	98	Proper scan speed: 0.5 mm/s Step size: 0.5 mm Frequency: 3 Hz Pulse duration: 10 ms	-	-	42	-		[179]
SLS	Cu-10wt.%Sn	Sn	36	Proper scan speed: 1.5 mm/s Proper laser power: 90 W Frequency: 1 Hz	-	-	0.2	-		[181]
EBM	Pure copper	Al ₂ O ₃ (2.28wt.%)	-	Proper scan speed: 3000 mm/s beam current: 1.67–26.67 ×10 ^{−3} A Layer thickness: 0.05 mm	-	-	-	-	-	[180]

* Calculated using Wiedemann-Franz law.

6.1. AM of Cu-C Composites

Carbon allotropes, including diamond, graphene, carbon nano-tubes (CNTs), carbon nano-particles, and fullerene, are among the most promising materials for fabricating metal matrix composites (MMC) due to their exceptional combination of mechanical properties and thermal/electrical conductivity [24,185,186]. With almost no equilibrium solid solubility in copper, carbon allotrope reinforcements can remain embedded intact in the copper matrix [187]. In addition, the high electrical conductivity, thermal conductivity, strength, and self-lubrication characteristics of copper-carbon MMCs make them excellent candidates for various applications in many industries, such as electrical, microelectronics, tooling, nuclear, and aerospace [188]. However, the inadequate wettability and bonding between copper and carbon can lead to segregation and degradation of the mechanical response, which must be taken into account [174]. Another issue is that graphite, as the most stable form of carbon, is incapable of enhancing the conductivity and mechanical properties of copper MMCs [189]. For instance, it has been shown that the graphitization of diamond in vacuum occurs at temperatures between 970 °K and 1670 °K. As this temperature range can be readily reached during laser or electron beam-based AM processes, careful attention should be paid to avoid this allotropic transformation during AM processing [190].

Diamond has high thermal conductivity and a low coefficient of thermal expansion (CTE) [174], making copper-diamond MMC an appropriate choice for electronic and tooling applications where rapid and efficient heat dissipation is required [175]. However, inadequate bonding between copper and diamond poses a significant challenge, as the interface between the matrix and the reinforcing agent plays a crucial role in the properties of MMCs [191]. To address the problem of low chemical affinity and poor bonding between diamond and copper, Constantin et al. [175] fabricated copper-diamond composites using L-DED by introducing TiO₂-TiC interlayers. They used a feedstock powder mixture of 95 vol.% copper and 5 vol.% diamond precoated with TiO₂-TiC. Figure 96 shows the precoated diamond particles, corresponding Raman spectra, and a schematic illustration of their adopted L-DED process.

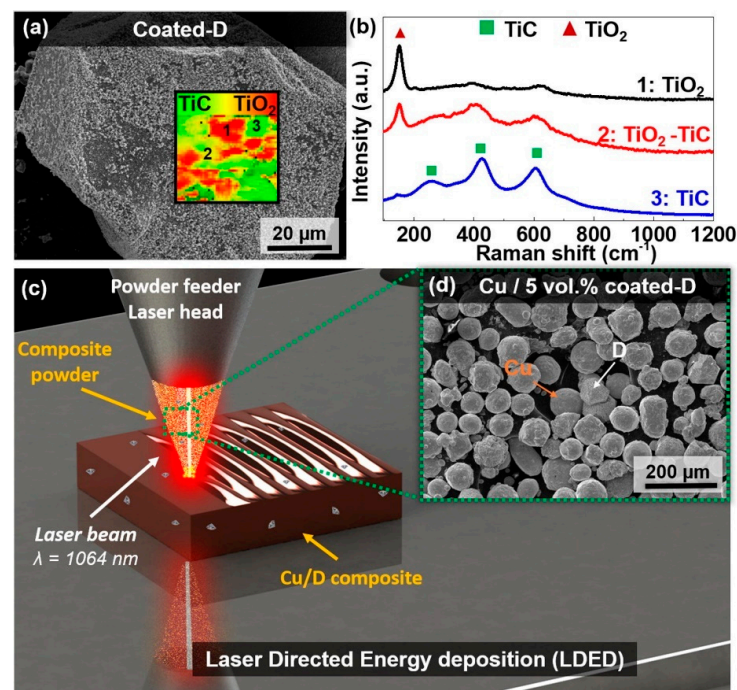


Figure 96. (a) TiO₂-TiC-coated diamond particles produced by the molten salt method, (b) Raman spectra of TiO₂-TiC powder taken from the selected area of interest, (c) schematic illustration showing the L-DED process, and (d) SEM image of the copper/diamond powder mixture (Reprinted with permission from [175]).

Figure 97 displays the printed surfaces obtained using various printing parameters. While they found a significant number of defects when using scan speeds ranging from 8.7 to 21.7 mm/s and laser power levels between 700 W and 1000 W, a narrow parameter window with a scan speed of 12.7 mm/s and laser power levels between 900 and 925 W resulted in the lowest level of defects.

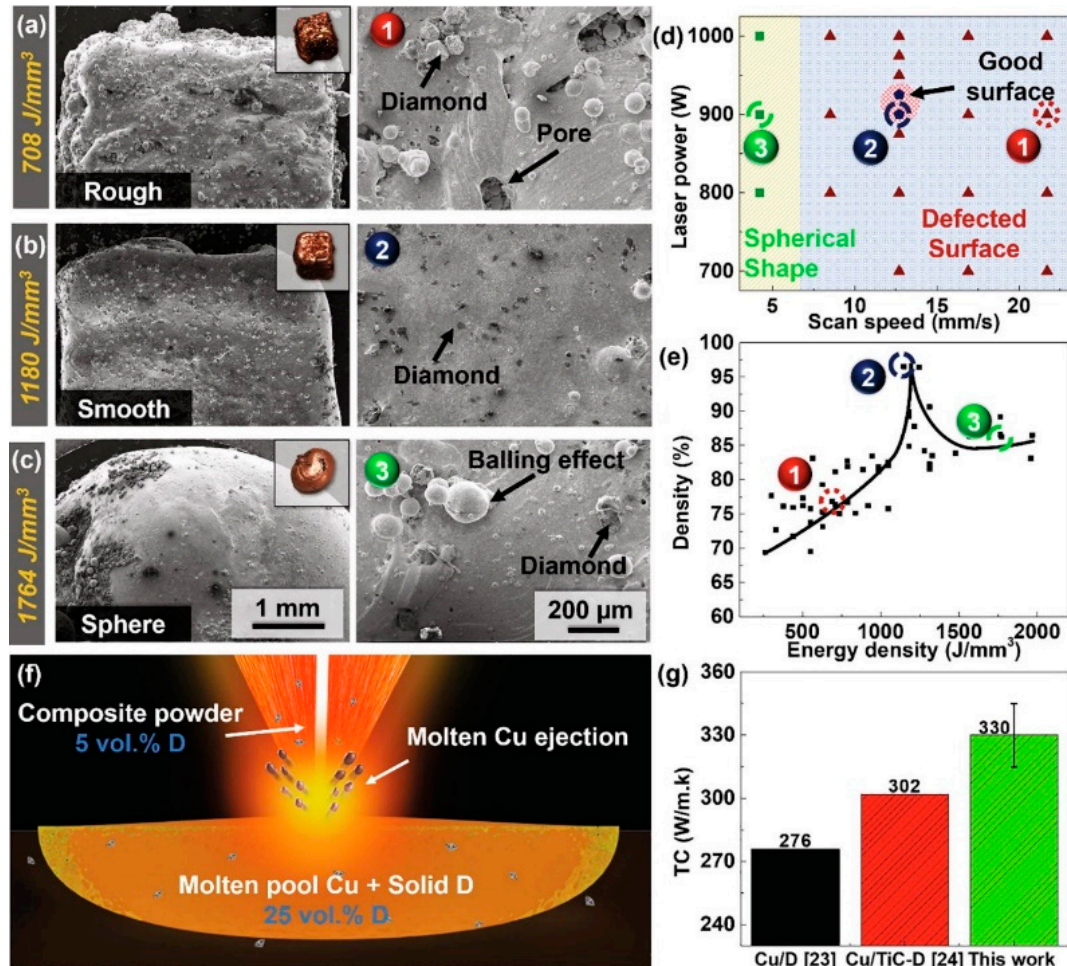


Figure 97. (a–c) SEM images taken from the surface of L-DED-fabricated copper-diamond composites with different energy densities, (d) effect of process parameters on the quality of the printed parts, (e) effect of laser energy density on the density of the printed parts, (f) schematic illustration showing the process of particle ejection during the deposition process, and (g) effect of interphase on the thermal conductivity (TC) of copper-diamond composites when using no interphase (black bar), only TiC interphase (red bar), and TiO₂-TiC interphase (green bar) (Reprinted with permission from [175]).

The HR-TEM images presented in Figure 98 show a smooth transition with no porosities at the interface of copper/TiO₂, TiO₂/TiC, and TiC/diamond, confirming a sound metallurgical bonding between the particles. Furthermore, comparing the micro-Raman spectra of the as-received diamond particles and the coated diamond after laser printing revealed no graphitization in the diamond structure (refer to Figure 99). They also reported an excellent thermal conductivity of 330 W/m·k, which is relatively higher than the values reported for the Cu/diamond composites fabricated using field-assisted sintering technology (302 W/m·k) [192] and mixing + sintering + hot-pressing (276 W/m·k) [193]. Although Constantin et al. [175] conducted extensive microstructural characterizations, they did not measure the mechanical properties in their study, which should be investigated in future research.

