Microstructural evolution and mechanical behavior of nickel aluminum bronze Cu-9Al-4Fe-4Ni-1Mn fabricated through wire-arc additive manufacturing

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\textbf{ABSTRACT}

As a step forward toward the development of the next generation of nickel aluminum bronze (NAB) components using wire-arc additive manufacturing (WAAM), square bars were printed in the vertical direction. The as-built microstructure was characterized using multi-scale electron microscopy techniques, where the differences in phase formation were compared to the reference cast-NAB based on the solidification characteristics. The as-cast microstructure typically consists of Cu-rich \(\alpha\)-matrix, and four types of intermetallic particles referred to as \(\kappa\)-phases. In the WAAM-NAB, the formation of \(\kappa\) was suppressed due to high cooling rates. The microstructure was finer and the volume fraction of intermetallic particles was significantly lower than that of the cast-NAB. Based on energy dispersive spectroscopy (EDS) technique and diffraction pattern analysis using transmission electron microscopy (TEM), the phases formed in the interdendritic regions were identified as \(\kappa_{\text{II}}\) (globular Fe\textsubscript{3}Al) and \(\kappa_{\text{III}}\) (lamellar NiAl), whereas numerous fine (5–10 nm) Fe-rich \(\kappa_{\text{IV}}\) particles were precipitated uniformly within the \(\alpha\)-matrix. Electron backscatter diffraction analysis revealed weak texture on both parallel and perpendicular planes to the building direction with (100) poles rotated away from the build direction. The WAAM-NAB sample exhibited considerably higher yield strength (\(\approx\)88 MPa) and elongation (\(\approx\)10\%) than the cast-NAB, but the gain in the ultimate tensile strength was marginal.

1. Introduction

Nickel Aluminum Bronze (NAB) alloys are valued for their high strength combined with good ductility and toughness, high resistance to all forms of corrosion (especially, in marine environments), and excellent wear, cavitation, and galling resistance \[1,2\]. They display outstanding biofouling resistance, excellent cryogenic properties, and good damping capacity (nearly twice that of structural steels). Further, they are non-sparking \[3\], and have a lower density (due to high aluminum content) as compared to most copper alloys and are about 10\% lighter than standard structural steels. NAB alloys have a long history of successful use in marine architecture, and aerospace applications \[4–6\]. Within the family of NAB, the most commonly used is cast alloy Cu-9Al-4Ni-4Fe-1Mn (C95800) that falls under the American Society for Testing and Materials standard (ASTM) B148 \[7\] and its wrought equivalent Cu-9Al-5Ni-4Fe alloy (C63200).

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NABs form a sub-class of aluminum bronzes and in addition to aluminum as the primary alloying element contain significant amounts of nickel, iron, and manganese. In the binary copper-aluminum system, alloys containing up to 9\% (wt\%) aluminum show a single-phase \(\alpha\) microstructure under the equilibrium conditions. However, under normal (non-equilibrium) cooling conditions, aluminum content of above 8–8.5\% results in a second phase known as \(\beta\) at high temperatures, which subsequently (below \(\approx\)565 \textdegree{} C) undergoes eutectoid decomposition to \(\alpha + \gamma_{\text{I}}\) \[8\]. The formation of \(\gamma_{\text{I}}\) (Cu\textsubscript{3}Al\textsubscript{2}) is undesirable as it affects the ductility and toughness of the alloy, which is also prone to preferential corrosion \[8\]. The formation of undesirable \(\gamma_{\text{II}}\) can be suppressed by nickel and iron additions (\(\approx\) 5\% each) that increase the solubility limit of aluminum up to 11\%, and precipitation of more desirable \(\kappa\)-phases can be obtained in the microstructure \[9\]. Aluminum addition enhances the mechanical properties of NAB alloy via solid solution strengthening \[10\]. Nickel increases the yield strength,
improves corrosion resistance, and also acts as microstructure stabilizer [9]. The addition of iron causes grain refinement and also increases the yield strength [11]. Manganese addition improves the castability and approximately 1 wt.% manganese is usually added to NAB alloy to retard the β-phase transformation. This amount of manganese is considered as equivalent to 0.15% Al on the phase diagram [9].

Unlike many non-ferrous alloys, NABs can undergo a wide range of solid-state phase transformations during solidification resulting in the presence of numerous phases at room temperature. The absorption of aluminum from the matrix by κ-phases extends the apparent range of the α-field. As a result, under equilibrium conditions, no eutectoid transformation occurs and β is not retained below 600 °C unless the aluminum content goes beyond 11%, compared to 9.5% in the Cu-Al binary system. The precipitation of κ-phases in the α-matrix increases the mechanical strength considerably without a significant reduction in ductility. This has been the most outstanding advantage of NABs over other aluminum bronzes. Various types of κ-phases were catalogued in the literature [6,12,13] based on their constitution and morphology, and are classified or designated as κ₌, κ₄, κ₅, and κ₆ in the order of their precipitation during cooling from high temperatures. Apart from α and κ-phases, some amount of martensitic β (β') may appear in the as-cast microstructures of Cu-9Al-4Fe-4Ni-1Mn alloy, but it is uncommon in sand castings because of the relatively slow cooling rates.

In general, casting defects such as segregation and porosity typically diminish physical properties, mechanical properties, and service performance. Due to long lead times and the complication in manufacturing large structures such as ship propellers, parts and components made of NAB are generally expensive. Hence, weld repair is usually preferred for extending the service life instead of replacing the parts. However, NAB alloys have some weldability issues such as porosity, hot cracking, and distortion [14] due to copper’s high thermal conductivity and coefficient of thermal expansion [15]. Friction stir processing (FSP) was used for cast-NAB as a weld repair technique [16], which enhanced the strength due to different strengthening mechanisms such as grain refinement, solid solutions, precipitation, and dislocation hardening. However, the formations of nano-level twins that are rich in martensitic phases (β') were observed in friction stir processed NAB alloys [16], which had a detrimental effect on the corrosion resistance. To improve the corrosion resistance, a post heat treatment is essential, which further increases the cost of production.

