Naval Surface Warfare Center Carderock Division

West Bethesda, MD 20817-5700

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June 2021

Platform Integrity Department Technical Report

Nickel-Aluminum Bronze (NAB) Review: Additive Manufacturing and Weldability

by

Sean M. Orzolek Jennifer K. Semple Charles R. Fisher



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ADMINISTRATIVE INFORMATION

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EXECUTIVE SUMMARY

Nickel-aluminum bronze (NAB) alloys are commonly used for marine applications such as propellers by the U.S. Navy. These NAB components are conventionally manufactured using casting techniques, but recent interest has shifted to the possibility of additive manufacturing (AM) processes. The following literature review discusses the microstructural evolution of (nominally) Cu-9Al-5Ni-5Fe-1Mn NAB alloys in the cast, wrought, arc-welded, and laser-welded conditions. NAB alloys exhibit a complex microstructure, consisting of a mixture of four κ precipitates distributed in an α or β ' martensitic matrix. The size, morphology, and distribution of these phases are sensitive to changes in cooling rate and thermal history such as those imposed by AM and welding. Although the microstructure is well documented under casting conditions, no continuous cooling diagrams have been developed to describe phase transformations under arc and laser processing conditions for NAB. As such, this review investigates recent reports related to arc- and laser-based additive manufacturing processes and the associated microstructures and properties.

Studies have reported additively manufactured NAB alloys with improved properties compared to cast material, due in part to the difference in microstructure. At moderate cooling rates such as those associated with arc-based processing, the microstructure consists of Widmanstätten α and various κ phases, which become more refined with increasing cooling rate. This leads to an improvement in the tensile properties of wire-arc direct energy deposited NAB, with >17% increase in yield strength and >90% increase in ductility when compared to cast material. At rapid cooling rates representative of laser-based processing, the microstructure consists primarily of a twin-related β ' martensite with nanoscale κ phases. This leads to a significant increase in vield strength (>60-100%) at the expense of ductility (<-30%) when compared to cast material. Additionally, previous studies have reported that the refined microstructure from these high cooling rate processes leads to an improvement in the corrosion resistance of as deposited NAB. There is also evidence that the conventional heat treatments for cast NAB alloys need to be optimized for additively manufactured materials. The report includes the methods and challenges associated with characterizing NAB alloys under these processing conditions and provides recommendations for future research.

BACKGROUND

The shipbuilding industry has seen great benefits from the use of nickel-aluminum bronze (NAB) alloys since the 1970s, especially in the construction of propellers for high-value ships [1]. These alloys have excellent mechanical properties, particularly strength, fatigue life, and toughness, allowing them to withstand repeated collisions with water. NAB alloys also exhibit high corrosion, erosion, and cavitation resistance, which are vital for any seawater application [2]–[5]. Recent studies examining NAB alloys have focused on applications of additive manufacturing (AM) techniques such as arc-wire directed energy deposition (DED), also commonly referred to as wire arc additive manufacturing (WAAM), where several studies have shown that additively manufactured NAB materials exceed the properties of conventional NAB castings [6].

NAB replaced simple aluminum-bronze alloys, which formed a brittle $\alpha + \gamma_2$ eutectoid that was detrimental to corrosion resistance [7]. NAB propellers also benefit from a density that is 15-19% lower than traditional brass propellers, improving the carrying capacity of marine propulsion systems while maintaining good strength, toughness, and corrosion resistance [1]. A substantial overview of NAB alloys has been summarized by the Copper Development Association and provides an excellent introduction into the applications and properties of NAB alloys [8].

NAB alloys are primarily copper, with substantial alloying additions of nickel, aluminum, and iron. At high temperatures, a body centered cubic (BCC) β phase forms, which typically transforms to a face centered cubic (FCC) α phase interspersed with various κ precipitates upon cooling [1]. The microstructure of NAB alloys is sensitive to changes in composition as well as to changes in cooling rate, all of which are discussed in detail in the following sections.

Microstructure of NAB

The solidification of a hypoeutectoid 11Al-6Ni-5Fe-1Mn NAB alloy and the solid state transformations have been described in detail by Pisarek and are shown schematically in Figure 1 [9]. This solidification process follows Stages I-VIII, where each stage corresponds to a different reaction temperature measured by differential thermal analysis. Stages I-III detail the primary solidification starting at the liquidus temperature of 1083 °C (1981 °F) and continuing with formation of the high temperature β solid solution, which nucleates heterogeneously on the interface of the mold (in the case of casting) or on undissolved precipitates. Below the solidus temperature of 1023 °C (1873 °F) (Stage III), all of the liquid is consumed, resulting in the formation of β grains, which grow unimpeded by grain boundary precipitates. At Stage IV (985) $^{\circ}C > T > 890 \ ^{\circ}C \ [1805 \ ^{\circ}F > T > 1634 \ ^{\circ}F]$), the κ_{II} precipitate nucleates on the β grain boundaries and interdendritic regions, growing to form the characteristic rosette morphology and locally depleting the surrounding β of iron and aluminum. This in turn stabilizes the α phase (945 °C > T > 760 °C [1733 °F > T > 1400 °F]) around the grain boundaries, according to the $\beta \rightarrow \beta + \alpha$ transformation. With decreasing temperature, the α phase consumes the majority of the β phase under equilibrium conditions, as shown in Stage V. With additional cooling, the eutectoid transformation of $\alpha \rightarrow \alpha + \kappa_{III}$ occurs (860 °C > T > 660 °C [1580 °F > T > 1220 °F]) resulting in the lamellar eutectoid constituent in Stage VI. This is associated with the formation of Ni-rich regions within α which partition into the NiAl κ_{III} phase. With further decreasing temperature (815 °C > T > 600 °C [1499 °F > T > 1112 °F]) the untransformed α regions locally exceed the solubility of iron, resulting in the intragranular precipitation of the Fe₃Al κ_{IV} phase as shown in Stage VII. Under equilibrium conditions and for NAB alloys with Al concentrations in excess of 11 wt. %, any remaining β transforms to α and the γ_2 intermetallic phase as shown by Stage VIII $(515 \text{ }^{\circ}\text{C} > \text{T} > 460 \text{ }^{\circ}\text{C} [959 \text{ }^{\circ}\text{F} > \text{T} > 860 \text{ }^{\circ}\text{F}])$. However, modern NAB alloys have lower concentrations of aluminum and preclude formation of the γ_2 intermetallic phase. Instead, low temperature transformations are associated with the β ' martensite phase under rapid cooling conditions and with the $\alpha + \kappa_{III}$ eutectoid at slow cooling rates. The reaction temperatures and microstructures presented by Pisarek are reported to vary with changes in composition and cooling rate but nevertheless, Figure 1 provides valuable insight into the complex microstructural transformations of NAB alloys [9]. The microstructural variations as a function of composition have been described in detail by Hyatt et al. [10] and Brezina et al. [11] but have not developed the microstructural model reported by Pisarek [9].



Figure 1. Model of crystallization and phase transformations under equilibrium conditions as observed by Pisarek for a hypoeutectoid 11Al-6Ni-5Fe-1Mn NAB alloy [9].

A more appropriate diagram for modern NAB compositions is described according to the calculated pseudo-binary phase diagram developed by QuesTek Innovations, LLC, showing the variation in phase formation as a function of Al content and temperature in **Figure 2** [12]. With increasing Al concentration, there is a stabilization of the β phase at the expense of α phase formation. As discussed previously, constituents observed in modern NAB alloys include β , β' , α , four distinct κ precipitates (κ_{I} , κ_{II} , κ_{III} , κ_{IV}) and the γ_2 intermetallic [7], [13]. A summary of these constituents is listed in **Table 1** and **Table 2**, detailing the morphology and composition,

respectively. These phases are labeled in the scanning electron microscope (SEM) micrograph shown in **Figure 3** and are explained in detail as follows.



Figure 2. Pseudo-binary phase diagram calculated using Thermo-Calc for a Cu-XA1-4.5Ni-4.0Fe-1.15Mn (wt.%) alloy for X=0-25 wt.% Al. Courtesy of QuesTek Innovations, LLC [12].

β and β ' Phases

The first phase to form upon solidification in any NAB is single phase β , reported to solidify above 1070 °C (1958 °F) [14]. This remains stable above the eutectoid temperature of approximately 800 °C (1472 °F) as a disordered body centered cubic (BCC) phase with a lattice parameter of 0.357 nm. At high cooling rates, the β phase becomes partially ordered between 400 °C (752 °F) to 600 °C (1112 °F) as a superlattice structure of Cu₃Al, designated as β_1 . With additional cooling to approximately 200 °C (392 °F), the β_1 phase transforms martensitically to β ', which has an ordered 3R or 2H martensitic structure interspersed with NiAl precipitates [14], [15]. The 3R structure in particular contains a high density of precipitates, the size of which depends on the cooling rate [7]. **Figure 3** shows a representative SEM micrograph of the β ' morphology. The β ' phase is undesirable due to its negative effect on corrosion resistance in a seawater environment and low ductility, and it has been noted to accelerate fatigue crack growth

[2], [14], [16], [17]. For modern NAB alloys with nickel and iron additions, a complete microstructural transformation to β ' will not occur, allowing remaining β to instead transform into α phase with a bainitic or Widmanstätten morphology [10]. Iron is an α phase stabilizer and favors a bainitic transformation, whereas nickel and aluminum are β stabilizers and favor the martensitic transformation [11]. Slow cooling rates such as those associated with casting or a quench and temper treatment can be used to mitigate formation of β ' [14]. The influence of phase formation as a function of cooling rate is discussed in a later section.

	110111 [10])	1		
Designation	Description	Crystallograph	Reference	
α	Copper rich solid solution	FCC	A1	[11]
β	High temperature solid solution	BCC	A2	[11]
κ _I	Cored iron-rich particles	Possibly iron ric DO ₃ / Fe	[13], [19]	
κ_{II}	Iron-rich Fe ₃ Al	BiF3	DO ₃	[11]
κ _{III/V}	Nickel-rich NiAl	CsCl	B2	[11]
$\kappa_{\rm IV}$	Fine iron-rich Fe ₃ Al	BiF ₃	DO ₃	[11]
β'	Martensitic phase from quenching β	Complex twin rel in the form of 3R, struct	[15]	
$\begin{array}{c} \text{Particles} \\ \text{retained in } \beta \\ (\kappa_V) \end{array}$	Nickel-rich NiAl	CsCl	B2	[19]

 Table 1.
 Summary of Microstructural Constituents in NAB (Adapted from [18])



Figure 3. SEM micrograph of an as-cast NAB alloy with phases labeled [8].