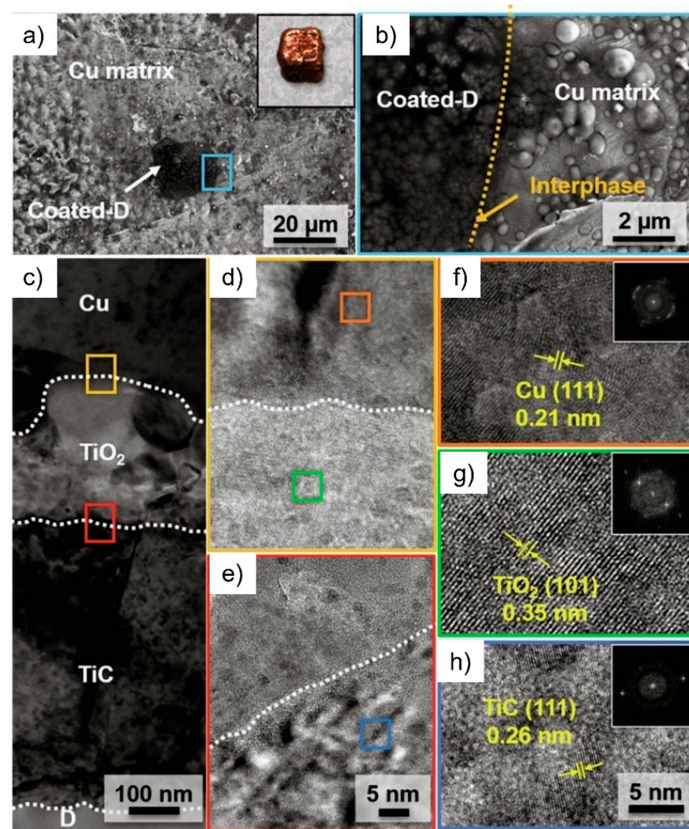


Figure 98. (a,b) SEM images of the L-DED-fabricated copper-diamond surface, (c) cross-sectional view of copper-(TiO₂-TiC)-diamond, (d) copper/TiO₂ interface, (e) TiO₂/TiC interface, and (f–h) HR-TEM micrographs of copper, TiO₂, and TiC, respectively (Reprinted with permission from [175]).

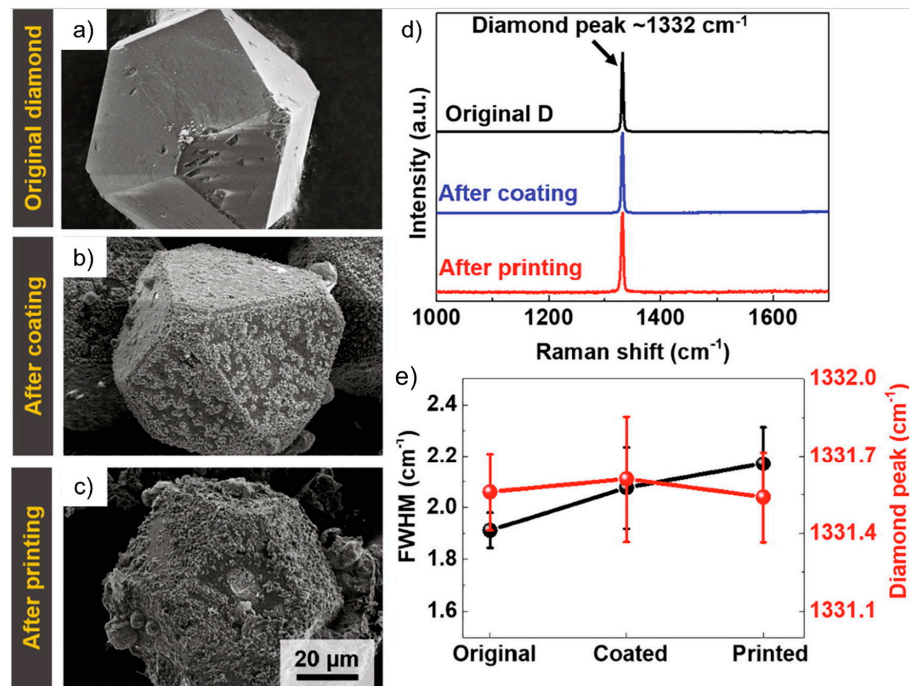


Figure 99. SEM images taken from (a) the original diamond particle, (b) the TiO₂-TiC-coated diamond particle before L-DED printing, and (c) after L-DED printing. (d) The corresponding Raman spectra from the powders at different states and (e) full width at half maximum (FWHM) and the diamond peak' position in different states of the powders (Reprinted with permission from [175]).

In another study, Li et al. [182] investigated the copper-diamond composites produced by binder jetting (BJT) as a low-temperature printing method compared to other AM techniques. The lower temperature in BJT not only reduces process costs but also decreases the possibility of graphitization, which was confirmed by the XRD results (see Figure 100a) in Li's study [182]. They used two different volume fractions of copper-coated diamond powders (10 vol. % and 50 vol. %) mixed with pure copper powder and implemented two different sintering temperatures of 800 °C and 900 °C. The bar chart in Figure 100b shows that the highest relative density (69.1%) was achieved in the case of 10 vol. % copper-coated diamond powders sintered at 900 °C due to the higher sintering temperature and better sinterability as a result of a larger fraction of pure copper in the powder mixture [182].

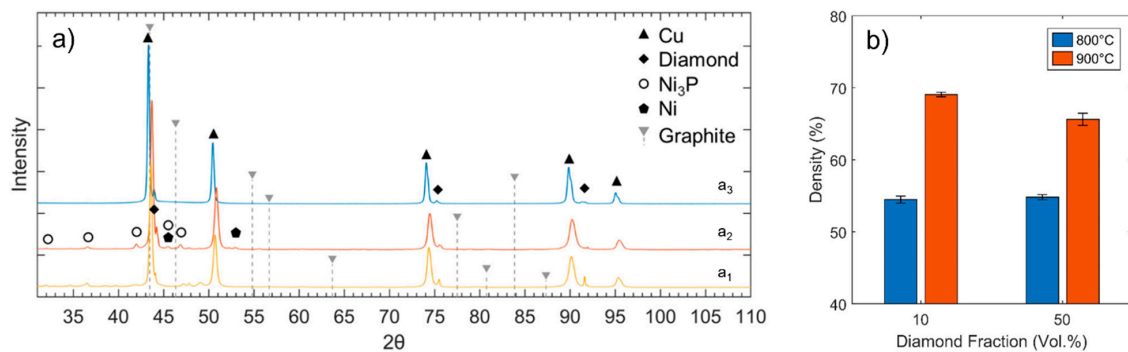


Figure 100. (a) XRD results of a BJT-fabricated copper-diamond composite in the (a₁) green state, (a₂) after sintering at 800 °C, and (a₃) after sintering at 900 °C, along with the (b) relative density of the samples fabricated with different volume fractions of diamond and different sintering temperatures (Reprinted with permission from [182]).

The effect of sintering temperature on the fracture behavior is shown schematically in Figure 101a, followed by fractography analysis (Figure 101b,c). At the higher sintering temperature (900 °C), a distinct matrix was formed by merging the pure copper powder and the copper coating on the diamonds, which surrounded the pure diamond particles. In contrast, at the lower sintering temperature (800 °C), only a limited number of necks formed among particles (see Figure 101a). Consequently, the 800 °C sintered samples exhibited a granular fracture, where the debonding occurred at the interface of the coating (copper) and the core (diamond particles), while the fracture in the 900 °C sintered samples occurred at the interface of the pure diamond particle and the copper matrix (see Figure 101b,c). However, the study did not report the effect of sintering temperature on the electrical/thermal conductivity, corrosion resistance, and mechanical properties of the BJT-fabricated copper-diamond composite [182]. Such performance analyses are crucial for determining the suitability of the composite for use in real-world service environments.

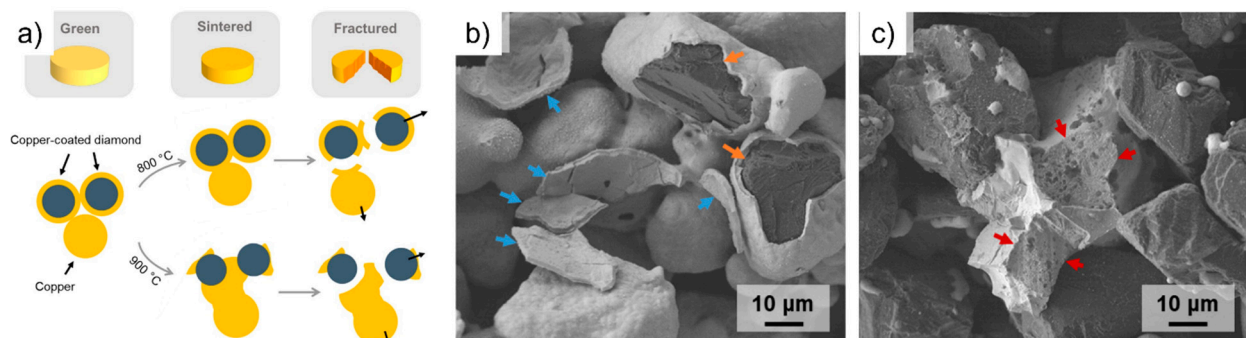


Figure 101. (a) An schematic illustration showing the effect of sintering temperature on the BJT-fabricated copper-diamond composite sample, along with the fracture surfaces of the samples sintered at (b) 800 °C and (c) 900 °C (Reprinted with permission from [182]).