In addition to heat treatment [17–19], some attempts were made to improve the mechanical properties and corrosion resistance of NAB alloys through changes in composition [20,21], plastic deformation [22–24], and surface treatment techniques such as friction stir processing [25], nickel ion implantation [26], thermal diffusion of Ni coating [27], laser surface melting [28], and laser surface alloying [29]. The limitation with surface modifying treatments is that they can only improve the corrosion resistance and mechanical properties of the surface layer instead of the bulk material. Heat treatment and plastic deformation techniques such as FSP have some limitations and are hard to use to process heavy castings such as ship propellers. Overall, NABs are metallurgically complex alloys in which small variations in the compositions can result in the formation of markedly different microstructures, which can, in turn, result in significant variations in seawater corrosion resistance [8].

In comparison with the conventional casting processes, superior mechanical properties can be achieved by additive manufacturing (AM) that results in certain microstructural benefits such as reducing segregation, uniform distribution of second phase particles, and finer grain sizes [30]. In addition, the defective and service-damaged components can be replaced by fabricating the required parts offshore or on a vessel instead of waiting for a long time to schedule and receive the new cast component. Among the various classes of AM, powder bed fusion techniques (Selective Laser Sintering, Direct Metal Laser Sintering, Selective Laser Melting, Electron Beam Melting) and powder metal deposition processes (Direct Metal Deposition, Lasform, Controlled Metal Buildup, Laser Engineering Net Shaping) are the most suitable for the fabrication of small metallic parts [31]. In recent years, wire-arc additive manufacturing (WAAM) techniques are becoming attractive for the manufacturing sector due to their ability to produce large size components with full density, high deposition rate, high material utilization, and low equipment cost [32]. WAAM does not need a vacuum environment to operate as required in electron beam based processes [33] and the use of an electric arc offers a higher efficiency fusion source than laser-based methods [34]. WAAM process was employed as a fabrication process for various engineering materials such as Ti alloys [35–38], Al alloys [39], Ni alloys [40], and steels [41,42]. Wire-based deposition produces stronger adhesion of deposited layers as the wire melts fully, where geometry restrictions are quite minimal with WAAM. As this process uses a wire instead of an atomized powder like in other AM processes, WAAM can also be used for repair purposes where wires of matching composition can be used to deposit the material on damaged parts that have complicated or complex chemical compositions. In WAAM process, an electric arc is used as a heat source and employs either gas metal arc welding (GMAW) [43], gas tungsten arc welding (GTAW) [44] or plasma arc welding (PAW) [45] to melt the wire as the feedstock.

GTAW and PAW processes are extremely sensitive to the arc length, and the wire is not fed coaxially in those two technologies which lead to variations during the process with a change in the welding direction [46]. This limits the applicability of those two processes as a rotary axis is required in the robotic welding systems to orient the wire-feed nozzle to match with the welding direction. Coaxial nature of GMAW process reduces machine complexity and provides high flexibility when combined with a positioning system such as a robot. To the author’s knowledge, at present, there has been no work reported on additive manufacturing of NAB alloys using other than the WAAM process. In an earlier work [47], WAAM process was used to deposit NAB on as-cast base metal in the form of straight thin walls of 10 mm width with typical length and height of 100 mm and 40 mm, respectively, manufactured under three different heat inputs (653, 874, and 1114 J/mm) for deposition. In another study [48], a bulk NAB alloy cubic sample (100 × 100 × 100 mm) was built up on the as-cast NAB alloy (substrate) by using the robotic WAAM system, and the influence of orientation on the mechanical properties was studied. As WAAM process is an inherently non-equilibrium thermal process, it is important to study its underlying physical metallurgical mechanisms to provide a guidance for the process optimization and improvement, and to adjust the process parameters according to target material characteristics. The subject of this paper is to employ lower heat input (170 J/mm) to deposit NAB alloy (Cu-9Al-4Fe-4Ni-1Mn) in form of square bars on 316L stainless steel substrate using WAAM process, and to characterize the microstructure evolution and mechanical behavior. The objective of the present study is to identify the morphology and crystal structure of the phases, understand the microstructural development during deposition, and to correlate the microstructure with the mechanical properties. This study also intends to compare the microstructure evolution in NAB during WAAM with its typical cast microstructure as a reference.

2. Experimental work

2.1. Materials and methods

A reference cast-NAB sample for microstructural characterization and mechanical testing was sectioned from a NAB salt-water impeller (a brackish water pump) that was 170 mm in diameter. The cast NAB specification corresponded to UNS C95800 and the nominal composition (in wt.%) of this material was: Cu: 79% minimum, Al: 8.5–9.5%, Ni: 4–5%, Fe: 3.5–4.5%, Mn: 0.8–1.5%.

Berlin (Germany)-based GEFERTEC has invented a new-patented technology called 3D Metal Printing (3DMP) process [49] that uses a metal wire feedstock. Their new GTarc 60-5 WAAM equipment was...
used to fabricate all samples in this study. The machine uses gas-metal arc welding (GMAW) technology, in which a wire passes through the feedstock, is melted, and then deposited in successive layers. The GTarc 60-5 offers five motion axes and can produce metallic parts up to 0.8 m³ volume with 500 kg maximum mass. The machine is equipped with a SIEMENS control unit to correctly position the welding head enabling high levels of precision to handle CAD models.