α Phase

Upon further cooling, β begins transforming into a face centered cubic (FCC) copper-rich α phase with a lattice parameter of 0.364 ± 0.004 nm according to $\beta \rightarrow \beta + \alpha$ [7], [20]. The

transformation start temperature has been reported at temperatures below 1030 °C (1886 °F) in sand mold castings cooled at approximately 0.001 °C/s (0.0018 °F/s), although older literature has reported transformation temperatures as low as 1100 °C (2012 °F) under equilibrium [7], [14]. The α formation temperature is sensitive to changes in nominal aluminum concentration, where increasing the aluminum concentration decreases the α formation temperature [11]. Nucleation of α occurs preferentially at β grain boundaries and grows along crystallographic planes as Widmanstätten sideplates [7], [14]. Intragranular formation of α has been reported in addition to these grain boundary allotriomorphs, with that intragranular formation increasing with heat input and subsequent decreasing cooling rate [21]. Coarse Widmanstätten α grains can significantly decrease yield strength, but can be suppressed with cooling rates in excess of 200 °C/s (360 °F/s) for some alloy compositions [2], [10]. As shown in **Table 2**, the chemical composition of α is similar to the bulk, with typical values of copper being approximately 6% higher.

		Compositi		7 moys m 1	wo blueles	<u>, , , , , , , , , , , , , , , , , , , </u>	
P	hase	Cu	Al	Ni	Fe	Mn	Source
]	Bulk	80.55	9.42	4.7	4.24	1.09	
	α	85.4 ± 4	8.3 ± 1.7	2.5 ± 1.4	2.7 ± 2	1.4 ± 0.1	
	β	85.2	8.7	3.5	1.6	1	
	KI	15 ± 5	13 ± 5	15 ± 3	55 ± 7	2 ± 0.4	[7]
	K _{II}	21 ± 5	19 ± 3	27 ± 4	32 ± 3	2.2 ± 0.6	
KIII		26 ± 4	18 ± 6	32 ± 2	22 ± 0.7	2 ± 0.3	
	KIV	13 ± 1	20 ± 3	4 ± 1	62 ± 4	1.5 ± 0.3	
Bulk	(Alloy 1)	80	9.4	4.9	4.4	1.2	
Bulk	(Alloy 2)	80.1	9	4.4	5.1	1.4	
α	(Alloy 1)	85.8 ± 0.4	7.2 ± 0.4	3 ± 0.2	2.8 ± 0.3	1.1 ± 0.1	
κ_I	(Alloy 2)	10.5 ± 1	9.3 ± 0.5	3.5 ± 0.4	72 ± 1.4	2.9 ± 0.5	[13]
κ_{II}	(Alloy 1)	12.1 ± 3.1	12.3 ± 1.3	8 ± 1.8	61.3 ± 4.9	2.2 ± 0.2	
K _{III}	(Alloy 1)	17 ± 4.6	26.7 ± 1	41.3 ± 6	12.8 ± 1.6	2 ± 0.4	
κ_{IV}	(Alloy 1)	2.6 ± 0.7	10.5 ± 1.7	7.3 ± 1.5	73.4 ± 2.3	2.4 ± 0.2	

Table 2. Chemical Composition of Each Phase as Compared to the Bulk

 Composition for NAB Allovs in Two Studies [7], [13]

κ₁ Precipitate

Further cooling shifts transformation to a $\beta \rightarrow \alpha + \kappa_I$ eutectoid reaction. There are four distinct κ precipitates, each with characteristic reaction temperature regimes, morphology, and composition [11]. The first to form is κ_I , which has been observed at temperatures from 900 °C (1652 °F) to 920 °C (1688 °F) at equilibrium cooling rates [11]. Rapid cooling typically depresses transformation temperatures, and previous studies observed the formation of α and κ_I in the lower temperature range of 820 to 830 °C (1508 to 1526 °F) for a cooling rate of 0.13 °C/s (0.23 °F/s) [7]. **Figure 3** shows the characteristic rosette morphology of the κ_I phase, outlined by the lamellar κ_{III} phase [7], [8]. Early literature stated that κ_I precipitates randomly in both α and β , but was traditionally expected to form in β [7]. Modern studies acknowledge κ_I as forming only in the α grains [13], [14].

The κ_I phase is nominally Fe₃Al and nucleates around small, copper-rich particles with minor additions of nickel, silicon, and manganese and can grow to be on the order of 20-50 µm in diameter [13], [14], [22]. κ_I does not have a single crystal structure; particles are instead

composed of a number of different structures, including disordered iron-rich solid solution (BCC), Fe₃Al (DO₃), and FeAl (B2). Therefore, the formation of κ_1 is sensitive to iron additions and was reported by previous work from Hasan *et al.*, where κ_1 formation only occurred in the alloy with higher iron content as shown in **Table 2** [13]. However, an earlier study by Culpan *et al.* [7] observed κ_1 formation in an alloy with even less iron than those tested by Hasan *et al.* [13]. In Culpan's study, samples were held at 1000 °C (1832 °F) for one hour before slowly cooling to a particular temperature, followed by quenching to room temperature [7]. This suggests that κ_1 may readily form in lower-iron alloys given enough time in the high-temperature regime, but its formation in as-cast microstructures is dependent on iron content. In general, the iron content must exceed 5 wt.% in order for κ_1 phase to form, but it has been reported to form in alloys with nominal concentrations below 5 wt.% iron associated with local, residual segregation after solidification [22], [23]. Neither Culpan nor Hasan commented on the relative amounts of iron and nickel, though ASTM B505 specifies for at least one NAB alloy (C95800) that "iron content shall not exceed nickel content," suggesting that this relationship may also have an impact on formation of κ_1 [24].

κ_{II} Precipitate

кш Precipitate

The third κ precipitate that forms during cooling is a NiAl intermetallic designated as κ_{III} , which forms according to the eutectoid reaction $\beta \rightarrow \alpha + \kappa_{III}$ [7]. A typical lamellar eutectoid morphology is shown in **Figure 3** and forms in the range of 800 to 860 °C (1472 to 1580 °F) at equilibrium, or 750 to 775 °C (1382 to 1427 °F) at a cooling rate of 0.13 °C/s (0.23 °F/s) [7], [13], [14], [17], [22]. κ_{III} exhibits an ordered BCC structure with a lattice parameter of 0.288 nm and is nickel- and aluminum-rich, with minor solubility of copper iron and manganese (**Table 2**) [13], [14]. The formation of the κ_{III} phase reduces the nickel in the eutectoid α constituent and the high surface area of the lamellar structure increases the susceptibility to galvanic corrosion [8], [26], [27].

Previous literature has reported the formation of intragranular acicular NiAl precipitates after heat treating, designated as κ_V [28]. However, this phase has the same crystal structure and composition of the κ_{III} precipitate, so there is a disagreement over the use of the κ_V terminology [11], [18], [29]. Additionally, as these precipitates nucleate within the α grain, they have occasionally been misclassified as κ_{IV} , but can be differentiated by composition and morphology [28], [30].

KIV Precipitate

When the temperature reaches 860 °C (1580 °F) during cooling, nucleation of κ_{IV} begins within α grains as the solubility of iron in α is exceeded [16]. κ_{IV} manifests as nano-scale (5-10 nm) spherical precipitates distributed throughout the center of the α grain [22]. After heat treating or for slow cooling rates, the κ_{IV} precipitates grow to the sub-micron scale, with a precipitate free zone (PFZ) at the periphery of the α grain as illustrated in **Figure 3** [8], [22]. Nucleation occurs preferentially in the center of α grains because this region does not experience local iron depletion from the κ_{I} or κ_{II} formation. The κ_{IV} phase has a DO₃ structure with a lattice parameter of 0.577 nm [7]. Similar to κ_{II} , it is nominally Fe₃Al with minor solubility of silicon, nickel, manganese, and copper [13].

Influence of Composition

When compared to binary aluminum-bronze alloys, the addition of nickel and iron to modern NAB alloys results in significant changes to the microstructure and properties. Nickel increases both corrosion resistance and yield strength, while nickel and iron both serve to suppress the $\alpha + \gamma_2$ eutectoid transformation when cooling from the β high-temperature regime, as illustrated in the phase diagrams in **Figure 4**.



Vertical Section of the Cu-Al-Ni-Fe system at 5% Ni, 5% Fe. Binary Cu-Al system.

Figure 4. Phase diagram of a typical NAB in comparison to a binary Cu-Al system, illustrating the decreased likelihood of $\alpha + \gamma_2$ formation in the former resulting from 5% Ni and Fe additions [7]. The γ_2 (Cu₉Al₄) intermetallic increases corrosion susceptibility in seawater environments, has poor strength, and is common in Cu-Al binary systems [7], [11], [23]. Nickel concentrations in excess of 7 wt.% can lead to the formation of continuous networks of the κ_{III} phase, embrittling the microstructure and increasing the susceptibility to thermal shock [31]. High amounts of iron can also lead to the excessive formation of κ_{I-III} precipitates, intermetallics that decrease ductility, and thus its addition is limited [8]. Manganese is added to increase the fluidity of the liquid metal during casting, and has been reported to inhibit the formation of β ' martensite during cooling [28].