Spierings et al. [184] employed a different approach for the fabrication of copper-diamond composites through L-PBF. They used a mixture of Ni-coated diamond particles and Cu-Sn-Ti-Zr brazing alloy powder as the feedstock material. Ni-coating was chosen to improve the bonding strength and provide better thermal stability for diamond particles during the laser treatment. They found that using a single-scanning strategy, a hatch spacing of 0.08 mm, and energy density of 42 J/mm³ resulted in the best optically evaluated density. Their microstructural analysis showed the formation of TiC interlayers at the interface of the diamond and copper matrix, which has been reported to improve the bonding between the reinforcements and the matrix [194]. Notably, their XRD analysis confirmed that there was no graphitization during the L-PBF process [184].

Graphene is a 2D material with a honeycomb structure, high electrical/thermal conductivity, a great Young's modulus, and high tensile strength, making it an ideal reinforcement for copper matrix composites to achieve a combination of superior mechanical response and high conductivity [176,195,196]. In addition, its high melting point temperature ensures stability during laser-based AM processing. Hu et al. [176] prepared a mixture of 1.9 g copper micro-powders, 0.1 g graphene nanoplatelets, 2 g polyvinyl alcohol (PVA), and 46 g of deionized water, which was dried and coated on an AISI 4140 substrate. They used the SLS process with a laser intensity of 70 W, a laser beam size of 0.8 mm, a scanning speed of 2 mms⁻¹, and a step size of 0.25 mm. Their microstructural analysis showed the uniform distribution of graphene sheets in the copper matrix and revealed different microstructural characteristics of the SLS-fabricated composite sample. Hu et al. [176] also evaluated the mechanical properties of the SLS-fabricated copper-graphene composite by Vickers microhardness and nano-indentation. The Vickers hardness of the AM copper-graphene composite was found to be 68.75% higher than that of the as-received copper plate due to the superior mechanical properties of graphene reinforcements. Moreover, the load-displacement curves obtained from nano-indentation confirmed that the SLS-fabricated copper-graphene composite had higher hardness, strength, and modulus, as evidenced by a deeper penetration of the copper under the same load.

Corona et al. [23] investigated the L-PBF fabrication of copper-graphene oxide (GO) composites. In their study, they added 0.1 wt.% GO to the Cu powder and mechanically mixed it for 12 h, followed by L-PBF treatment. Figure 102 illustrates the mixed composite powder containing GO flake (a) and the surface of the 3D-printed Cu-GO composite specimen, revealing the presence of pores containing pristine copper particles (b). They found that the addition of graphene oxide reduced the reflectivity by 30% and improved the density from around 83% for pure copper to approximately 90% for the Cu-GO composite. They also reported that the Cu-GO matrix shows 43% higher electrical and 42% higher thermal conductivity in comparison with the L-PBF-fabricated pure copper. As shown in Figure 102c, the tensile testing in horizontal and vertical directions demonstrated 160% and 660% increases in vertical strength and strain, while only 37% and 236% increases in strength and strain to break point were recorded for the horizontal direction, respectively [23]. It should be noted that while anisotropic mechanical response is a characteristic feature of the L-PBF-fabricated parts, the addition of GO to copper could contribute to a more homogenous mechanical performance.

Carbon nano-particles can also be utilized as an alternative reinforcement for highly reflective copper powders to enhance optical absorption and improve the functional properties of L-PBF printed components [177]. Jadhav et al. [177] studied the effect of carbon nano-particle addition to the surface of copper powders with the aim of improving the laser absorptivity of the copper. The maximum part density of 98% was achieved using a laser power of 725 W, a scan speed of 400 mm/s, and a hatch spacing of 0.12 mm [177]. Figure 103a,b depict the unpolished top view of the L-PBF-fabricated composite sample, showing carbon segregation and crack formation on the surface of the material. Figure 103c,d show the corresponding polished samples, indicating that the cracks were filled by segregated carbon, phosphorous, and oxygen, as proved by EDS analysis. Further

examination of the samples through etching (see Figure 103e,f) revealed that the cracks were formed along the grain boundaries.

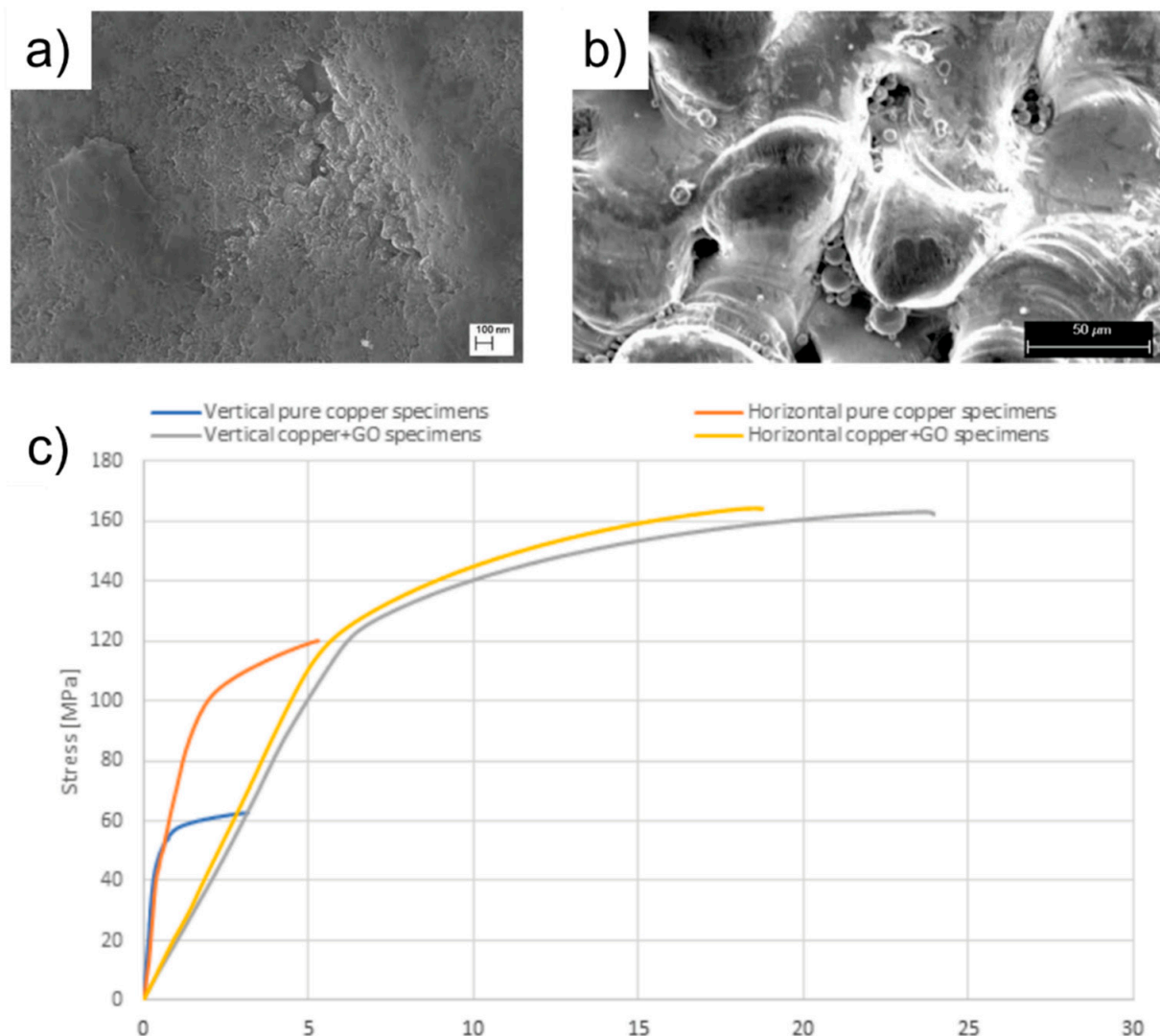


Figure 102. SEM images taken from (a) mixed composite powder before the L-PBF process and (b) surface of the L-PBF-fabricated Cu-GO composite specimen, along with the (c) stress–strain curves of as-printed samples in vertical and horizontal directions (Reprinted with permission from [23]).

The optical absorption values for laser wavelengths of 1060 nm–1080 nm showed a 38% increase for copper powders coated with carbon nano-particles compared to virgin copper [177]. However, their fractography analysis revealed that impurity segregation along the grain boundaries and cracks resulted in an insufficient mechanical response (tensile strength of 125 MPa and strain of 3%), which was relatively lower than other references [197].