Nickel aluminum bronze filler wires corresponding to AWS A5.7 ERCuNiAl (nominal composition same as that of cast-NAB) were used in the WAAM process to produce the samples. The NAB was printed at wire feed rate of 6.5 m/min, travel speed of 480 mm/min, and voltage of 12.5 V at 114 A current. These deposition parameters are listed in Table 1 along with the heat input. Relatively low value of 170 J/mm was obtained with an assumption on process efficiency as 95%. If the efficiency drops, heat input on the samples decreases to much lower values.

2.2. Microstructural characterization

The samples of cast- and WAAM-NAB were cut from the cross-sectional plane and were mounted, mechanically ground, and polished by standard metallography methods to a 1 μm finish, and then etched for 30 s using Klemm’s reagent. The microstructures of the samples were examined using Zeta-20 optical microscope and JEOL JSM6400 scanning electron microscope (SEM) fitted with an energy dispersive spectroscopy (EDS). Electron probe micro-analyzer (EPMA) characterization technique was used to identify the elemental distribution of the cast-NAB alloy. The individual elemental distribution maps were produced in an SEM (JEOL 733 Microprobe located at UNB’s Microscopy and Microanalysis facility) to identify the presence of elements in the matrix and in the second-phase (or intermetallic) particles.

The WAAM-NAB samples were prepared by mechanical polishing to a thickness of 30 μm followed by further thinning via ion-beam milling using a Gatan Precision Ion Polishing System (Gatan model 695) operating at an accelerating voltage of 200 kV for transmission electron microscope (TEM) study. For characterization of phases present in the microstructure, FEI Tecnai Osiris TEM equipped with a 200 keV X-FEG gun was used. High angle annular dark field (HAADF) detectors were used in combination with EDS to generate elemental maps; where spatial resolutions in the order of 1 nm were obtained using a sub-nanometer electron probe. Selective area diffraction (SAD) and convergent beam electron diffraction (CBED) was used to obtain patterns from the matrix and intermetallic particles, respectively. Electron backscatter diffraction (EBSD) analysis was performed on WAAM-NAB samples along x–z and x–y planes (marked in Fig. 1). Field emission gun scanning electron microscope (FEG-SEM-FEI Nova NanoSEM-650) with an OIM 6.2 EBSD system (EDAX) was used to obtain the EBSD scan. The scans at low magnification (500 ×) were run over an area of 500 μm × 500 μm with a step size of 0.25 μm. At high magnification (2000 ×), the scan was performed on an area of 75 μm × 75 μm using a step size of 0.05 μm.

2.3. Mechanical testing

Mechanical properties were evaluated under quasi-static uniaxial tensile loading for both WAAM- and cast-NAB at room temperature.
Sample dimensions for tensile testing corresponded to ASTM E-8 standard [50]. Cylindrical Samples for WAAM-NAB were machined such that the tensile axes were parallel to the print direction (z-axis in Fig. 1). A computer-controlled Instron model 1332 universal testing machine was used to conduct the uniaxial tensile tests. This machine was accompanied by a 25 mm Instron extensometer to accurately obtain displacement during the tensile test. Samples were pulled to failure at a constant cross head displacement rate (0.001 mm/min) and the data for engineering stress was simultaneously recorded throughout the test. Tests were carried out on multiple (3–5) samples to confirm repeatability of the tests, where typical tensile engineering stress-strain curve was plotted. Fracture surfaces were characterized using a JEOL 6400 SEM operating with a tungsten filament. In addition, optical microstructural examination was performed on a plane normal to the tensile axis for further investigation of the fracture mechanism.

3. Results

3.1. Microstructures of cast-NAB

Microstructural examination (Fig. 2) of the cast-NAB samples revealed a number of intermetallic particles dispersed in a matrix of relatively coarse \( \alpha \)-dendrites. As can be seen in the SEM micrograph shown in Fig. 2(b), the intermetallic phases consisted of \( \kappa _{I} \) in rosette morphology, \( \kappa _{II} \) in the form of small roughly globular particles, \( \kappa _{III} \) in lamellar morphology, and \( \kappa _{IV} \) in the form of numerous fine particles.

Fig. 3. (a) SEM-Backscattered electron (BSE) image of cast-NAB, and corresponding EPMA elemental maps for (b) Cu, (c) Al, (d) Ni, and (e) Fe.
precipitated homogeneously within the \( \alpha \)-dendrites. It may be noted that, intermetallic phases \( \kappa_1 \) to \( \kappa_{IV} \) are mainly present in the interdendritic regions. No evidence of retained \( \beta \) or acicular \( \beta' \) martensite is observed in the as-cast samples. These microstructural features are very typical of a NAB alloy in the as-cast condition [6,13]. The precipitates \( \kappa_1 \) to \( \kappa_{II} \) primarily appear in the interdendritic regions due to the interdendritic segregation of alloying elements during solidification, while the \( \kappa_{IV} \) intermetallic homogeneously precipitates within the primary \( \alpha \)-dendrites. In the microstructural examination, the \( \kappa_1 \) appeared as micro-sized rosette-shape particles as they form during solidification. On the other hand, the \( \kappa_{II} \) precipitates are seen as essentially finer, globular particles. The \( \kappa_{III} \) precipitates exhibit a distinct lamellar morphology because of their formation as a result of eutectoid decomposition of \( \beta \) phase to \( \alpha + \kappa_{III} \). Finally, the \( \kappa_{IV} \) precipitates as numerous sub-micron-sized globular particles homogeneously distributed within the \( \alpha \)-dendrites. It may be noted that precipitates \( \kappa_1 \) to \( \kappa_{IV} \) are essentially intermetallic phases. The results of EPMA elemental mapping studies on cast-NAB are shown in Fig. 3. In the as-cast sample, the dendrite cores can be seen to be relatively lean in Al, Ni, and Fe, whereas the interdendritic intermetallic phases were rich in Ni and/or Fe as well as Al. While \( \kappa_1 \), \( \kappa_{II} \), \( \kappa_{IV} \) precipitates are rich in iron and aluminum, \( \kappa_{III} \) precipitates are rich in nickel and aluminum. However, some amount of nickel is typically measured in \( \kappa_1 \), \( \kappa_{II} \), \( \kappa_{IV} \) precipitates as is some iron in \( \kappa_{III} \) precipitates.