Sadayappan et al. reported the influence of trace element additions that lead to minimum specification changes to the ASTM standard [32]. Their work identified that the addition of lead in excess of 0.03 wt. % lead to cracking during welding and heat treating at 900 °C (1652 °F). Other alloving additions were found to be detrimental to the elongation but the allovs did not drop below the minimum ductility requirement of 15%. Hyatt et al. evaluated the influence of alloying addition of chromium, titanium, and zirconium as well as standard additions for low heat input laser welds [33]. Their results showed that the addition of aluminum increased the hardness of the fusion zone, increased the cavitation erosion resistance and made the alloy more resistant to tempering. High nickel concentrations resulted in an increase in the proportion of martensite, whereas iron additions favored the formation of α . Chromium increased the hardness of the as deposited material, suppressing the formation of α and increasing the cavitation erosion resistance. The addition of titanium and zirconium lead to the formation of a fine-grained equiaxed structure, likely due to the formation of high temperature oxides, which act as heterogeneous nucleation sites. The additions of these elements lead to a dual phase α + martensitic constituent and was found to be detrimental to the cavitation erosion resistance. However, the additions of chromium, titanium, and zirconium are not included as part of the chemistry requirements of common NAB alloys, as specified by ASTM B505 [24], B150 [34], and AWS A5.7 [35] as shown in Table 3. These alloy grades represent the modern variant of NAB alloys, which are generally Cu-9Al-5Ni-5Fe-1Mn and will be the focus of the remainder of the review.

Standard	Designation	Condition	Cu (min)	Al	Ni (incl. Co)	Fe	Mn	Si	Zn	Sn	Pb
Standard Designation ASTM C95500 B505 C95520 C95820 C95820 C95820 C63000 ASTM C63020 B150 C63200	C95500	Cast	78	10.0- 11.5	3.0-5.5	3.0- 5.0	3.5				
	C95520		74.5	10.5- 11.5	4.2-6.0	4.0- 5.5	1.5	0.15	0.3	0.25	0.03
	C95800		79	8.5- 9.5	4.5-5.0 ^A	3.5- 4.5 ^A	0.8- 1.5	0.1			0.03
	C95820		77.5	9.0- 10.0	4.5-5.8	4.0- 5.0	1.5	0.1	0.2	0.2	
	C63000		BAL	9-11	4-5.5	2-4	1.5	0.25	0.3	0.2	
ASTM B150	C63020	Wrought	74.5	10-11	4.2-6	4.0- 5.5	1.5		0.3	0.25	0.03
D 130	C63200		BAL	8.7- 9.5	$4.0-4.8^{A}$	3.5- 4.3 ^A	1.2-2	0.1			0.02
AWS A5.7	ERCuNiAl/C63280	Wire	BAL	8.5- 9.5	4-5.5	3-5	0.5- 3.5	0.1	0.1		0.02

Table 3.Chemical Composition for NAB Alloys in Cast, Wrought, and
Wire Form. Values Represent Maximum or Ranges in Weight
Percent Unless Noted Otherwise [24], [34], [35].

^{*A*} Iron content shall not exceed the nickel content.

MATERIAL PROCESSING

Although the microstructure of NAB alloys is sensitive to differences in composition, the microstructure is also sensitive to processing conditions such as cooling rate, aging, and thermal cycles from welding to AM. The following sections describe the microstructures and properties of NAB alloys starting with slow cooling rates (casting/wrought material), moderate cooling rates (arc welding/WAAM) and high cooling rates (laser cladding, laser-wire/powder direct energy deposition, and laser powder bed fusion).

Slow Cooling

Cast and Wrought NAB

A summary of the microstructural transformations under equilibrium conditions has been summarized by Fuller in **Figure 5** [16]. At slow (approaching equilibrium) cooling rates (< 0.1 °C/s [0.18 °F/s]), such as those observed during casting, the β phase undergoes a complete transformation into α and κ phases [11]. This is because the $\beta \rightarrow \alpha + \kappa_{III}$ transformation is diffusion-controlled and therefore is dependent upon time and temperature, unlike the $\beta \rightarrow \beta$ ' martensitic reaction, which is a diffusionless transformation and therefore can occur at faster cooling rates [11]. The microstructural characterization of NAB alloys has been discussed in detail by Culpan *et al.* [7] and Hasan *et al.* [13] in the previous section.



Temperature Equil. Cooling

Figure 5. Microstructural transformations of NAB alloys under equilibrium conditions. Adapted from [16].

NAB alloys designated as C63000, C63200 and C63020 are also available in wrought form, with requirements described in ASTM B150 [34]. The microstructure of wrought NAB alloys has been described in detail by Cook *et al.* and generally consists of fine κ phases in an α matrix, with distorted $\kappa_{I/II}$ rosettes observed after hot rolling [36]. Banding is observed after rolling and is similar to what is observed in carbon manganese steels. Differences in hardenability have been observed in association with the banded microstructure [36]. An SEM micrograph and a microstructural schematic of wrought NAB is shown in **Figure 6** [36], [37].



Figure 6. A) Scanning electron micrograph of banding in wrought NAB plate. Adapted from [36]. B) Microstructural schematic of banding in wrought NAB plates. Adapted from [37].

The variations between wrought and cast microstructure can result in different heat affected zone (HAZ) microstructures created by welding. Hasan *et al.* reported that the HAZ of welds made with cast NAB exhibited a mixture of β ' martensite and Widmanstätten α [15].

However, the welds with wrought NAB material exhibited alternating bands of α and β ' in the HAZ, associated with the compositional banding and difference in hardenability [15]. Given the different possible HAZ microstructures, the base metal selection for welding and AM is important to consider as it may lead to differences in the HAZ microstructure.

Heat Treatments

In order to comply with ASTM B505, all castings of copper alloy UNS No. C95800 except propeller castings are required to undergo a temperature anneal heat treatment at 675 ± 10 °C (1250 ± 50 °F) for a minimum of six hours. Cooling for all other components is required to be done at the fastest rate possible that will not cause excessive distortion or cracking [24]. According to former NSWCCD engineer Steve Fielder, propellers are exempt from this requirement due to the associated logistical difficulties (*i.e.*, the difficulty of cooling the extremely large thermal mass of a propeller). For perspective, it takes on the order of a month for a large propeller casting to cool to room temperature. This difficulty is coupled with the lack of necessity for heat treatment, as propellers generally use a sacrificial zinc anode or other cathodic protection to prevent corrosion of as-cast material [38].

Copper alloy UNS No. C95520 is only used in the quench-hardened and tempered (TQ30) condition, while C95500 has two suggested heat treatments: solution heat treatment and annealing heat treatment as shown in **Table 4**. The AWS Welding Handbook Vol. 5 recommends a temper anneal at 620 - 663 °C (1150 - 1225 °F), followed by rapid cooling in air, for NAB alloys that will be exposed to corrosive environments [39]. This thermal cycle effectively tempers the β ' phase, improving corrosion resistance and resulting in the precipitation of additional κ_{TV} precipitates.

Copper Alloy UNS No.	Solution Treatment (not less than 1 h followed by water quench), °F [°C]	Annealing Treatment (not less than 2 h followed by air cool), °F [°C]
C95500	1600–1675 [870–910]	1150–1225 [620–660]
C95520	(2 h followed by water quench) 1600–1700 [870–925]	925–1000 [495–540]

Table 4. Suggested Heat Treatments for NAB Castings [24]

Recommended heat treatments for stress relief after machining or other post-processing have been noted to have no influence on the mechanical properties. These are typically conducted between 300 and 450 °C (572 and 842 °F) for a minimum of one hour followed by air cooling [8]. This was described in detail by C. Wang *et al.*, who evaluated the stress relief as a function of time and temperature after shot peening the surface of a 10Al-4Fe-3.6Ni-0.3Mn NAB alloy [40]. The residual stress was characterized using an x-ray diffraction technique. Stress relief as a function of temperature for an annealing time of five minutes is shown in **Figure 7**.

Measured residual stress decreased with increasing annealing temperature, and a heat treatment of 500 °C (932 °F) for five minutes resolved nearly 95% of the residual stress. However, this heat treatment may lead to undesirable microstructural transformations and as such, annealing temperatures between 200 and 400 °C (392 and 752 °F) were used to evaluate the differences in stress relief as a function of time up to two hours, as shown in **Figure 8**. The initial stress relief occurs rapidly for all tested annealing temperatures and reaches a steady state at time intervals of less than one hour. This is in agreement with the conventional treatments described previously for castings. The fine grain size and high residual stresses induced by the shot peening process suggest that these treatments may be similarly applicable to parts produced by welding and AM.



Figure 7. Residual stress in the surface layer of a shot peened 10Al-4Fe-3.6Ni-0.3Mn NAB alloy as a function of temperature with a holding time of five minutes [40].



Figure 8. Isothermal stress relaxation as a function of annealing time for a shot peened 10Al-4Fe-3.6Ni-0.3Mn NAB alloy [40]

It must be considered that as the microstructure is not uniform for NAB alloys, neither is the distribution of the residual stress. This was reported by Lv et al. using in-situ electron backscatter diffraction (EBSD) and neutron diffraction during tensile tests of a 9.5Al-4.2Ni-4Fe-1.2Mn NAB alloy after heat treating at 675 °C (1247 °F) for six hours [41]. Tensile testing was conducted with peak stresses of 300 MPa (44 ksi), 400 MPa (58 ksi), 450 MPa (65 ksi), 500 MPa (73 ksi), and 600 MPa (87 ksi). Residual stress was measured following unloading of each sample. The imposed tensile stresses caused a change in peak position intensity and position, associated with the accumulation of residual stress in the α matrix and the κ phases as shown in **Figure 9A-D**. However, the direction of the peak shifting is opposite for the α and κ phases, resulting in compressive stresses in the matrix and tensile stresses in the k phases. The magnitude of the residual was calculated using Hooke's law using the data in Figure 9C, where the stress accumulation is concentrated in the κ phases (Figure 9D). Transmission electron microscopy (TEM) characterization and EBSD related this to the dislocation pileup at the α/κ interface. As the k precipitates act as barriers to dislocation motion, this was found to be primarily associated with the κ_{II} and κ_{III} phases. With an imposed stress of 300 MPa (44 ksi) negligible residual stress was observed, as this is in the elastic region of the NAB alloy. With increasing stress, the residual stresses increased to a maximum of -135 MPa (20 ksi) in the α phase and 560 MPa (81 ksi) in the κ phases following a tensile load of 600 MPa (87 ksi).



Figure 9. In-situ neutron diffraction results of a 9.5Al-4.2Ni-4Fe-1.2Mn NAB with A) neutron diffraction peaks of α matrix, B) diffraction peaks of the κ phases, C) calculated lattice strain based on the peak shifts, D) microscopic residual stress of each phase [41].