In a subsequent study, the same authors utilized CuCr0.3 pre-alloyed powder and a lower concentration of carbon nano-particles (0.05 wt.%) [63]. Figure 104a–d shows the SEM images taken from the virgin CuCr0.3 alloy powder before and after mixing with carbon nano-particles used for L-PBF fabrication of copper-carbon composites. They observed that the presence of chrome in the feedstock played a positive role in reducing carbon segregation in comparison with their previous study (compare Figure 104e,f with Figure 103a,b). This was ascribed to in-situ deoxidation during the L-PBF process and the formation of nano-sized metallic chrome and chromium-carbides in the matrix [63].

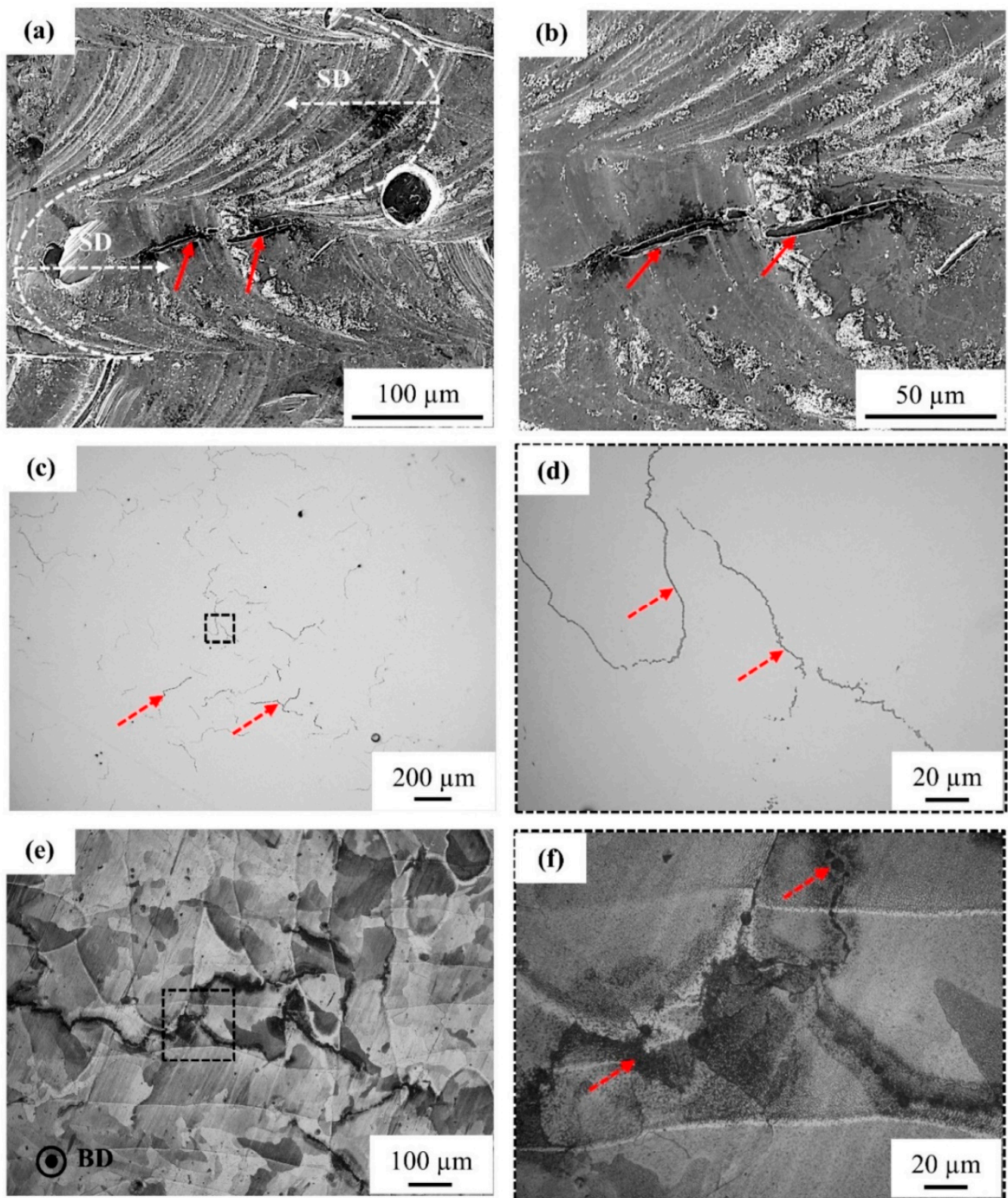


Figure 103. (a,b) Unpolished top view of the L-PBF-fabricated copper-carbon composite, (c,d) the corresponding polished (unetched) samples, and (e,f) the corresponding etched samples (Reprinted with permission from [177]).

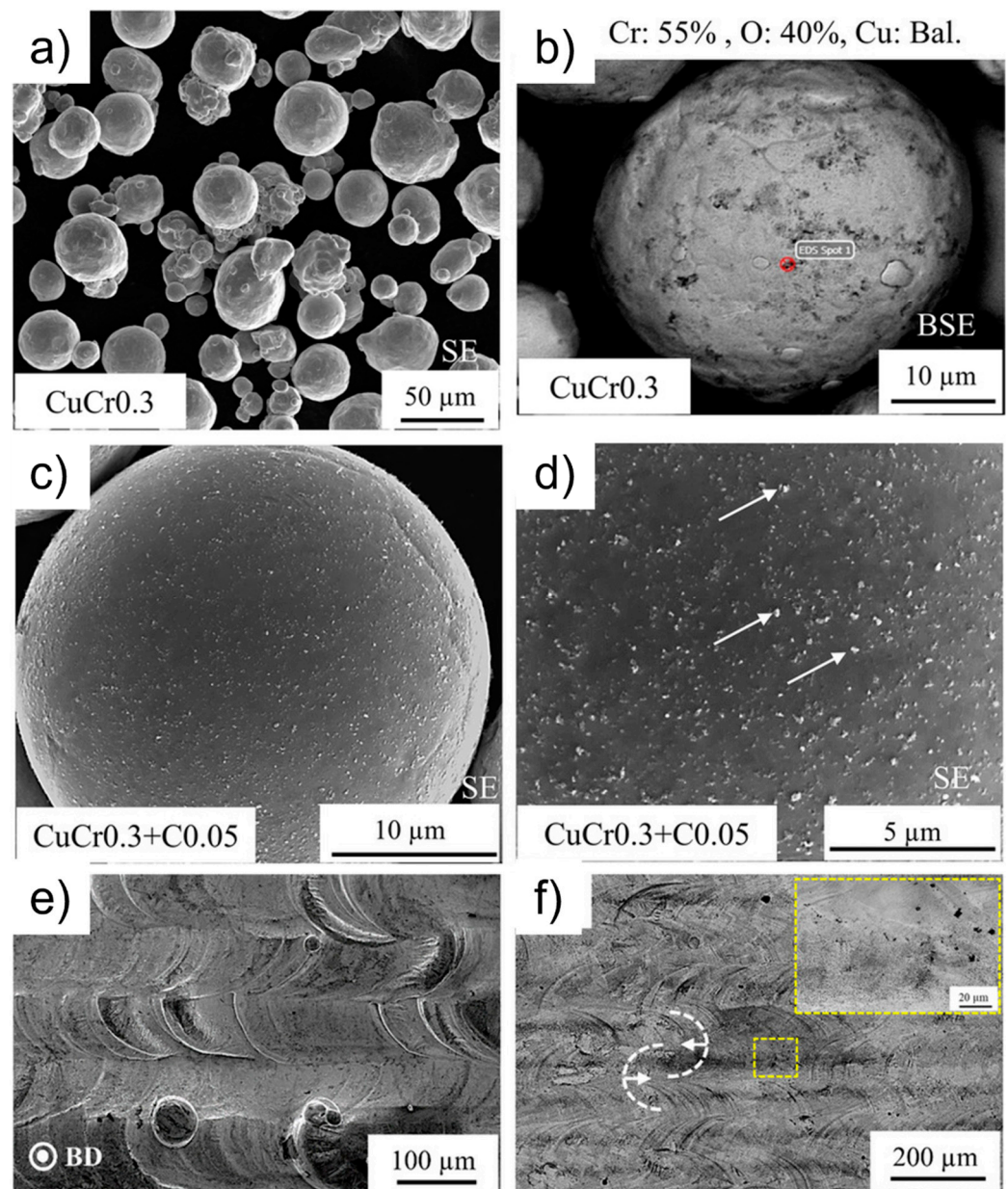


Figure 104. (a,b) Virgin CuCr0.3 alloy powder, (c,d) mixed CuCr0.3 powder and carbon nanoparticles, along with the SEM images taken from the top view of the L-PBF-fabricated (e) CuCr0.3 alloy, and (f) carbon-mixed CuCr0.3 composite used for L-PBF fabrication of copper-carbon composite (Reprinted with permission from [63]).

Mechanical response, strain rate sensitivity, and time-dependent deformation behavior (creep) of L-PBF-fabricated Cu-0.5 wt.% CNT composite were studied by Sadeghilaridjani et al. [183]. The Cu-CNT composite exhibited higher porosity content and lower hardness, which was attributed to weak physical interaction between CNTs and Cu particles. This resulted in inefficient energy transfer from CNTs to Cu particles. This study also found higher strain rate sensitivity (SRS) and creep displacement in the Cu-CNT composite due to the higher porosity, which facilitates the annihilation of the dislocations.