### 3.2. Microstructures of WAAM-NAB

A low magnification optical micrograph at a melt pool boundary of a WAAM-NAB sample is shown in Fig. 4(a). The bulk of the sample consisted of very fine \( \alpha \)-dendrites with some dark-etched interdendritic regions, as can be seen in Fig. 4(b). Below each melt pool boundary, as marked in Fig. 4(a), a region of coarser microstructure in varied thicknesses up to 500 \( \mu m \) was observed. These coarser microstructural regions also consisted of bright-etched \( \alpha \)-dendrites and dark-etched interdendritic regions, as can be seen clearly in Fig. 4(c). As in the as-cast NAB samples, no \( \beta' \) martensite was noticed in the WAAM samples. However, unlike in the as-cast NAB samples, optical microscopy did not reveal any intermetallic phases in the WAAM samples. Fig. 5 shows the SEM image of the WAAM-NAB at higher magnifications, which revealed some fine globular \( \kappa_{II} \) particles in the interdendritic regions. These fine \( \kappa_{II} \) particles precipitated in the dark etched regions seen in Figs. 4(b) and (c).

Examination of the WAAM samples in TEM (Fig. 6) more clearly revealed the presence of various intermetallic phases in the interdendritic regions. In Fig. 6(a) and (b), \( \alpha \)-dendrites and interdendritic regions can be clearly seen. The interdendritic regions displayed two-types of intermetallic phases, \( \kappa_{II} \) in globular form and \( \kappa_{III} \) in lamellar morphology in between fine \( \alpha \)-lamellae (Fig. 6(b) and 6(c)). These intermetallic phases were found to be \( Fe_3Al \) and \( NiAl \), respectively, based on the diffraction pattern analysis as shown in Fig. 7. While some
amount of Fe or precipitation of $\kappa_{II}$ in NiAl precipitate is noticed (Fig. 7(b)), some Fe$_3$Al ($\kappa_{III}$) particles (shown in Fig. 8) seem to be free from any NiAl precipitation. From Figs. 7(b) and 8, both NiAl and Fe$_3$Al particles appear to exhibit semi-coherency with the matrix as indicated by misfit dislocations observed at their interfaces with the matrix. There is a Burger's orientation relationship (lattice correspondence relation) between Fe$_3$Al and surrounding NiAl, where $[001]_{\text{Fe}_3\text{Al}} \parallel [010]_{\text{NiAl}}$.

Further, EDS elemental mapping (Fig. 9) studies also distinctly revealed the Fe-rich $\kappa_{III}$ globular particles and Ni-rich $\kappa_{II}$ in lamellar morphology. The interdendritic regions were rich in Al, Ni, and Fe. The nucleation of $\kappa_{II}$ occurs at relatively high temperatures in the $\beta$-phase with precipitating $\alpha$-phase envelopes around it during cooling [6]. $\kappa_{III}$ particles are in various ranges of sizes, mostly very fine to the size of few nanometers (Figs. 6(b) and 7(b)), and precipitated mainly in the regions of lamellar eutectoid mixture (mainly $\kappa_{III}$). $\kappa_{II}$ precipitates (Fe$_3$Al, Iron aluminide) typically have DO$_3$ crystal structure at low temperatures with a lattice parameter of $5.71 \pm 0.06$ Å [13]. $\kappa_{III}$ particles that are based on NiAl belong to B2 (ordered BCC) crystal structure with a lattice parameter of $2.88 \pm 0.03$ Å [13].

It must be noted from the EDS elemental map corresponding to Fe (Fig. 9(f)) that, the matrix contains a distribution of fine precipitates throughout the $\alpha$-grains. To reveal them more clearly, TEM imaging (Fig. 10(a)) was done at a very high magnification of 630000x and corresponding EDS elemental maps for Al, Ni, and Fe are shown in Figs. 10(b)-(d), respectively. The $\kappa_{IV}$ precipitates are in 5 to 10 nm in size, and believed to have a composition and crystal structure similar to...
based on Fe$_3$Al [13]. Superlattice reflections from these precipitates can be noticed in diffraction pattern that corresponds to α-matrix in Fig. 7(a).