The relationship between the residual stress accumulation and the susceptibility to stress corrosion cracking was evaluated through the immersion of NAB alloys in a 3.5% NaCl solution while exposed to a constant stress for 20 days. No change in the corrosion resistance was observed with a sample subjected to a stress of 300 MPa (44 ksi), whereas significant corrosion was observed in samples that underwent stresses of 450 MPa (65 ksi) and 600 MPa (87 ksi), shown by the microstructural characterization in **Figure 10**. Preferential corrosion was observed at the α/κ interface for the samples subjected to plastic deformation, associated with high concentration of dislocations. These observations are important to consider for welding and AM applications, where changes in microstructure and high residual stresses influence the susceptibility to stress corrosion cracking [21], [42].



Figure 10. SEM characterization of surface and cross-sectioned microstructure of NAB alloys immersed in 3.5% NaCl solution for 20 days under tensile stresses of A) unstressed, B) 300 MPa (44 ksi), C) 450 MPa (65 ksi), D) 600 MPa (87 ksi) [41].

Moderate Cooling

Moderate cooling rates (> 1 °C/s [1.8 °F/s]), representative of arc welding processes, result in the diffusionless transformation of β into the β ' martensitic phase [11]. However, these reactions depend not only on the cooling rate but also on the peak temperature experienced by the material, as indicated by Fuller's work shown in **Figure 11** [16].



Figure 11. Temperature and cooling rate dependence of NAB [16].

These transformations are described by the continuous cooling transformation (CCT) diagrams in **Figure 12A-C** developed by previous work by Brezina *et al.* for three unique compositions [11]. At the time of this writing, these are the only CCT diagrams known to the authors. Though they were developed for NAB alloys that included iron, nickel, manganese, and aluminum additions, they are consistent with previous work by Gorecki, where CCT diagrams were developed for a nickel-free aluminum bronze alloy (Cu-10A1-3Fe-2Mn) [43].

Unlike traditional CCT diagrams where temperature is plotted as a function of time, the diagrams are plotted as a function of cooling time in the critical range of 950 to 500 °C (1742 to 932 °F). At rapid cooling rates, the martensite start temperature (M_s) occurs around 200 °C (392 °F) and is preceded by an ordering reaction, designated as β_1 between 400 and 500 °C (752 and 932 °F) according to $\beta \rightarrow \beta_1 \rightarrow \beta$. Other researchers have noted that the β_1 ordering reaction has been observed at cooling rates in excess of 2000 °C/s (3600 °F/s), but is dependent on the aluminum addition as a long range ordered martensite is observed in Al-Cu binary alloys with

aluminum concentrations in excess of 11 wt. % [10]. These diagrams also describe the influence of aluminum content, where with decreasing aluminum concentration there is a decrease in the ordering and martensite reaction temperatures. Figure 12C shows the CCT diagram for a composition representative of a modern NAB alloys, where β martensite is expected to form for any cooling rate greater than 0.1 °C/s (0.18 °F/s). This is consistent with the observation of Gorecki where without the addition of nickel (β stabilizer), a cooling rate greater than 1 °C/s (1.8 $^{\circ}$ F/s) was needed to form β ' [43]. These figures also indicate that the proportion of β ' is primarily dependent on the peak temperature and alloy composition rather than cooling rate. This is because the formation of β ' is dependent upon the amount of β phase present, which is expected to increase with increasing peak temperatures above the eutectoid and is highly dependent on the concentration of aluminum (Figure 4). In order to maximize the amount of β phase that formed in the microstructure, Hyatt et al. used a Gleeble 2000 to partially melt NAB alloys by using a thermal cycle with a peak temperature in the L + β region [44]. The study reported that no significant increase in β ' was observed for a sample cooled at 3000 °C/s (5400 $^{\circ}$ F/s) compared to a sample cooled at 300 $^{\circ}$ C/s (540 $^{\circ}$ F/s), indicating that the proportion of β ' is not sensitive to differences in cooling rate [21], [45].



Figure 12. CCT diagrams of NAB alloys solution heat treated at 950 °C (1742 °F) for one hour, shown as a function of cooling time between 950 and 500 °C (1742 and 932 °F) for A) Cu-11.5Al-5.3Fe-5.1Ni-0.9Mn, B) Cu-9.9Al-5.3Fe-5.1Ni-0.9Mn, and C) Cu-8.8Al-5.4Fe-5Ni-0.9Mn [11].

Although the diagrams in **Figure 12** provide insight into the microstructural changes for the cooling rates representative of casting and high heat input welding, there is insufficient information regarding the very high cooling rates experienced when welding with low heat inputs or during additive manufacturing. This is in part due to the difficulty in measuring the reaction temperatures by dilatometry as shown in **Figure 13**, where a comparison is made between a bainitic steel and a Cu-Al bronze. Although the transformations are from BCC to FCC ($\beta \rightarrow \alpha$), the changes in lattice parameter are very small 0.357 nm \rightarrow 0.364 nm and therefore the change in volume is only on the order of 1% or less [46].



A more recent study by Anantapong *et al.* was able to overcome the challenges of dilatometry with a 9.3Al-3.3Ni-2.6Fe-0.2Mn NAB alloy according to the test procedure in **Figure 14A**, resulting in the dilatometry curve presented in **Figure 14B** for a sample heated to a peak temperature of 1000 °C (1832 °F) [30]. The authors used hollow cylindrical specimens with an outer diameter of 5 mm (0.20 in.), inner diameter of 3 mm (0.12 in.), and a length of 10 mm (0.39 in.) with a linear variable differential transducer to measure the length of the specimen. Although the use of solid pins is more common for dilatometry testing, the tubular geometry allows for higher cooling rates as it provides a larger surface area for gas quenching. Peak temperatures of 750 °C (1382 °F) and 800 °C (1472 °F) were selected to evaluate the $\alpha + \kappa_{III}$ phase formation, 870 °C (1598 °F) and 900 °C (1652 °F) were selected to evaluate the $\alpha + \kappa_{II}$ phase and 950 °C (1742 °F) and 1000 °C (1832 °F) were selected to evaluate the $\alpha + \beta$ phase formation. The reaction temperatures as a function of peak temperature and cooling rate were not reported but the observed microstructures are consistent with the observations by Brezina [11] in **Figure 12C**.



Figure 14. A) Dilatometry test procedure and **B**) example result for a 1000 °C (1832 °F) peak temperature [30].

Although this study was successful in identifying reaction temperatures, the use of a dedicated dilatometer limited the evaluated heating and cooling rates. A common apparatus for dilatometry of thermal cycles far outside of equilibrium is a Gleeble thermomechanical simulator. This machine typically uses resistive heating and either conductive cooling via watercooled grips alone or combined with gas- or water-quenching for fine temperature control at rapid heating and cooling rates. The only studies documenting successful Gleeble dilatometry characterization of NAB were shown by Gianetto et al. [47] and Hyatt et al. [45], who each used a Gleeble 2000 to study the microstructure of the simulated fusion zone and HAZ of arc welded NAB with heat inputs between 300 and 500 J/mm (7.62 and 12.7 kJ/in.). A schematic of the test specimens used is shown in **Figure 15**. The HAZ simulations used a specimen geometry with a 6 mm (0.24 in.) reduced cross-section (Figure 15A), and the simulated fusion zone was evaluated using a solid cylinder with a diameter of 9.84 mm (0.39 in.) and surrounded by a quartz sleeve. Fusion zone specimens were heated to a peak temperature to induce melting and subsequently water quenched to break the quartz sleeve and achieve cooling rates representative of weld metal. Samples that were thermally cycled to a peak temperature of 800 °C (1472 °F) exhibited a partial transformation to β upon heating and formed martensite on cooling in the interdendritic regions. No microstructural transformations were reported for samples heated to a peak temperature of 500 °C (932 °F).

The influence of cooling rate on the microstructural transformations of a 9.2Al-4.7Ni-3.4Fe-0.77Mn NAB alloy were reported by Gianetto *et al.* using radial dilatometry in the Gleeble [47]. The results of the dilatometry tests are presented in **Table 5** for various cooling rates and dwell times at a peak temperature of 1030 °C (1886 °F). The heating rate was not specified.



Figure 15. Schematic diagrams of the Gleeble specimens used by Gianetto *et al.* [47] and Hyatt *et al.* [45] for **A**) HAZ simulations and **B**) fusion zone simulations.

The samples with a faster cooling rate exhibited a fine Widmanstätten α structure with martensitic constituents, which coarsened with decreasing cooling rate. This is likely due to the longer dwell time at high temperature and an increase in the $\alpha + \beta \rightarrow \alpha + \beta + \kappa$ reaction temperature. This reaction temperature increased from 855 to 865 °C (1571 to 1589 °F) when cooling rate decreased from 300 to 9.7 °C/s (540 to 17.5 °F/s). The next reaction was labeled as $\alpha + \beta + \kappa \rightarrow \alpha + \kappa + \gamma_2$, but likely represents formation of additional $\kappa_{III/IV}$ phases as the γ_2 intermetallic would not be expected for the composition of the alloy evaluated [7], [13]. A similar trend would be expected for the first reaction, where an increase in cooling rate would likely suppress the reaction and decrease the reaction temperature. However, these reactions are associated with extremely minor volumetric changes and may be misinterpreted. Additional research is needed to provide a more complete understanding of the reaction sequences and effect of cooling rate. The martensite reaction was only identified in dilation curves of the highest cooling rate specimen despite its presence in micrographs for all of the specimens.