6.2. AM of Cu-Ceramic Composites

Ceramic materials, such as zirconium diboride (ZrB_2), are excellent reinforcements for copper alloys due to their high strength, wear resistance, and hardness [198]. Other manufacturing techniques, such as powder metallurgy and hot-pressed sintering, have

been utilized to take advantage of the beneficial effect of ZrB_2 on the mechanical properties of copper [199,200]. While the high-temperature stability and melting point of ZrB_2 make it a suitable reinforcement for high temperature additive processes [201], poor wetting of ZrB_2 in contact with liquid copper remains a challenge [202]. To overcome this challenge, multicomponent systems have been introduced. For example, Lv et al. [178] used a pre-mixed powder with a final composition of 70 wt.% Cu, 13.96 wt.% Ni, 10.41 wt.% ZrO_2 , 3.04 wt.% Al, and 2.59 wt.% $\text{Ni-B}_4\text{C}$ to develop in-situ needle-like ZrB_2 -reinforced Cu composites using the L-DED process. Figure 105 shows an SEM image taken from the powder mixture used as the feedstock for the L-DED fabrication of the copper- ZrB_2 in-situ composite. The addition of Ni to the mixture improved the bonding between the copper and ceramic and also enhanced the stability of the melt pool.

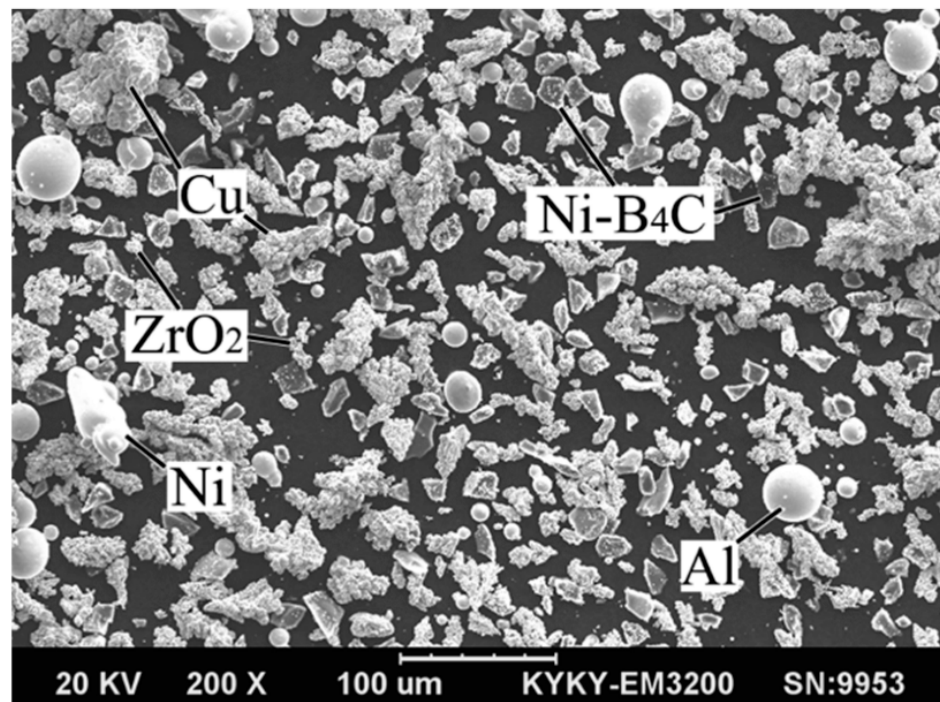


Figure 105. SEM image taken from the powder mixture used for the L-DED fabrication of the copper- ZrB_2 in-situ composite (Reprinted with permission from [178]).

Theoretically, the in-situ synthesis reaction described by Equation 1 was expected to occur, as the Gibbs free energy of the reaction is negative. Experimental confirmation of this reaction was obtained through SEM and XRD analyses of the fabricated sample, as shown in Figure 106.



According to Figure 106a, the microstructure of the fabricated samples mainly consisted of needle-like ZrB_2 and Ni dendrites embedded within a Cu matrix. Mechanical properties testing revealed that the average hardness of the L-DED-fabricated copper- ZrB_2 composite ($294.26\text{ HV}_{0.2}$) was approximately five times higher than that of pure copper, which was attributed to the presence of hard needle-like ZrB_2 and dendritic Ni phases. Additionally, the maximum ultimate tensile strength achieved in these L-DED-fabricated copper- ZrB_2 composites was 535 MPa, a significant improvement compared to pure copper.

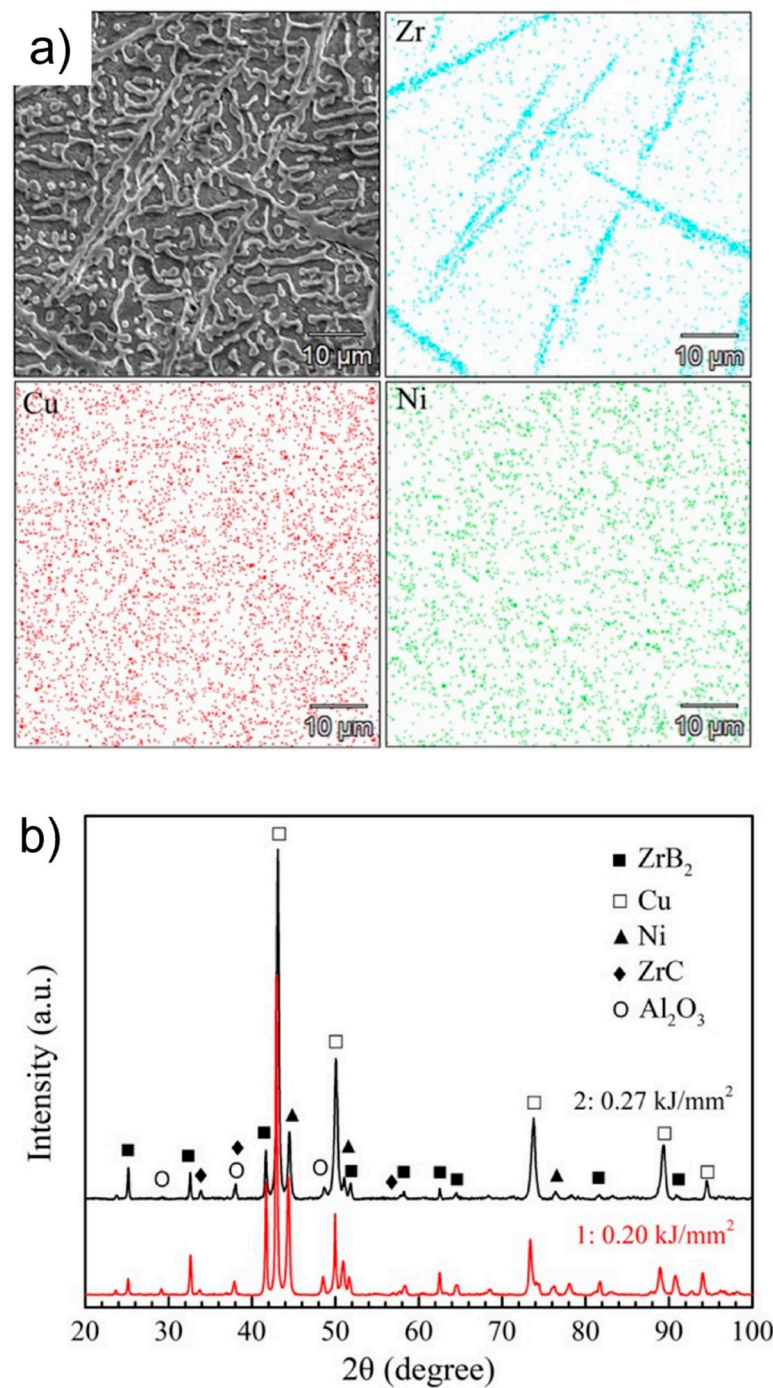


Figure 106. (a) Microstructure and elemental distribution maps of Zr, Cu, and Ni taken from the L-DED-fabricated copper-ZrB₂ in-situ composite and (b) the corresponding XRD results (Reprinted with permission from [178]).

In situ synthesis of reinforcing ZrB₂ particles in a copper matrix was also investigated in another study. Stašić et al. [179] used two sets of feedstock materials, that is, a mixture of Cu-1wt.%Zr and Cu-4.1wt.%Zr-1.1wt.%B, for the SLS processing of the composite. XRD and SEM analyses revealed the formation of non-uniformly distributed ZrB₂ particles and a metastable CuZr phase (Figure 107). The highest density and microhardness (135–180 HV) were found for the ternary alloy, compared to pure copper (60–64 HV) and the binary alloy (97–108 HV). The hardness improvement in the binary alloy (Cu-Zr) was attributed to the formation of Cu₅Zr phases, while the ternary alloy (Cu-Zr-B) resulted in the formation of ZrB₂ phases and metastable Cu₅Zr particles, ultimately leading to a higher degree of

hardening. However, the addition of alloying elements reduced the IACS factor from 96–98% for the pure copper to 82–89% for the binary alloy and 28–42% for the ternary alloy.