Fig. 11 shows the EBSD microstructural and crystallographic characterization of WAAM-NAB along the build direction (z-axis). Fig. 11(a) shows the inverse pole figure (IPF-Z) map that reveals the grain structure (high and low angle grain boundaries), without any pronounced grain elongation along the build direction. This is in contrast to the characteristic of the directional growth along the build direction in AM processes [51]. The dotted lines in the IPF map show the orientation of grains that are elongated along the melt pool boundaries. Grains that appear somewhat bigger in the map seem to be dominated by green color i.e. in <101> orientation. Rest of the grains are oriented either on <001> or <111> direction. Grain boundary misorientation map (Fig. 11(b)) reveals that high-angle grain boundaries are predominant. It can also be observed in Fig. 11(a) that the color associated with crystallographic orientations within individual grains is uniform. This may be indicating that low local stresses and low dislocation densities (less population of low-angle grain boundaries in Fig. 11(b)) are present in the WAAM-NAB. The average grain size is estimated to be 16.4 μm from the grain size distribution plot in Fig. 11(c). Fig. 11(d) shows the texture analysis of the EBSD data in the form of pole figures. It
demonstrates that, the WAAM-NAB had a weak to moderate texture denoted by the locations of the peaks in (001) tilted away from the build direction (y-axis in pole figures) and the four on-axis peaks in the (111) map. The maximum texture intensity is 1.85 times the random. The evolution of the texture may be related to the grain formation during repeated heating and cooling cycles, and strongly dependent on the heat input [52].

Fig. 12(a) shows the EBSD inverse pole figure (IPF) map of a WAAM-NAB sample on the section (x–y plane) perpendicular to the build direction (z-axis). The map shows only random orientations, similar to the texture of an as-cast material (mostly random texture). The dotted line indicates the melt pool track and somewhat larger dendrites are oriented towards <101> direction, similar to the EBSD scan on plane parallel to the build direction. The grain boundary misorientation map representing the grain-to-grain misorientation angle distributions in the α-phase is shown in Fig. 12(b). The distribution of misorientation angles shows a distinct random component and the population of the high-angle boundaries (> 15°) is the highest. From the grain size distribution plot (Fig. 12(c)), the average grain size measured was about 17.4 μm. Fig. 12(d) shows the pole figures measured on the x–y plane. Though the maximum texture intensity is the same to that on the x–z plane, changes in the rotations of (001) and (111) poles are distinctly visible. Changes in the direction of wire-feed deposition for two successive layers appear to modify the solidification conditions enough to cause low thermal gradients and to inhibit the development of a texture. The random texture is indicative of the solidification of the equiaxed grains that was promoted by heterogeneous nucleation in the presence of fine κIV particles in the matrix. To see the grain shapes more clearly, high magnification (2000x) EBSD images (IPF and grain size distribution) are presented in Figs. 12(e) and (f), where most of the α-grains are elliptical in shape. Networks of fine equiaxed grains (typically about 5 μm) are evolved in the interdendritic regions in random orientations.

Overall, when compared to the as-cast NAB samples, the WAAM samples showed a distinctly finer microstructure without any κI intermetallic phases. The WAAM samples did contain κII, κIII, and κIV phases, but their amounts and sizes were significantly lower than in the cast condition.

3.3. Mechanical properties

Fig. 13 shows the typical tensile stress-strain curves of the cast- and WAAM-NAB samples. The results of tensile testing on multiple samples are summarized in Table 2. As can be seen, the WAAM samples were found to exhibit considerably higher yield strength (YS) and percent elongation as compared to the as-cast samples. However, the increase in the ultimate tensile strength (UTS) was only marginal. Examination of the fracture surfaces revealed ductile fracture features in both cases, as can be seen in Fig. 14. In the as-cast samples, especially, some regions of flat fracture were seen occasionally (Fig. 14(b)). Examination of the microstructural features close to the fracture location of the WAAM samples (Fig. 15) revealed no preferential fracture along layer interfaces or in the areas (heat-affected zones (HAZ)) adjacent to the melt-pool boundaries.

4. Discussion

4.1. Solidification characteristics

Solidification in cast Cu-9Al-4Fe-4Ni-1 Mn alloy occurs by the formation of α-dendrites, where it may also involve a peritectic reaction L + α − β [53]. Some pre-primary Fe-Al intermetallic particles can also form directly from the melt, especially under relatively slow cooling conditions, and are known to aid in the nucleation of α-crystals [54]. During solidification, the alloying elements show a strong tendency to segregate into the liquid and the last-to-solidify liquid develops considerably higher concentration of solute elements. As a result, some rosette-like κI particles generally form in the interdendritic regions during cooling to about 1040 °C. It may be noted that, the severity of segregation of the alloying elements depends on the cooling rate and faster cooling helps to minimize the segregation if it is beyond the critical rate of 10³ K/s [55]. After solidification, the alloy successively passes through α + β, α + β + κ, and α + κ regions on the cooling path to the room temperature. The β phase essentially forms in the interdendritic regions. Some precipitation of relatively coarser κI particles generally form at high temperatures as the alloy cools through the α + β + κ region. Here again, the amount of precipitation in the form of κI particles depends on the cooling rate, but typically occurs at about 930 °C. Subsequently, as the alloy cools into the α + κ region, a eutectoid reaction β −→ α + κ takes place (at about 800 °C) [8]. Unless the cooling rate is very high, the β phase is entirely consumed in the eutectoid reaction. The eutectoid mixture exhibits a characteristic lamellar structure and consists of a nickel-rich κII phase in between α-lamellae. The scale of the eutectoid mixture is also dependent on the cooling rate. Finally, as the alloy cools further, precipitation of very fine κIV particles disperse homogeneously in the primary α-dendrites. It may be noted...
that, the eutectoid reaction can get fully suppressed if the cooling rates are very high. In such a case, the $\beta$ phase undergoes a martensitic transformation (diffusion-less) leading to some acicular $\beta'$ martensite in the room-temperature microstructure. If the diffusion-less transformation occurred, all phases ($\kappa_{II}$ and $\kappa_{IV}$) consist of the same chemical composition \[13\] though they differ in morphology. However, under equilibrium or slow cooling conditions, both $\kappa_{II}$ and $\kappa_{IV}$ particles correspond to the same phase, albeit with slightly different composition, which may be attributed to different temperatures for precipitation during cooling.