Thermal cycle	Heating transformation	Transformation sequence	Cooling transformation	Transformation sequence
condition	temperatures		temperatures	
	•C		"C	
Tp=1030°C Δt ₈₀₀₋₅₀₀ =1 s (Fig. 19(a))	~ 335		~ 855*	$\alpha + \beta \rightarrow \alpha + \beta + \kappa$
	~780*	$\alpha + \kappa + \gamma_2 \rightarrow \alpha + \beta + \kappa$	~720	$\alpha + \beta + \kappa \rightarrow \alpha + \kappa + \gamma_2$
			565	
	~955	$\alpha + \beta + \kappa \rightarrow \alpha + \beta$	~150	martensite
Tp=1030°C Δt ₈₀₀₋₅₀₀ =11 s	295		~ 865*	$\alpha + \beta \rightarrow \alpha + \beta + \kappa$
	755*	$\alpha + \kappa + \gamma_2 \rightarrow \alpha + \beta + \kappa$	~685	$\alpha + \beta + \kappa \rightarrow \alpha + \kappa + \gamma_2$
			~425	
	~970	$\alpha + \beta + \kappa \rightarrow \alpha + \beta$		
Tp=1030°C Δt ₈₀₀₋₅₀₀ =31 s (Fig. 19(b))	~ 170		~ 865*	$\alpha + \beta \rightarrow \alpha + \beta + \kappa$
	~405		~725	$\alpha + \beta + \kappa \rightarrow \alpha + \kappa + \gamma_2$
			615	
	~965	$\alpha + \beta + \kappa \rightarrow \alpha + \beta$	~400	
Tp=1030°C Slow Heat Hold 10 s	-		~ 860*	$\alpha + \beta \rightarrow \alpha + \beta + \kappa$
	795	$\alpha + \kappa + \gamma_2 \rightarrow \alpha + \beta + \kappa$	~620	$\alpha + \beta + \kappa \rightarrow \alpha + \kappa + \gamma_2$
∆t800-500=1 s			~535	
	025	$\alpha + \beta + r \rightarrow \alpha + \beta$	~425	

Table 5.Dilatometry Results for a 9.2Al-4.7Ni-3.4Fe-0.77Mn NABAlloy with Variations in Cooling Rate and Peak Hold Time[47]

* denotes major transformation

An increase in peak temperature hold time had a significant effect on the resultant microstructure after cooling at 300 °C/s (540 °F/s) as shown in **Figure 16** [47]. These microstructures correlate to the dilatometry results from the top and bottom of **Table 5**, where the sample held at peak temperature for 10 seconds was also "slowly heated." The authors did not report the exact difference in heating rate between the samples. The longer time at high temperature resulted in a more complete transformation of α to β , which decreased the amount of primary α constituent in the high temperature regime. On cooling, the supersaturated β phase transformed to the acicular, "basket-weave" $\alpha + \kappa_{III}$ eutectoid, which is coarser then the one second hold time sample. Although the resultant microstructure is quite different between these two samples, the measured hardness was identical at 253 HV₁₀₀.



Figure 16. Influence of hold time for Gleeble samples cycled to a peak Temperature of 1030 °C (1886 °F) with a cooling rate of 300 °C/s (540 °F/s) and a hold time of **A**) one second and **B**) 10 seconds [47].

Arc Welding

NAB alloys are readily weldable when using the appropriate procedures as described in more detail within **Appendix B**. Although these welds generate a relatively homogeneous fusion zone, the sensitivity of NAB alloys to thermal cycles induces microstructural changes in the HAZ. These transformations have been studied in detail for friction stir welds, but there is a lack of detailed information regarding the HAZ of arc welds. One such study was conducted by Fuller et al. who characterized the microstructure in the fusion zone as well as regions of HAZ of a NAB multipass gas tungsten arc weld (GTAW), as shown in Figure 17A-B [23]. In the nonreheated fusion zone (regions 1 and 2), the microstructure consisted of Widmanstätten α and β ' martensite, which were more coarse at the top of the weld, associated with a decrease in cooling rate with subsequent weld passes. The microstructure along the fusion line and HAZ is shown for three regions designated as 3-i, 3-ii and 3-iii. Unlike the even distribution of α and β ' phases observed in the fusion zone, the HAZ contained large blocks of β ' martensite, as shown in region 3-i and 3-iii. It is likely that this region reached a peak temperature in the β phase field, resulting in the complete dissolution of the κ_{III} constituent, and that the high cooling rates resulted in β ' upon cooling. Region 3-ii of the HAZ exhibited significant coarsening of the lamellar κ_{III} when compared to the base metal in region 4, with β ' martensite replacing the eutectoid α . The authors attributed this to the material reaching a peak temperature below the β solid solution phase field and above the eutectoid temperature, resulting in only partial dissolution of the α phase.

Micro tensile samples were extracted throughout the fusion zone, HAZ, and base metal, and identified a significant reduction in tensile strength, yield strength, and ductility in the HAZ. This relative reduction in mechanical properties was associated with the coarsening of the κ constituents and the formation of β ', which provided a brittle pathway for crack propagation.



Figure 17. A) Optical microscopy montage of longitudinal and transverse cross-sections of a NAB fusion weld and B) light optical micrographs representing different regions of the sample as marked in A. Sub-parts 3i-3iii refer to regions along the fusion line in the HAZ [23].

These phase transformations were also detailed in work conducted by McCaw *et al.*, who evaluated the weldability of NAB via longitudinal Varestraint testing [48]. The welds on both cast, (C95800) and NAB plate (C63200) base materials were found to be resistant to solidification and liquation cracking with no cracks observed in the fusion zone or HAZ at strain levels up to 3.85% [48]. Additional welds were made with gas tungsten arc welding (GTAW), (1651 J/mm [41.9 kJ/in.]) and gas metal arc welding (GMAW), (1016 J/mm [25.8 kJ/in.]) according to a double bevel joint with a 60° angle. Samples were extracted perpendicular to the

welding direction and subjected to three-point bend tests with a 3T bend radius. Bend tests consistently resulted in failure in the HAZ for all the samples tested, except for one sample that failed in the fusion zone. The authors did not report why one sample had failed in the fusion zone but the fracture in the HAZ was associated with the formation of β ' martensite. The microstructure of the HAZ compared to the base metal for the GTAW and GMAW scenarios are shown in Figure 18A-D. For each process significant microstructural changes occurred in the HAZ as compared to the base metal, including the coarsening of the κ phases (most notably κ_{III}) and the formation of β '. Additionally, when compared to the base metal, the fine, intragranular κ_{IV} coarsened, forming a more acicular morphology. Microstructural features were similar for the GTAW (Figure 18A) and the GMAW (Figure 18C) HAZs. However, the higher heat input used for the GTAW weldment resulted in a slower cooling rate and therefore, the GTAW HAZ remained at high temperatures for longer than the GMAW HAZ. This is evidenced by the larger overall width of the HAZ, resulting from more overall absorption of thermal energy by the baseplate. There was a corresponding coarsening of microstructures in the GTAW HAZ, a phenomenon which is associated with time spent in high temperature regimes where sufficient thermal energy is available for precipitate and grain growth [49].



Figure 18. Light optical micrographs of representative microstructures of a GTAW **A**) HAZ and **B**) base metal and a GMAW **C**) HAZ and **D**) base metal [48].

Microhardness traces from the fusion zone to the base metal of each weldment are shown in **Figure 19A-B**. For both welds, the highest hardness is observed in the HAZ, associated with the large β '/bainitic constituent. However, the peak hardness is much higher for the GTAW than the GMAW scenario. The authors did not comment on the difference but it is possible that the HAZ in **Figure 19B** was sufficiently reheated by the second pass to temper the β ' constituent and reduce the hardness [48]. Alternatively, the difference in the base metal microstructure (**Figure 18B/D**) may explain the difference in properties, where there is a finer distribution of the κ_{IV} precipitate for in the base metal and HAZ of the GTAW weldment. Additional research would be needed to confirm the exact cause of the discrepancy in hardness between the HAZ of the two weldments [21].



Figure 19. Vickers microhardness traces for the A) GTAW weld and B) GMAW cross-sections [48].

Microstructural characterization of thermally cycled specimens can provide insight to the effects of welding thermal histories by using the procedure discussed previously in **Figure 14A**, as documented by Anantapong *et al.* [30]. The microstructures of the NAB alloys following the
thermal cycling procedure are shown by the backscatter electron micrographs in Figure 20 for each peak temperature with Brinell hardness (HB) specified for each scenario. In the as-cast condition (not depicted) the microstructure consisted of α , various κ phases with some residual β ' correlating to a hardness of 207 HB. After being subjected to a peak temperature of 750 °C (1382 °F) (**Figure 20A**), the authors did not observe any β ' martensite and observed that the κ_{II} , κ_{III} , κ_{IV} had not dissolved, indicating that the measured eutectoid temperature of 750 °C (1382 °F) in Figure 14B was not reached and likely varies with heating rate. Therefore the 750 °C (1382 °F) peak temperature can be identified as the subcritical region, where no high temperature β is formed and results in a tempering of the existing martensite according to $\beta' \rightarrow \alpha + \kappa_{III}$, reducing the hardness to 191 HB. For the sample with a peak temperature of 800 °C (1472 °F) (Figure **20B**), no κ_{III} was observed and instead, β ' martensite formed at the α grain boundaries, indicating that the eutectoid temperature was surpassed. The formation of the brittle β ' constituent increased the hardness to 224 HB. This trend continued for the peak temperatures of 870 and 900 °C (1598 and 1652 °F) (Figure 20C-D), which brought about only minor differences in the microstructure, including increased amounts of the β ' martensite and complete dissolution of the κ_{III} and κ_{IV} phases with blocky untransformed α present as well. Additionally, these peak temperatures reduced the size of the κ_{II} precipitates, indicating either a partial dissolution or a reprecipitation upon cooling. As a result of the increased phase fraction of β ', increases in hardness were observed with increasing peak temperature with 281 HB for the 870 °C (1598 °F) sample and 322 HB for the 900 °C (1652 °F) sample. At peak temperatures of 950 °C (1742 °F) and 1000 °C (1832 °F) (**Figure 20E-F**), the amount of β ' martensite increased and the α phase changed from a blocky to Widmanstätten morphology with no k precipitates. The microstructure was finer for the sample heated to 1000 °C (1832 °F). This change from microstructures present in samples heated to lower peak temperatures resulted in an increase in hardness to 328 HB for the 950 °C (1742 °F) sample and 343 HB for the 1000 °C (1832 °F) sample. During welding and AM, the HAZ is subjected to variable peak temperatures, and therefore, variable microstructures and mechanical properties.



Figure 20. Backscatter electron images of the microstructure after the heating cycle in Figure 14A for a peak temperature with Brinell hardness (HB) listed: A) 750 °C (1382 °F), B) 800 °C (1472 °F), C) 870 °C (1598 °F), D) 900 °C (1652 °F), E) 950 °C(1742 °F), F) 1000 °C (1832 °F) [30].