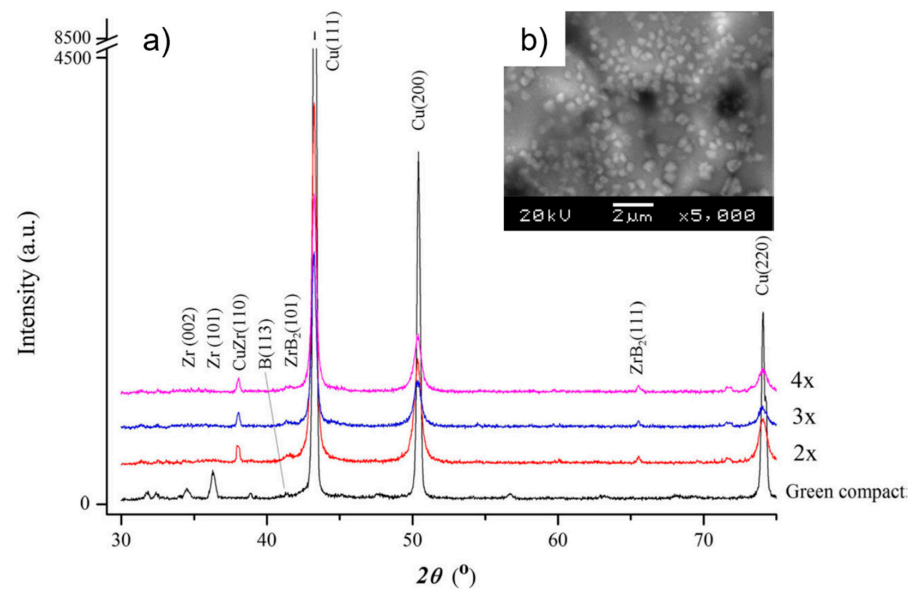


Figure 107. (a) XRD analysis and (b) SEM images taken from the SLS processed copper-ceramic composite using ZrB₂ reinforcing particles (Reprinted with permission from [179]).

Pobel et al. [180] produced an oxide dispersion-strengthened (ODS) copper powder with 5 vol. % alumina by using a ball milling process on a powder mixture of pure copper, pure aluminum, and copper oxide (see Figure 108) to be processed by selective electron beam melting (SEBM). All printed samples contained porosities and tunnel-shaped defects (see Figure 109a–c), with the lowest porosity levels found in samples with scan speeds of 3000 mm s^{−1} and 4000 mm s^{−1}, regardless of the energy density. At an energy density of 40 J mm^{−3}, porosity levels did not change when altering the scan speed, but at other energy density levels, the lowest scan speed had the highest porosity level. However, no clear general correlations were found between porosity level and scan speed or energy density, indicating that phase separation and melt pool dynamics are more dominant than processing parameters. Heavy de-mixing of copper and alumina was observed in all printed samples, indicating the occurrence of phase separation in the microstructure (Figure 109d–f). The authors identified three main driving forces for the phase separation of alumina and copper in the as-printed state: (i) high interface tension between molten copper and solid alumina, (ii) poor wettability of alumina by molten copper, and (iii) partial melting of alumina.

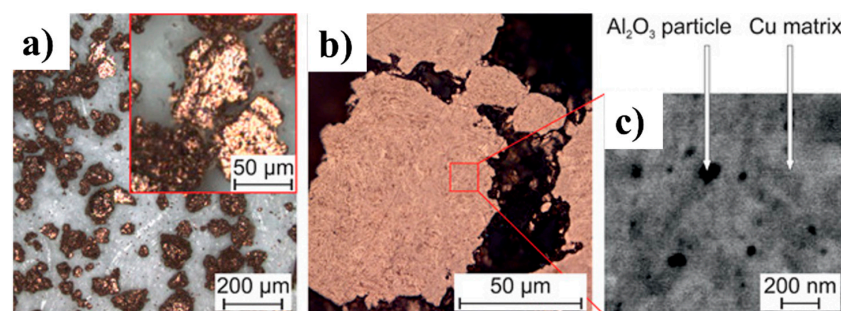


Figure 108. (a) An overview of the ODS-Cu powder used for SEBM-fabrication of copper-alumina composite, (b) a low-magnification cross-sectional view, and (c) a high-magnification SEM image showing the uniform dispersion of Al₂O₃ with an approximate size of 35 nm (Reprinted with permission from [180]).

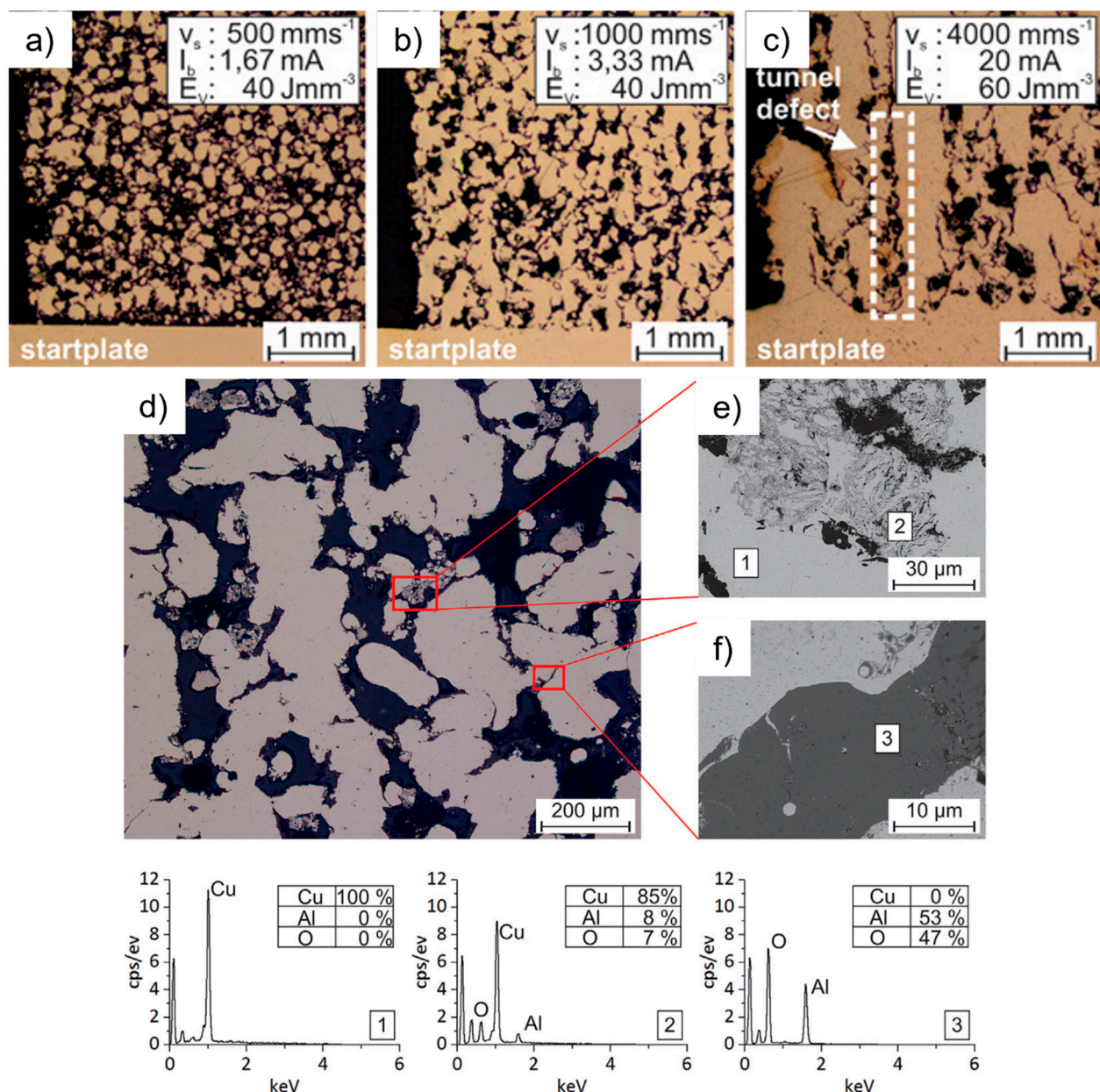


Figure 109. Longitudinal cross-sectional overview of SEBM-fabricated copper-alumina composite showing a porous structure in (a–c) all different sets of process parameters, along with (d–f) higher magnification SEM images showing the occurrence of phase separation in the microstructure of the as-printed specimens, that is, region (1) consists of pure copper, region (2) reveals copper/alumina structure, and region (3) contains alumina (Reprinted with permission from [180]).

The formation of alumina reinforcements and porosities are two opposite contributing factors to the mechanical performance of the fabricated parts. Therefore, assessing the mechanical properties of the SEBM-fabricated copper-alumina parts is essential, which was not addressed in Pobel's study [180].