Fig. 9. (a) STEM-HAADF images of WAAM-NAB in an interdendritic region, (b) composite map of the main elements, (c)-(f) show the corresponding EDS elemental maps for Cu, Al, Ni, and Fe, respectively. The lamellar precipitates are NiAl ($\kappa_{III}$) and the fine globular precipitates are Fe$_3$Al ($\kappa_{IV}$) that are formed in the core of the NiAl ($\kappa_{III}$) precipitates. Note the precipitation of Fe-rich $\kappa_{IV}$ in the matrix in (f).
As compared to conventional casting, the cooling rates during WAAM are significantly higher (around 10^2 °C/s) [30]. This has a strong bearing on the microstructural development in alloy Cu-9Al-4Fe-4Ni-1 Mn. The high cooling rates in WAAM results in a significantly finer solidification structure as compared to conventional casting. WAAM process is identical to that of multi-pass welding as arc (i.e. heat source) locally melts the NAB as it passes, and the deposited layer solidifies before the upper portion of it partially re-melts again during the next scan for successful bonding between the layers. The lower portion below the bottom of the melt pool drives the solidification process and thus, the microstructural evolution. In general, under slow cooling rates, solute atoms have enough time to diffuse, where micro-segregation does not occur. At relatively high cooling rates (non-equilibrium conditions), diffusion of solute atoms into solid get suppressed, which leads to interdendritic micro-segregation. However, if the cooling rate is further increased to critical cooling rates such as in WAAM, the velocity of the growing dendrite increases and approaches its atomic diffusive speed [56]. In such situation of solute trapping, diffusion of solute atoms becomes very difficult not only in solid state, but also in liquid phase.

4.2. κ-Precipitates

In WAAM process, the high cooling rates in newly deposited layer minimize the thermal gradient with lower portion of the layer beneath it. This can reduce the segregation of alloying elements during solidification and suppress the formation of rosette-like κ particles in WAAM samples. Even if some precipitation occurs in the upper portion of the layer, those precipitates get dissolved, when that portion reheated to solidus temperature again during subsequent deposition of the next layer. It may be important to note that, specifying a single cooling rate value for the whole AM deposition process is likely inappropriate as it is a strong function of temperature and the location at which it is measured as each layer experiences multiple thermal cycles and temperature peaks. In AM, typically, two different temperature ranges are important to consider. Firstly, cooling rate from the liquidus to solidus...
temperature range, which determines the features of solidification microstructures such as cells and dendrites [57], and another cooling rate is during the solid-state phase transformations. Perhaps, the most well-known range for NABs is the 850 to 500 °C, where the microstructure is significantly affected by the cooling rate [8,13,58]. While the κ particles contribute very little to the strength, they have a marked detrimental effect on the ductility and toughness of the alloy [8]. Hence, the absence of coarse κ particles in WAAM samples is a significant advantage.

The TEM diffraction data shown in Figs. 7 and 8 indicate that there are two structurally distinct κ-phases in the interdendritic region; one (κ_{II}) based on Fe₃Al and the other (κ_{III}) based on NiAl. This agrees with the findings of Weill-Couly et al. [59] that κ_{II} particles are Fe-rich, while the lamellar eutectoid decomposition product κ_{III} is Ni-rich. There is no comprehensive information in the literature on the phase relationships in the Cu-Al-Ni-Fe quaternary system (i.e., ternary phase diagrams at moderate or high cooling rates) to comment on the potential composition range of the κ_{II} and κ_{III} intermetallic phases. The size of κ_{II} precipitates (in few nanometers) in WAAM-NAB is significantly lower than that of the cast-NAB (5–10 μm). In cast-NAB, it was reported that both κ_{II} (Fe₃Al) and κ_{III} (NiAl) particles exhibit Kurdjumov-Sachs (K–S) orientation relationships with the α-matrix (Cu) [13], which means that the close-packed planes in the two structures (precipitate and matrix) are parallel or nearly-parallel. The subsequent evolution of texture during solidification depend on this crystallographic orientation relationships.

Fine Fe-rich κ_{IV} particles uniformly precipitated throughout the α-grains. However, their size is very small to the level of 5–10 nm. Their shape is neither acicular nor globular, and appears likely to be rhombohedron from Fig. 10(d). Short available time for diffusion under fast

![EBSD results from a WAAM-NAB sample at 500x on plane (x–z) parallel to the build direction (z-axis, which is vertical in the images): (a) inverse pole figure (IPF) map, (b) grain boundary misorientation map, (c) grain size distribution plot, and (d) pole figures. Dotted lines in (a) indicate melt pool boundaries. The build direction is marked as BD in pole figures.](image-url)
Fig. 12. EBSD results from WAAM-NAB on x–y plane (perpendicular to build direction i.e. z-axis): (a) inverse pole figure (IPF) map at 500x, (b) grain boundary misorientation map, (c) grain size distribution plot, (d) pole figures, and (e) IPF map at higher magnification (2000x) and corresponding (f) grain boundary misorientation map. Dotted line in (a) represents for scan track. The build direction is marked as BD in pole figures.
cooling rates of WAAM process probably restricted the solid-state transformation of $\kappa_{IV}$. These $\kappa_{IV}$ particles contribute to strength significantly. It may be possible to induce satisfactory increase in their volume fraction and size in WAAM samples by conducting an annealing heat treatment in the temperature range of 500 to 600 °C. Further work is needed in this regard.