Wire Arc Additive Manufacturing / Wire-Arc Directed Energy Deposition

Although components created from NAB alloys are traditionally produced via casting or wrought fabrication processes, recent research has focused on the use of wire-arc directed energy

deposition (DED), also known as wire arc additive manufacturing (WAAM). Wire-arc DED is an application of multipass welding and therefore the previously discussed microstructural transformations and welding metallurgy apply. One comprehensive study using a GMAW process with a synergic pulse spray transfer mode for wire-arc DED was carried out by Ding *et al.* using a 8.8A1-5Ni-5Fe wire and a cast C95800 NAB base metal [17]. Three different sets of welding parameters were used and are outlined in **Table 6** with 100% argon shielding. Three representative samples were produced with a six-axis robot on an as-cast NAB substrate, as shown in **Figure 21A**. The components were each approximately 100 mm (3.94 in.) long and 44 mm (1.73 in.) tall, with thicknesses increasing from 10 to 14 mm (0.39 to 0.55 in.) as heat input increased from 653 to 1114 J/mm (16.6 to 28.3 kJ/in.) [17].

Test Number	Wire Feed Speed (m/min [ft./min])	Travel Speed (mm/min [in./min])	Average Current (A)	Average Voltage (V)	Heat Input (J/mm, [kJ/in.])
1	5.4 [18]	400 [15.8]	175.5	24.8	653 [16.6]
2	6.7 [22]	400 [15.8]	218.3	26.7	874 [22.2]
3	8.0 [26]	400 [15.8]	256.1	29.0	1114 [28.3]

Table 6. Welding Parameters for Three Tests of WAAM-Based NAB

 Fabrication [17]

Figure 21B shows the as-deposited fusion zone with a microstructure consisting of Widmanstätten α interspersed with very fine, dark-etched retained martensite (β '). Approximately 0.2 mm (0.008 in.) of each pass was reheated by the subsequent pass, with a distance between reheated layers of approximately 2 mm (0.08 in.). The last layer was 3 mm (0.12 in.), indicating that each layer is partially re-melted by the deposition of the subsequent layer. Figure 21C shows the heat-affected zone (HAZ) microstructure in the first weld pass. The HAZ for each set of welding parameters was less than 1 mm. It appears that the material exceeded the eutectoid temperature, partially transforming to β at the peak temperature and formed β ' upon cooling surrounding α grains. These microstructures are similar to those observed for multipass welding as shown in Figure 18 and Figure 19. These microstructures are compared to the unaffected base metal in **Figure 21D**, where no β ' constituent is observed and instead the microstructure consists of α grains and various κ precipitates [17]. Samples were cut in half, and one half of each underwent post weld heat treatments (PWHT) to relieve residual stress and homogenize microstructures, which are shown in Figure 21F and G. The treatment consisted of annealing at 675 °C (1247 °F) for six hours followed by air cooling. This heat treatment made little change to the base material, as the as-cast microstructure was already stable. The martensite in the HAZ was refined and large sections of α were retained, as shown in **Figure 21F.** Near the fusion line, the α phase was partially decomposed and martensite was replaced with a fine-grained α phase with κ precipitates. The PWHT decomposed the Widmanstätten α and β ' in the WM, leaving a fine homogenized microstructure of α phase and κ precipitates Figure 21G.



Figure 21. Representative microstructure of the deposited NAB components: A) macro photography of the cross-section of the wall structure, B) representative microstructure in the fusion zone (weld metal), C) morphology of the HAZ, D) representative microstructure of the base metal, E) evolution of on-cooling transformation products in NAB alloys, F) typical microstructure of the HAZ after PWHT, and G) typical microstructure of the fusion zone after PWHT [17].

Tensile tests were performed at room temperature for each sample, with specimen geometry and orientation perpendicular to the build direction. Measurements were repeated for both as-welded and PWHT samples. Little difference was found between the samples produced with different welding parameters, as illustrated in **Figure 22**. Likewise, the PWHT had little effect on the base material. The weld metal increased in strength and decreased in ductility following PWHT, with results shown below in **Figure 23**. This was associated with the formation of additional κ constituents, resulting in increased precipitation hardening.



Figure 22. Effect of heat input on mechanical properties of as-deposited WM. Each data points represents the average of more than 10 specimens from one of the three welding heat inputs [17].



Figure 23. Effect of heat treatment on mechanical properties of as-cast BM and as-deposited WM. Each data point represents the average of samples from three difference welding parameters, corresponding to the three wall samples that were produced [17].

Overall, Ding *et al.* achieved deposition rates of upwards of 5 kg/hour (11 lb/hour) and determined that the process was relatively insensitive to process parameters [17]. This lack of sensitivity was echoed in another study by Li *et al.* [27]. Annealing the material increased strength and decreased ductility, likely caused by evolution of κ constituents. Tensile tests were only measured in the direction of deposition, rather than normal to deposited layers. Corrosion was not examined in either study.

Shen et al. evaluated the properties of wire-arc DED using 8.8Al-4.2Ni-4.4Fe-1.1Mn NAB as a function of build orientation and heat treatment conditions, with representative light optical microstructures shown in Figure 24 [2]. In the as-deposited (AD) condition (Figure 24A), the microstructure consisted of Widmanstätten α and dark-etched regions, consisting of the β ' and other constituents, in agreement with Ding *et al.* (Figure 21) [17]. After normalizing at 900 °C (1652 °F) for two hours and then quenching (Figure 24B), equiaxed α grains were observed with residual β ' along the grain boundaries. Figure 24C-F shows samples that were normalized at 900 °C (1652 °F) for two hours, quenched and then tempered for six hours at 450 °C (842 °F), 550 °C (1022 °F), 650 °C (1202 °F), and 750 °C (1382 °F). No β' was observed after tempering at 550 °C (1022 °F) or above, which is consistent with observations made previously by Hyatt et al. [2], [10]. SEM characterization was used to identify the microstructural constituents in the as-deposited, quenched, as well as quenched and tempered conditions, with representative micrographs for each shown in Figure 25A-F. For all test conditions κ_{II} , κ_{III} , and κ_{IV} were observed, with constituent size increasing with tempering temperature. The most notable change is identified for the κ_{III} and κ_{IV} precipitate after tempering at 650 °C (1202 °F) and 750 °C (1382 °F), in which case a significant increase in particle size was observed and the morphology transitions from acicular to spherical. However, the authors did not perform energy dispersive spectroscopy (EDS) characterization and may have misclassified this precipitate as the NiAl $\kappa_{III/V}$ identified by other researchers [50].



Figure 24. Optical microstructures of additively manufactured NAB alloy before and after heat treatments: A) as-deposited, B) quenched, C) QT450, D) QT550, E) QT650, and F) QT750, where QT stands for "quench and tempered", with the number designating the tempering temperature [2].



Figure 25. SEM micrographs of the additively manufactured NAB samples in the following conditions: A) as-deposited, B) quenched, C) QT450, D) QT550, E) QT650, and F) QT750 [2].

The implications of the microstructural transformations were revealed by the tensile results, shown in **Figure 26A-C** as a function of build condition and orientation. The authors noted no significant difference in elongation with build orientation and therefore plotted the average elongation of all orientations. The highest tensile and yield strengths correlated with the

lowest ductility, with similar values observed for the as-deposited and OT650 sample. The strengthening mechanisms for these samples were not described by the author, but as shown in Figure 24 and Figure 25, there are significant differences in the microstructure. In the asdeposited condition, the high strength is likely associated with residual stress from the fabrication process (work hardening) and the presence of the brittle β ' constituent. For the QT650 sample, the strengthening can likely be attributed to κ precipitate strengthening, as residual stresses would be minimized by the tempering step. A reduction in strength was observed for the QT750 sample, likely associated with the coarsening of the κ_{IV} and κ_{III} precipitates. Although no anisotropy was indicated by elongation results, significant differences in the yield and ultimate tensile strengths were observed with orientation. The authors claimed that heat treatment improved the anisotropy by reducing the columnar grain texture produced by additive manufacturing, but the mechanical performance shown Figure 26A and B does not show a significant improvement. In a following study, Shen *et al.* reported similar tensile and yield strengths for wire-arc DED samples heat treated at 675 °C (1247 °F) for six hours with and without a normalization treatment [51]. Although slightly lower elongation was observed for the non-normalized sample, these results indicate that the expensive and time consuming normalization process is not necessary for industrial applications [2].



Figure 26. Mechanical properties as a function of build orientation and sample condition for A) tensile strength, B) yield strength, and C) elongation (%) [2].

Queguineur et al. conducted an evaluation of wire-arc DED specifically for large marine components [52]. They constructed copper-aluminum test specimens using FRONIUS Cold Metal Transfer (CMT®) and pulsed mode gas metal arc welding (GMAW-P) using a three-axis machine and achieved a maximum deposition rate of 3.3 kg/hour (7.3 lb./hour). The filler wire was described as 1.2 mm (0.047 in.) Cu-Al9Ni6, but no full composition or trade name was provided [52]. It was noted that the lower heat input associated with the CMT® allowed for a more consistent bead geometry, with a more regular bead shape than that produced by GMAW-P. CMT® deposits had a microhardness of 140 HV, compared to the lower microhardness of 125 HV measured in samples deposited using GMAW-P. This difference in microhardness was attributed to the heat input, which is typically lower for CMT® than for GMAW-P. As the heat input is expected to be inversely proportional to the cooling rate, the low heat input associated with CMT® likely induced rapid cooling of the weld metal. The higher temperatures associated with GMAW-P may have also provided an opportunity for tempering of previously deposited material by subsequent passes or coarsening of the κ phases. The authors noted no significant difference in microstructures between the two welding modes, with observed microstructures comprising of a majority columnar a phase microstructure for each condition, as illustrated in the macrographs in Figure 27 [52]. These microhardness values are significantly different than the results previously discussed as the deposited alloy was Cu-8Al-2Ni-2Fe, where significantly less κ constituent was observed and no β ' formed.



Figure 27. Pulsed mode (left) and CMT mode (right) on Cu-Al8Ni2Fe2 builds using wire-arc DED techniques [52].