6.3. AM of Cu-Metal Composites

Selective laser sintering (SLS) is an additive manufacturing technique that aims to produce dense parts through laser sintering without fully melting the feedstock powders. However, controlling the process can be challenging, especially when working with mixed feedstock powders, due to limitations in the wetting and diffusion of different metal powders. One beneficial method to provide sufficient liquid phase required for sintering

without melting the primary alloy is by adopting powders coated with a low-melting-point metal. This technique can also be used to fabricate composite structures [203]. In a study by Walker et al. [181], immersion tin plating was used to produce 90–10 wt.% Cu–Sn composite powders using electrochemical means. They compared the SLS parts fabricated using the composite powders with those made from mechanically mixed Cu and Sn powders. Figure 110 depicts the different feedstock powders used in their study, including virgin Cu powders, mechanically mixed Cu and Sn powders, and composite Cu–Sn powders.

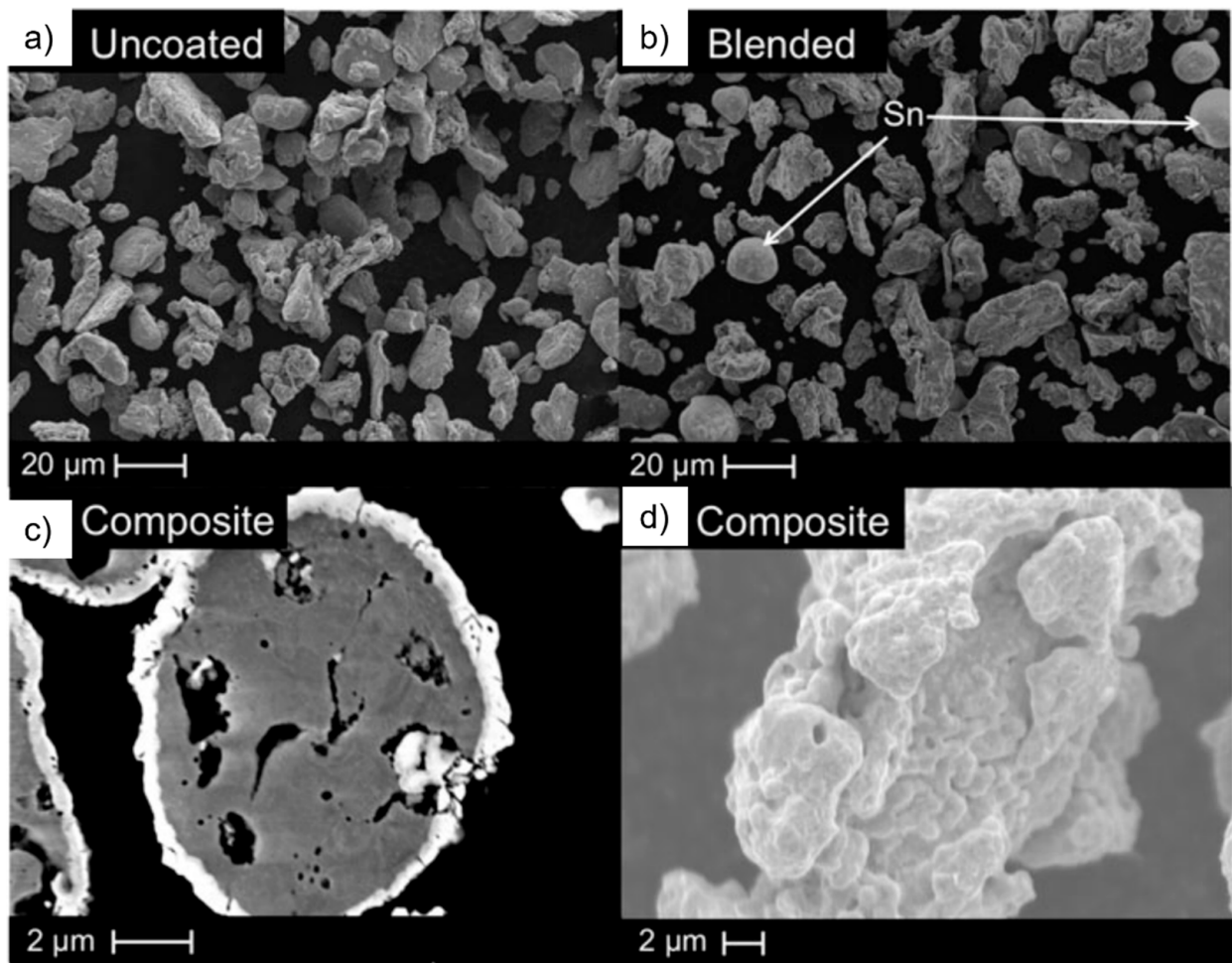


Figure 110. Different feedstock powders used for SLS fabrication of Cu–tin alloy, including (a) virgin Cu powders, (b) mechanically mixed Cu and Sn powders, and (c,d) cross-section and surface of composite Cu–Sn powders, respectively (Reprinted with permission from [181]).

In their study, they utilized a pulsed Nd:YAG laser with a maximum pulse power of 0.09 kW, a travel speed of 1.5 mm/s, and a pulse duration of 0.2 ms at a pulse frequency of 30 pulses/s. While insufficient interparticle bonding without much Cu–Sn interaction was found in the sample fabricated using mechanically mixed Cu and Sn powders (Figure 111a,b), extensive interparticle bonding and significant necking were observed in the sample fabricated with composite Cu–Sn powders (Figure 111c,d). This observation was correlated to the formation of Cu–Sn intermetallic phases, such as ϵ , metastable β , and γ , at the interfacial regions. The micrograph of the Cu–10wt.% Sn composite structure can be seen in Figure 111e,f), which shows necking between two Cu particles as a result of the formation of a Sn-rich interparticle layer.

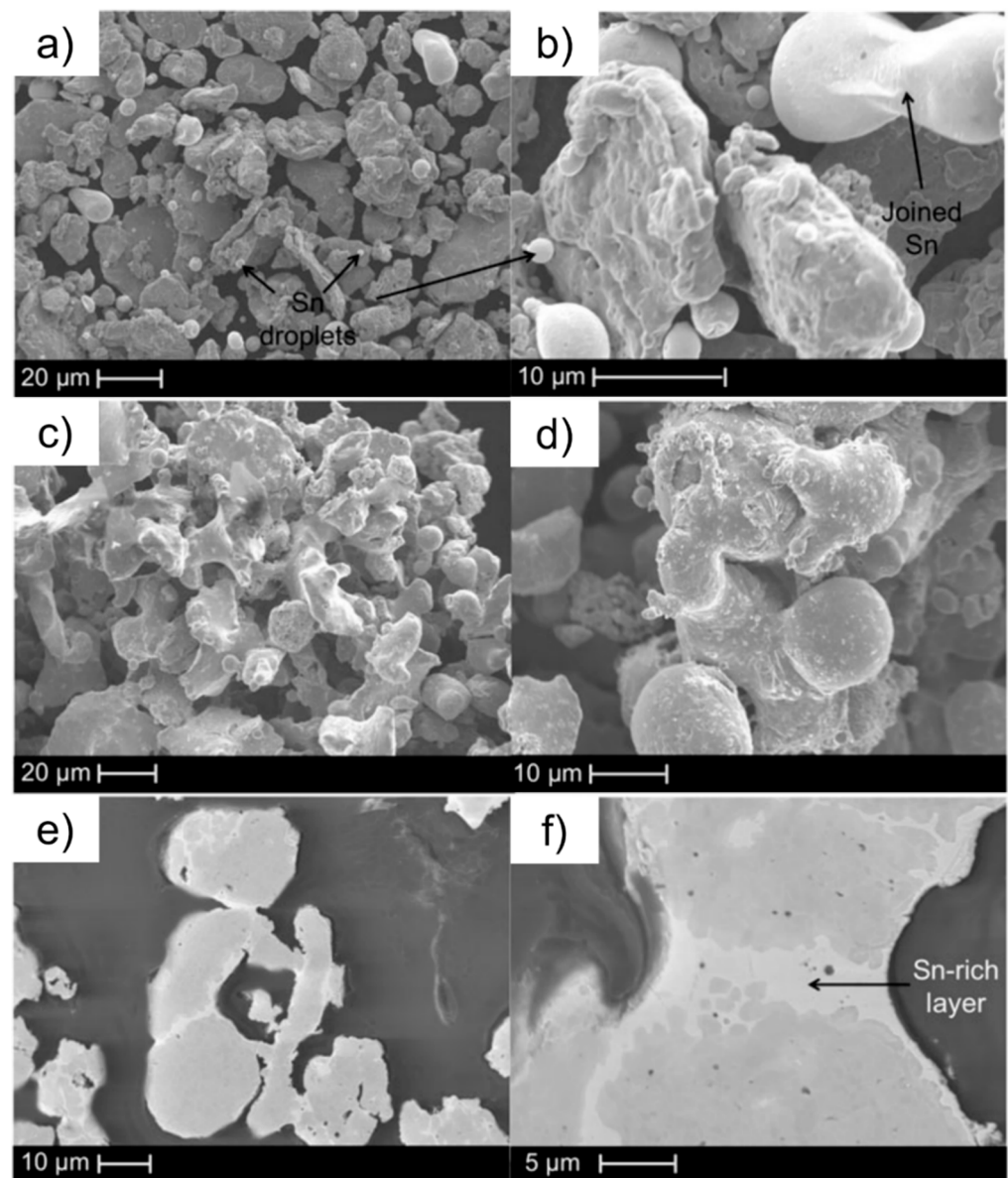


Figure 111. SEM images at different magnifications taken from the SLS-fabricated Cu-based sample using (a,b) mechanically mixed Cu and Sn powders, (c,d) composite Cu-Sn powders, along with (e,f) a detailed microstructural feature showing the necking between two Cu particles in the presence of a Sn-rich interparticle layer (Reprinted with permission from [181]).