It is obvious as to why the cooling rates in WAAM are high enough to suppress the formation of $\kappa_{II}$ precipitates, but not so in the case of $\kappa_{II}$, $\kappa_{III}$, and $\kappa_{IV}$ precipitates. It is known that, the rate at which the weld metal cools gradually drop off with temperature [60]. Therefore, any precipitation events in both high and low temperature regimes are more likely to get suppressed during weld metal cooling. While high cooling rates are responsible for suppression of precipitation reactions at high temperatures ($\kappa_{II}$ formation in the present case), the cooling rates are not typically high enough and the diffusivities are not typically low enough to suppress any precipitation reactions in intermediate temperature ranges. For this reason, the formation of $\kappa_{II}$, $\kappa_{III}$, and $\kappa_{IV}$ precipitates was not suppressed in the WAAM-NAB and solid-state phase transformations did occur.

During WAAM, each layer is subjected to significant reheating when the next layer is being deposited. The peak temperatures experienced in the reheated region decrease as a function of distance away from the fusion boundary. The region that (re)heated above the phase transformation temperature undergoes noticeable microstructure change, which is seen as the heat-affected zone (HAZ) underneath each weld bead (Fig. 4(a)). Normally, the HAZ of each weld bead appears thicker at the bottom of the weld bead as the temperatures would be the highest at the center of the weld pool. In alloy Cu-9Al-4Fe-4Ni-1 Mn, the HAZ can be expected to experience peak temperatures above the $\beta$ solvsus temperature (830 °C) [8]. Consequently, any $\kappa_{II}$, $\kappa_{III}$, and $\kappa_{IV}$ precipitates in the reheated region get partially or completely dissolved during the heating part of the reheat thermal cycle. Further, some coarsening of $\alpha$ and $\beta$ regions can take place (Fig. 4(c)). During cooling, the $\kappa_{II}$ precipitates initially form in the $\beta$ regions and then eutectoid decomposition of the $\beta$ phase into $\alpha + \kappa_{II}$ phases takes place. Because the reheat thermal cycle involves a slower cooling rate as compared to the cooling rate in a newly deposited weld bead, the $\kappa_{II}$ precipitates as well as the eutectoid mixture in the HAZ may appear slightly coarser. It may be noted that reheating to temperatures below the $\beta$ solvsus, but well into the $\alpha + \beta + \varphi$ phase field, can also result in noticeable coarsening of the microstructure. In this case, the $\kappa_{II}$ precipitates do not undergo any dissolution (some coarsening can be expected instead), where the reverse eutectoid reaction ($\alpha + \kappa_{III} \rightarrow \beta$) takes place. During cooling, the $\beta$ phase once again undergoes transformation to a coarser $\alpha + \kappa_{II}$ lamellar mixture. In any case, the microstructural changes occurring in the HAZ of alloy Cu-9Al-4Fe-4Ni-1 Mn are not seriously detrimental as the HAZ bands are discontinuous.

4.3. Microstructure evolution

Low heat input employed in the WAAM process might have increased the cooling rate, prevented the significant grain growth, and yielded to fine grains as evidenced in the EBSD maps (Figs. 11 and 12). Although the scale (fine/coarse) of microstructure is noticeably different (Fig. 4), the phase constitution (i.e. presence of $\kappa_{II}$ and $\kappa_{III}$ in the HAZ and in the unaffected weld metal regions is essentially the same.

From the EBSD IPF map in Fig. 11(a), it may be noted that the region between the melt pool boundaries exhibit slightly finer grains. The presence of fine grains in alternating bands is observed more clearly in the optical microscopy, which is presented in Fig. 4. Texture formation in WAAM-NAB showed that the texture was almost random. This may be attributed to the nucleation, which lead to the formation of random oriented nuclei of the solid phase. The growth of some of the nuclei, however, takes place by selecting a specific orientation, here probably <001>, thereby produced somewhat sharp texture in the (100) pole figure (Fig. 11(d)). It is noted that, <001> orientation, parallel to the build direction, is the easiest growth direction for the columnar grains in most FCC metals and alloys [61]. (001) is a less close-packed plane, which can provide more comfortable locations for the moving atoms in the liquid phase to adhere. Even in such scenario, texture on (001) for WAAM-NAB is not very significant. Development of solidification texture might be controlled due to the low heat input employed and the corresponding low thermal gradients. EBSD images at high magnification (Fig. 12(e) and (f)) clearly revealed the grain structure evolution of WAAM-NAB. The grain size is finer than the cast-NAB (shown in Fig. 2) and small equiaxed grains nucleated on the grain boundaries of primary-$\alpha$, which are interdendritic regions. Nucleation of these fine grains is attributed to the heterogeneous nucleation from the globular $\kappa_{II}$ particles and also to the higher cooling rates where shorter growth times are available for the growth of the nucleated grains.

4.4. Mechanical properties

As noted in Section 3.3, the WAAM samples in as-fabricated condition exhibited considerably higher yield strength as compared to the as-cast samples. The increase in yield strength in WAAM samples can be attributed to the finer and homogenous solidification structure (grain boundary strengthening), presence of fine $\kappa_{IV}$ precipitates, and the absence of $\kappa_{I}$ that is detrimental for mechanical properties. It may be noted that the strength levels displayed by the WAAM samples are particularly impressive given that the samples did not contain significant volume fraction of $\kappa_{IV}$ strengthening precipitates in as-fabricated condition. Finer microstructural features, such as finer cell or dendrite spacing as observed from the EBSD images, enhanced yield strength of the WAAM-NAB significantly. In the perspective of NAB component engineering design, yield strength is more relevant than UTS [7,8]. The WAAM samples may prove to be even more superior to

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast-NAB</td>
<td>300 ± 15</td>
<td>670 ± 8</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>WAAM-NAB</td>
<td>388 ± 12</td>
<td>685 ± 10</td>
<td>26 ± 1</td>
</tr>
</tbody>
</table>

Fig. 13. Typical tensile stress-strain plots of cast and WAAM samples.
conventional castings after a simple annealing treatment in the temperature range of 500 to 600 °C [8], which would result in homogeneous $\kappa_{IV}$ precipitation in the $\alpha$-matrix.