A CMT® test block was produced with dimensions of 35 mm (1.38 in.) wide, 230 mm (9.06 in.) long, and 100 - 140 mm (3.94 - 5.51 in.) tall. Each weld bead was approximately 7 mm (0.28 in.) wide, with an interval of 4 mm (0.16 in.), showing an overage overlap of 55%. Tensile specimens that were longitudinal and transverse to the travel direction were excised from this deposit, with tensile tests performed in accordance with NF EN ISO 6892-1 [53]. Transverse tensile tests referred to those taken in the Z-direction (*i.e.*, along the height of the part). Tensile test results for each orientation are shown below in **Figure 28**, compared to a supplementary sample composed of a higher weight percent nickel alloy, which was included in an attempt to reproduce the tests carried out by Ding *et al.* discussed previously [17], [52]. Unfortunately, little information is given on this second alloy, but it does confirm the findings by Ding *et al.* [17]. The high strength was attributed to the microstructure, consisting of Widmanstätten α phase along with fine martensitic β ' and various κ constituents. Longitudinal and transverse elongation was found to be 44% and 56%, respectively. This is much better elongation than that achieved by traditional cast NAB, and exceeds the minimum standard requirement of 15% ductility [54].



Figure 28. Comparison of YS and UTS for specimens taken on Cu-Al8Ni2Fe2 multipass sample with specimens taken on a Cu-Al9Ni5 sample [52].

Ongoing investigations into wire-arc DED of NAB by Dharmendra *et al.* [22], [29], [50], [55], [56] have shown similar results to those of Queguineur [52], Ding [17], Shen [2], [51], and Li [27]. The authors have carried out extensive testing to evaluate the feasibility of wire-arc DED for a Cu-9Al-4Fe-4Ni-1Mn alloy within specifications for UNS C95800 using a 5-axis GMAW system called GTarc 60-5 WAAM, produced by GEFERTEC [50]. A relatively low heat input was used, reported as 170 J/mm (4.32 kJ/in.). The fabricated specimens had a square cross-sectional area with a side of 25 mm (0.98 in.) and a height of 160 mm (6.3 in.) and were deposited directly onto a 316L stainless steel plate. A following study characterizing microstructure of the dissimilar metal weld between the deposited NAB and the 316L build plate revealed liquation cracking [55].

Specimens for microstructural characterization were extracted from deposited material 80 mm (3.2 in.) away from the base plate. Optical and scanning electron microscopy revealed fine α

dendrites interspersed with a dark-etched phase containing fine, globular κ_{II} precipitates. Highangle annular dark-field scanning transmission electron microscopy (STEM-HAADF) imaging revealed fine lamellar κ_{III} phases in the same dark-etched region, shown in **Figure 29** [50]. No β ' was observed in the HAZ of the reheated weld passes or in the fusion zone, where instead regions of the fine $\alpha + \kappa_{III}$ eutectoid were observed. As many of the previous studies conducted microstructural characterization by light optical or SEM methods, it is possible that the fine $\alpha + \kappa_{III}$ constituents were misclassified as β '. A following study used atom probe tomography (APT) for additional characterization and revealed that the α dendrites in the as-deposited condition were populated with nano-scale (5-10 nm) κ_{IV} precipitates [28].





Figure 29. STEM-HAADF images of wire-arc DED: **A**) and **B**) show the general microstructure with interdendritic regions and primary α -dendrites, **B**) and **C**) show interdendritic α -lamellae with lamellar and globular intermetallic phases [50].

The wire-arc DED builds were subjected to heat treatments of 350 °C (662 °F) for two hours, 550 °C (1022 °F) for four hours, and the more conventional heat treatment of 675 °C (1247 °F) for six hours. The 350 °C (662 °F) heat treatment was conducted as a stress relief treatment, resulting in no change in dendritic structure, grain size, or κ_{II} or κ_{III} precipitates, but did coarsen the κ_{IV} precipitates to 20 nm. The 550 °C (1022 °F) heat treatment was selected as an intermediate time and temperature between the 350 °C (662 °F) and 675 °C (1247 °F) treatments. Coarsening of the κ_{II} precipitates and partial spherodization of the κ_{III} was observed with the precipitation of NiAl phases within the α dendrite, designated as κ_{V} . Following the 675 °C (1247 °F) treatment, significant coarsening of the κ_{II} precipitates were observed. No change in κ_{IV} precipitate size or morphology was observed for heat treatments at temperatures greater than 350 °C (662 °F).

The tensile properties of the wire-arc DED NAB alloys were reported in an associated study by Dharmendra *et al.* and are summarized for the conditions evaluated in **Table 7** [29]. Tensile samples were extracted parallel to the build direction with the dimensions according to the sub-size flat specimen geometry according to ASTM E-8 [57]. No significant change in tensile properties were observed following the stress relief treatment at 350 °C (662 °F), indicating that the coarsening of the κ_{IV} precipitates did not affect mechanical properties. The authors suggested that such a treatment may improve the resistance to stress corrosion cracking, which has been confirmed by previous work [41]. The 550 °C (1022 °F) heat treatment results in a significant increase in tensile and yield strength at the expense of ductility, associated with the precipitation of the κ_V precipitates. The author noted that the six hour treatment at 675 °C (1247 °F) provided the best balance of strength and ductility due to the coarsening of the various κ precipitates. While the 675 °C (1247 °F) treatment is more commonly used to temper β ' martensite, this phase was not reported to form in the wire-arc DED deposit studied by Dharmendra *et al.* and may be unnecessary [29].

Condition	0.2% Offset Yield Strength (MPa [ksi])	Ultimate Tensile Strength (MPa [ksi])	Elongation (%)	
As-built	$380 \pm 9 \; [55 \pm 1]$	$708 \pm 8 \; [103 \pm 1]$	35 ± 1	
350 °C (662 °F) for two hours	$380 \pm 12 \ [55 \pm 2]$	710 ± 7 [103 ± 1]	32 ± 2	
550 °C (1022 °F) for four hours	471 ± 8 [68 ± 1]	$767 \pm 10 \ [111 \pm 1]$	14 ± 1	
675 °C (1247 °F) for six hours	$413 \pm 14 \ [60 \pm 2]$	$745 \pm 8 \ [108 \pm 1]$	28 ± 1	

Table 7.Tensile Properties of Wire-Arc DED NAB As-Deposited and
After Heat Treatment for Sub-Size Flat Specimens in
Accordance with ASTM E8 [59] with Data Adapted from [29]

Rapid Cooling

As documented in **Figure 12** and discussed previously, there is a significant lack of understanding regarding microstructural changes accompanying rapid cooling rates (> 1000 °C/s [1800 °F/s]) associated with laser processing techniques. A previous literature review conducted

by Hyatt [10] provides an excellent overview of the NAB laser processing research prior to 1997 and therefore, the following section provides a supplement to that review that encompasses only more recent literature.

Laser Wire/Powder Directed Energy Deposition

Xue *et al.* evaluated the influence of processing conditions on NAB using laser-wire DED [58]. Their study used a 3 kW CO₂ laser with a 190 mm (7.5 in.) focal length in order to evaluate the influence of laser power, wire feed speed, and gas flow rate on the as-deposited bead morphology. Their results showed that changes in gas flow rate do not affect the morphology of the deposited bead (not shown), while changes in power and wire feed speed have a significant influence, as observed in **Figure 30**. At a constant power and travel speed, an increase in the wire feed speed had minimal effect on the width of the deposited bead but resulted in a consistent increase in bead height with a decrease in the extent of penetration (**Figure 30B**). Increases in laser power increased the penetration and the width of the bead while also reducing the height (**Figure 30C**). Although these are for single pass bead on plate laser welds, the processing conditions may assist in adjusting the weld bead shape in future laser-based applications involving NAB [58].



Figure 30. Results adapted from [58] with A) schematic weld bead, B) bead morphology as a function of wire feed speed (rate) and C) bead morphology as a function of laser power.

X-ray diffraction was used to evaluate the micro-strains associated with as-deposited laser cladding for heat inputs of 150 and 350 J/mm (3.81 and 8.89 kJ/in.). Measured microstrains were then converted to the residual stress estimates shown in **Figure 31**. Although the magnitude of heat input was doubled for the high heat input condition, the estimated residual stresses were not significantly different due to the standard deviation of the measurement. However, these results provide a frame of reference for future residual stress studies.



Figure 31. Residual stress measurements of laser clad NAB with variable heat input [58].

Several previous studies have documented the use of low heat input laser welding and cladding for NAB alloys, which has been shown to be beneficial to the corrosion resistance [10], [45], [59]. Hyatt *et al.* documented that the microstructure NAB alloys exhibit a sensitivity low heat input welding through the evaluation of wire-fed laser welds made with a 5 kW CO₂ laser and heat inputs between 42.5 and 595 J/mm (1.08 and 15.11 kJ/in.) [21]. Microstructures for each case are shown in **Figure 32** [21]. At the lowest heat input of 42.5 J/mm (1.08 kJ/in.), no significant amount of α phase was observed, and the microstructure instead consisted of a 9-R martensite and κ_{IV} precipitates (**Figure 32A**). With increasing heat input (> 47.5 J/mm [1.21 kJ/in.]), bands of allotriomorphic α phase were observed along the prior β boundaries coupled with the formation of secondary Widmanstätten α (**Figure 32B**). The allotriomorphic α along the prior β boundaries is more continuous with increasing heat input, and fully outlines the boundaries at a heat input of 150 J/mm (3.8 kJ/in.) (**Figure 32C-D**). At high heat inputs (> 390 J/mm [9.9 kJ/in.]), there is an increase in the amount of α constituents, bearing a close resemblance to the microstructure observed in arc welds.



Figure 32. Optical micrographs of laser clad specimens with heat inputs of A) 42.5 J/mm (1.08 kJ/in.), B) 47.5 J/mm (1.21 kJ/in.), C) 64.3 J/mm (1.63 kJ/in.), D) 150 J/mm (3.81 kJ/in.), E) 390 J/mm (9.91 kJ/in.), and F) 595 J/mm (15.1 kJ/in.) [21].