7. Future Perspective

Despite recent advancements in AM processing of copper-based alloys and composites, industrial implementation of copper in AM technology has been limited compared with other engineering metals, such as steels, nickel, aluminum, and titanium alloys. While there have been some recent industrial studies, most studies in the literature have primarily focused on processing feasibility, process parameter optimization, and the general demonstration of AM-fabricated parts' properties.

The slower progress in AM of copper alloys could be due to processing challenges, specific requirements for AM machines, for example, L-PBF systems equipped with green lasers, difficulties in process parameter optimization, and a lack of general support for AM feedstock materials. This lag indicates that further applied research is required to support industrial sectors in the smoother adoption of AM-fabricated copper alloys. Based on the

present review of the literature, the following gaps have been identified in the AM of each specific copper alloy that need to be addressed in future research:

- (i) Copper-chrome alloys: Future research should systematically investigate the corrosion behavior of additively manufactured copper-chrome alloys. Moreover, the in-service performance of EBM-fabricated copper-chrome alloys needs to be comprehensively studied to understand their potential for industrial applications.
- (ii) Copper-nickel alloys: Based on the present literature, the feasibility of manufacturing Cu-Ni alloys has been evaluated in a few studies, revealing anisotropic mechanical properties, microstructural inhomogeneities, and a relatively porous structure in the fabricated parts. To overcome these issues, future research should focus on optimizing the composition of the feedstock materials and production process parameters based on the specific applications of the intended end-products. A comprehensive study on the in-service performance and corrosion behavior of additively manufactured Cu-Ni alloys is also required.
- (iii) Tin-bronzes: While most of the available studies in the literature on tin-bronze alloys have focused on the L-PBF fabrication method, exploring the feasibility of arc-DED or WAAM, followed by process optimization, could provide a new opportunity for the production of large-scale tin-bronzes suitable for marine applications. Therefore, further research should be conducted on WAAM fabrication to determine its potential advantages and limitations for producing tin-bronzes.
- (iv) NAB alloys: Future research is necessary to comprehensively investigate the seawater corrosion performance of AM-fabricated NAB alloys in both as-printed and heat-treated conditions, followed by comparison with the corrosion properties of their conventionally fabricated counterparts. Since NAB alloys are widely used in the marine industry, these studies could have significant practical applications.
- (v) Reinforced copper composites: As most of the existing research on these materials is in the feasibility stage, there is a significant potential for future studies focused on optimizing the process parameters for additive manufacturing of MMCs. This can be followed by an investigation of the resulting physical and mechanical properties. Such studies could lead to a better understanding of the behavior of these materials and open up new possibilities for their industrial applications.

Another limitation in the literature is the scarce adoption of BJT for the processing of copper alloys. Given the AM processing challenges associated with copper-based materials, BJT could serve as a suitable alternative to laser-based AM methods such as L-PBF and L-DED. BJT does not involve melting and solidification, which can eliminate the inherent AM challenges of copper alloys, such as low laser absorptivity, high oxygen affinity, and high thermal conductivity. Although the lack of extensive research implies substantial uncertainties in the processability and final properties of BJT-processed copper alloys, it is anticipated that the future of AM in copper alloys will shift towards BJT processing. Therefore, investigating potential challenges and developing optimized sets of processing variables and appropriate post-printing treatments involved in BJT of copper alloys are essential.

8. Summary and Conclusions

In this paper, a comprehensive review of the state-of-the-art in additive manufacturing (AM) of several industrial grades of copper alloys has been presented. These include tin-bronzes, NiAl bronzes, Cu-Cr, and Cu-Ni alloys, as well as Cu-based metal matrix composites produced using AM. The review covers various AM methods, process parameters, microstructure, and physical and mechanical properties of the AM-processed alloys, providing valuable insights for future research in this field. The following are some of the key conclusions drawn from the study:

1. The processability of copper-based materials using L-PBF presents several challenges due to: (i) the high laser reflectivity of copper, which can damage the optical coating on the laser mirror; (ii) the high thermal conductivity of copper, which leads to

a rapid heat transfer from the melt pool region to the surrounding area, causing layer curling and delamination in the as-printed material due to a significant local temperature gradient; (iii) the low laser energy absorptance rate of copper, leading to a porous as-printed part; and (iv) the rapid oxidation of copper feedstock powders during processing, leading to gas bubbles entrapped in the end-product as porosities. To address these challenges, the following solutions are suggested: (i) adopting a high-power laser, (ii) preheating the powder bed, (iii) using laser sources with lower wavelengths, (iv) employing a lower conductive material for the building platform, and (v) incorporating alloying elements or composite particles into the material.

2. The addition of alloying elements to pure copper can deteriorate its electrical and thermal conductivities. Therefore, developing copper-based MMCs can be an effective way to overcome the L-PBF processability challenges of copper-based materials and produce tailored-to-design parts. While most of the available studies in the literature have focused on employing carbon-based particles as reinforcements, it is important to consider the avoidance of in-situ graphitization during the AM process.
3. In the case of copper-chrome alloys, the high solidification rate associated with AM is advantageous in preventing the segregation of chrome, which is a common issue during traditional manufacturing methods of copper-chrome alloys such as casting. This results in AM-processed components with superior mechanical properties compared to their conventionally produced counterparts. However, post-printing processes, such as mechanical deformation or heat treatment, are required to balance the properties of additively manufactured copper-chrome parts. It is important to optimize the post-printing heat treatment cycles to achieve the desired characteristics, as the ideal microstructure is obtained at a threshold temperature that may differ from the recommended heat treatment cycles for conventionally fabricated copper-chrome counterparts. Specifically, conventionally fabricated copper-chrome parts yield the optimum properties with solution-aging heat treatment, while their additively manufactured counterparts exhibit the best combination of strength and conductivity with direct aging.
4. In the case of copper-nickel alloys, the higher cooling rates associated with the L-PBF process suppress the recrystallization process, leading to the formation of a quasi-amorphous (metal glass) microstructure and higher hardness in as-printed parts compared to the conventionally fabricated parts in the annealed condition. Faster scanning and higher layer thickness increase the porosity level and decrease the corrosion resistance and hardness of the as-printed Cu-Ni alloys. However, adopting a higher scan speed during L-DED processing of Cu-Ni alloys has been found to be detrimental to the soundness of the deposited tracks, primarily due to insufficient laser energy absorption by the feedstock material. L-DED processing of Cu-Ni alloys results in a crystalline microstructure with a mix of cellular and dendritic structure at the bottom/middle layers and equiaxed grains at the top regions, in contrast to the quasi-amorphous structure obtained in L-PBF processed Cu-Ni alloys. Compared to beam-based AM processes, the WAAM process is more effective in producing sound and defect-free Cu-Ni alloys with negligible discontinuities and internal porosities. However, WAAM-fabricated Cu-Ni alloys may exhibit anisotropic mechanical properties due to different grain sizes and the presence/absence of precipitates in different orientations.
5. Tin-bronzes fabricated using AM have a microstructure similar to those produced by traditional casting but with a finer microstructure due to the faster cooling rate associated with the AM process. Sequential melting and reheating cycles during AM lead to the formation of a low-volume fraction of ϵ secondary phases, which act as an artificial aging heat treatment cycle. The finer microstructure and presence of hard ϵ -precipitates in AM-fabricated tin-bronzes result in a better combination of strength and ductility compared to cast samples. However, the post-fabrication annealing process can eliminate the heterogeneous microstructure and consequently alter the

mechanical response, thermal properties, and corrosion resistance of AM-fabricated Cu-Sn alloys. In particular, the annealing process results in the formation of a coarse single-phase microstructure, improving ductility and corrosion resistance, but at the cost of reduced mechanical strength.

6. In the case of the NAB alloys, the α -Cu matrix in cast parts contains four different intermetallic phases (κ_I , κ_{II} , κ_{III} , and κ_{IV}), while WAAM produces a finer microstructure, eliminates κ_I , and reduces the content of other secondary phases due to the higher solidification rate. In contrast, beam-based AM processes, such as L-PBF, L-DED, and EBM, lead to the formation of a hard martensitic matrix due to even higher cooling rates. Overall, AM-fabricated NAB alloys exhibit higher mechanical properties than their cast counterparts due to the lower fraction and finer size of precipitates in WAAM parts and the formation of a martensitic matrix in beam-based AM processes. However, the columnar and heterogeneous microstructure of WAAM- and L-PBF-fabricated NABs results in anisotropic mechanical properties, while EBM-fabricated NABs contain a fairly homogeneous microstructure with a nearly equiaxed grain structure and near-isotropic tensile properties due to the relatively uniform heating cycles associated with EBM. Novel ultrasonic vibration-assisted WAAM systems or appropriate post-printing heat treatment cycles can minimize the columnar structure and anisotropic mechanical properties of AM-fabricated NABs.

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