The WAAM samples that are deposited under low heat input showed significantly finer and lower volume of intermetallic second-phases, and the absence of $\kappa_{I}$ as compared to the cast samples. As a result, the WAAM samples exhibited significantly higher tensile ductility than the as-cast samples. Fractographic examination as well as microstructural examination close to the location of fracture in WAAM samples did not show any cracking features such as micro-void coalescence or secondary cracks. The gain in the tensile ductility was very striking in spite of the fact that the WAAM samples were tested in the z-direction (layer interfaces oriented perpendicular to the loading direction), which is the orientation in which additive manufactured samples typically show their lowest tensile ductility [30,47,62]. The strength and ductility levels of as-built WAAM-NAB may be even higher than the cast alloy if it is deposited in the longitudinal or transverse directions.

The current study shows that the nickel-aluminum bronze alloy Cu-9Al-4Fe-4Ni-1 Mn can be readily used for part fabrication in WAAM process without any serious concerns about weld metal solidification cracking or HAZ liquation cracking. The parts may be considered for use in as-fabricated condition as the tensile properties of WAAM samples easily meet the minimum properties specified in ASTM B148 for alloy C95800 in as-sand-cast condition [7]. If necessary, a stress-relieving treatment in the temperature range of 300–350 °C may be carried out for improving stress-corrosion cracking resistance. As mentioned earlier, an annealing treatment in the temperature range of 500–600 °C may be considered for increasing the strength of WAAM parts in alloy Cu-9Al-4Fe-4Ni-1 Mn. For best corrosion resistance in seawater, an annealing treatment at 675 °C for a minimum of 6 h is generally recommended for alloy C95800 sand castings. The precipitates including globular or rosette shaped $\kappa_{II}$ and lamellar $\kappa_{III}$ are hard phases and less ductile. The improved corrosion resistance after annealing treatment is known to be due to globularization of the lamellar $\kappa_{III}$ and other intermetallic phases [63]. In future, it is appropriate to consider this heat treatment as well for WAAM parts in alloy Cu-9Al-4Fe-4Ni-1 Mn.

Fig. 14. SEM fractographs of (a and b): Cast, and (c and d): WAAM samples. Encircled region in (b) shows flat fracture features due to the presence of coarse intermetallic phase.
The microstructural features and mechanical properties of WAAM-NAB arc additive manufacturing (WAAM) to produce Nickel Aluminum Bronze (NAB) alloy bars, and to study the morphology, crystallography, and the distribution of the phases present using optical, scanning electron microscopy, and transmission electron microscopy techniques. The microstructural features and mechanical properties of WAAM-NAB are compared with the cast-NAB. The findings of this study are as follows:

1. WAAM process is suitable for additive manufacturing of NAB alloy with relatively low heat input (170 J/mm). In the current study, nearly full dense square bars (two) of 25 mm side and 160 mm height were successfully deposited in multiple layers with excellent layer bonding and no defects at the layer interfaces.

2. The process of WAAM significantly altered the microstructure. While the as-cast microstructure consists of copper-rich α-phase and all four types of κ-phases, κII phase is not precipitated in WAAM-NAB due to higher cooling rates.

3. In WAAM-NAB, κII and κIII phases are precipitated in the interdendritic regions whereas κI is uniformly nucleated in the α-matrix. κII particles are globular and Fe₃Al based; κIII is an eutectoid mixture in lamellar structure and NiAl based.

4. No retained β is observed in the WAAM-NAB. As the rate of cooling in weld metal drops off with decrease in temperature, eutectoid reaction in the intermediate temperature range is not suppressed, and the β-phase is entirely consumed and transformed to κII.

5. WAAM-NAB exhibited fine equiaxed grain structure and relatively weak texture. The (001) poles, which is typically an easy growth direction for FCC structure tilted away from the build direction. There is no significant difference in the texture evolution between x–z plane and x–y plane.

6. Reheating associated with multi-layer deposition cause no detrimental microstructural changes in WAAM-NAB. It exhibits relatively finer microstructure, and show higher yield strength and percent elongation. The gain in room temperature tensile properties which may attribute to the absence of κI is quite impressive even when WAAM tensile samples are tested along the normal direction (build direction). The ductile fracture mode was determined to be the main failure mode of both NAB alloys.

7. Heat treatments in the range of 500–600 °C may result in increasing the volume fraction of fine-κIV precipitates, which may increase the strength levels of WAAM-NAB.

8. Overall, the prospects of WAAM to produce NAB seem very bright and it can significantly widen the scope and applicability of additive manufacturing to produce NAB parts and components, mainly for the marine industry. Further work towards the effect of various heat treatments on microstructure, mechanical properties, and corrosion resistance would be highly beneficial.

5. Conclusions

The material chosen for this study was microstructurally complex. The intent of this work was to explore the feasibility of adopting wire-arc additive manufacturing (WAAM) to produce Nickel Aluminum Bronze (NAB) alloy bars, and to study the morphology, crystallography, and the distribution of the phases present using optical, scanning electron microscopy, and transmission electron microscopy techniques. The microstructural features and mechanical properties of WAAM-NAB are compared with the cast-NAB. The findings of this study are as follows:

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Declaration of Competing Interest

The authors declare that there is no conflict of interest.

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