The variation in microstructure lead to a variation in the mechanical properties, as evidenced by the range of peak microhardness in **Figure 33**. The primarily martensitic structure formed by heat inputs < 390 J/mm (9.91 kJ/in.) led to a high peak hardness in excess of 400 HV. The authors did not provide an explanation for the high peak hardness for the 64.3 J/mm (1.63 kJ/in.) weld, which exceeded 500 HV, but as the microstructure was similar to that of other low

heat input welds, it is likely that this datapoint was an outlier or within error. There was a reduction in hardness in welds produced with a high heat input > 390 J/mm (9.91 kJ/in.), dropping from over 400 HV to approximately 320 HV. This hardness decrease was associated with the reduction in martensitic constituents and corresponding increased phase fraction of Widmanstätten α .



clad NAB [21].

Although there is variation in the fusion zone microstructure with heat input, Gianetto *et al.* identified that there is a difference in microstructure within the laser weld bead associated with differences in cooling rate [60]. The microstructure along the fusion line of a 150 J/mm (3.81 kJ/in.) weld primarily consisted of martensitic constituents and transitioned to a mixed martensitic/Widmanstätten α at the top of the fusion zone, where the cooling rate was lower [60]. Electron microprobe characterization determined that there were no significant local variations in composition within the weld bead and therefore the change in microstructure was driven by differences in cooling rate [60]. Nonuniform microstructures are associated with nonuniform mechanical properties, as evidenced by a microhardness of 354 VH₁₀₀ within the martensitic region and a microhardness of 297 HV₁₀₀ in the martensitic/Widmanstätten α region [60]. However, the reheated fusion zone from a subsequent weld pass resulted in a tempering of the martensitic constituents, resulting in slightly lower microhardness values of 242 HV₁₀₀.

Hyatt *et al.* observed that the identity of microstructural constituents present in the reheated fusion zone of the laser clad NAB samples did not vary with weld heat input, but that reheated regions were characterized by a difference in scale of the constituents [44]. This resulted in a consistent reduction in microhardness to 200 - 260 HV compared to values in the

fusion zone **Figure 33**, with softening associated with a tempering of the martensitic constituents. This constituent coarsening phenomenon was also observed to correspond to peak temperature dwell time, as shown in **Figure 34A-B**, where an increase in dwell time from one to 10 seconds at a peak temperature of 1000 °C (1832 °F) resulted in a substantial coarsening of α constituents [61]. The authors noted that the reheated fusion zone microstructure consisted of allotriomorphic α along prior β boundaries, in addition to intragranular Widmanstätten α and minor quantities of β ' martensite.



Figure 34. Optical micrographs of laser clad weld metal reheated to 1000 °C (1832 °F) with a cooling rate of 600 °C/s (1080 °F/s) and a peak dwell time of **A**) one second, **B**) 10 seconds [61].

Hyatt *et al.* also evaluated the cavitation erosion behavior of the fusion zones for high heat input (390 J/mm [9.91 kJ/in.]) and low heat input (68 J/mm [1.73 kJ/in.]) multipass laser welds, as shown in **Figure 35** [21]. There was a significant improvement in the cavitation resistance with decreasing heat input, and although the ductility decreased with heat input, the authors noted that the improvement cavitation resistance could be associated with an increase in the corrosion fatigue limit. The corrosion tests were conducted in the as-deposited condition without any stress relief or PWHT, and localized corrosion was consistently observed in the reheated HAZ of the weldment. This may be associated with the accumulation of residual stress within the HAZ or the coarsened microstructure. Despite promising initial results, further research is needed to understand both optimization of corrosion resistance and the effect of heat treatments on laser weldments.



Figure 35. Cavitation erosion behavior comparison between the base metal, high heat input weld (390 J/mm [9.91 kJ/in.]) and low heat input weld (68 J/mm [1.73 kJ/in.]) [21].

Li *et al.* utilized laser-powder directed energy deposition with a Cu-9Al-5Fe-5Ni powder and 5-axis Trulaser Cell 3000, where an overview of the process is shown in **Figure 36** [62]. Specimens with geometries of 20 x 20 x 20 mm (0.79 x 0.79 x 0.79 in.) and 106 x 16 x 30 mm (4.17 x 0.63 x 1.18 in.) were deposited for microstructural characterization and tensile specimens, respectively. Tensile tests were conducted using an extracted coupon with dimensions of 100 x 2 x 3 mm (3.94 x 0.08 x 0.12 in.) using a universal testing machine with a 50 kN load cell under a constant strain of 0.01/min.



Figure 36. A) Schematic illustration of the laser-powder DED process, referred to here as laser metal deposition (LMD) and B) asdeposited Cu-9Al-5Fe-5Ni specimen with optimized parameters [62].

Laser processing parameters were assessed with variations in laser power from 500 - 2500 W and scanning speed from 0.25 - 2 m/min (0.8 - 6.6 ft./min) with results shown in **Figure 37**. The width and deposition rate of the single track beads generally increased with laser power

and decreased with scan speed (**Figure 37A-B**). At high laser powers and low scan speeds, the authors noted that the excessive laser power led to "severe sputtering and poor deposition" [62]. Optimal processing parameters were determined to be between 1250 - 1750 W laser power with scanning speeds between 0.25 - 2 m/min (0.8 – 6.6 ft./min). The highest density of 99.55%, as determined by light optical cross-sections, was achieved with a laser power of 1500 W, a scan speed of 1 m/min (3.3 ft./min), and a hatch spacing of 2 mm (0.08 in.). The most common discontinuities observed in deposits made with the laser-powder DED process at the highest laser power conditions were porosity (associated with gas entrapment in the gas atomized powder) and hot cracking in the fusion zone (**Figure 37E**). The hot cracking was associated with the high residual stress imposed from the high laser power and therefore high heat input conditions. The primary discontinuity observed at the low laser power conditions was unmelted powder, resulting on poor deposition (**Figure 37D**) [62].



Figure 37. Process optimization of a single pass of laser powder-blown DED Cu-9Al-5Fe-5Ni alloy as a function of A) width, B) building rate of printed single tracks with variations in laser power and scanning speeds, C) laser processing window of the NAB alloy with D-G) morphology of single tracks color coded to the processing window [62].

The authors noted unique microstructures in the as deposited sample in the center of the melt pool and at the melt pool boundaries, where there was reheating of the previous weld pass.

The differences in observed microstructure from these regions are shown in the SEM images in **Figure 38**. At the center of the melt pool, allotriomorphic α was observed along the prior β boundaries, with secondary Widmanstätten α needles forming in the intragranular β ' martensite (**Figure 38A-B**). This microstructure was similar to those discussed previously and observed by Hyatt *et al.* in the fusion zone of multipass laser claddings in **Figure 32D** [21]. However, in the melt pool boundary regions, there was significant coarsening of the Widmanstätten α phase (**Figure 38C-D**). The basketweave morphology was similar to what was observed by Anantapong *et al.* in **Figure 20E** [30], suggesting that this region was subjected to a peak temperature of 950 °C (1742 °F) or greater.



Figure 38. SEM images showing the microstructure of the as-deposited laser-powder DED NAB specimens A/B) melt pool center and C/D) melt pool boundary [62].

High resolution TEM and EDS mapping characterized the martensitic constituents observed in the melt pool center and boundary as shown in **Figure 39**. The martensitic plate morphology observed in the melt pool center were found to exhibit a twin orientation relationship, alternating from the dark and bright plates shown in **Figure 39A-C**. EDS characterization shows that these boundaries are separated by regions enriched in Al (**Figure 39F-G**) and that there are iron- and nickel-rich precipitates within the martensitic plates (**Figure 39F-G**). These were characterized as the Fe₃Al κ_{IV} and the NiAl κ_{III} phase respectively, indicating that even under the rapid heating and cooling conditions of laser powder blown DED, these nanoscale precipitates are still observed. The microstructure is different at the boundary of the melt pool (**Figure 39H-O**), where the α phase is more apparent and the β ' martensitic phase no longer exhibits the twin related morphology. The α and β ' phases were both characterized as face centered cubic (FCC) with minor differences in lattice spacing (**Figure 39J-K**). Additionally there is growth of the κ_{IV} and κ_{III} phases and a more homogeneous distribution of

Al as evidenced by the EDS maps (**Figure 39L-O**). These results suggest that the martensitic β ' is not tempered by subsequent weld passes for the laser weld processing conditions used in their study.



Figure 39. TEM images showing the phases and elemental distributions within the laser-powder DED specimens with: A) high-angle annular dark field (HAADF) image, at the melt pool center; B) HAADF image of the inset of A, comparing the selective area diffraction (SAD) patterns of a, b, c, and d; C) bright field image of the interface between c and d; D-G) EDS maps of the elemental distribution in A; H) HAADF image at the melt pool boundary; I) HAADF image and SAD patterns for the phases; J) High resolution TEM image of the α phase; K) High resolution TEM image of the β* phase; L-O) EDS maps of the region in H [62].

The measured yield strengths and elongations of the as-deposited laser-powder DED (labeled LMD) specimens are compared to values previously reported for the wire-arc DED (labeled WAAM), laser powder bed fusion (L-PBF) (labeled SLM), and cast material with some specimens in the heat treated (HT) condition as shown in **Figure 40**. The residual β ' martensite and the fine κ phases led to a significant increase in the yield strength at the expense of ductility when compared to the wire-arc DED results. However, none of these specimens meet the minimum ductility requirement of 15% specified by NAVSEA for sand cast NAB propellers, a common benchmark discussed further in **Appendix A** [54]. The authors did not assess the influence of heat treatment on the tensile properties of the laser-powder DED, which provides the motivation for future research, where a heat treatment would likely restore the ductility of the material at the expense of the strength.



Figure 40. Comparison of the mechanical properties reported by Li [62], Murray [42], Ding [17] and Dharmendra [50] for various additive manufacturing processes.

Laser Powder Bed Fusion

While most of the recent work has focused on the application of DED processes to NAB fabrication, Murray *et al.* used L-PBF with Cu-9.8A1-5.2Ni-4.6Fe-0.3Mn powder and a Concept Laser Mlab Cusing R [42]. Due to the slow deposition rates of L-PBF in comparison with DED, comparatively small deposits with length and width of 10 mm (0.39 in.) and 20 mm (0.79 in.) with a height of 3 mm (0.12 in.) were deposited on a 316L baseplate for the purpose of parameter optimization. The optimized parameter set used a laser power of 90 W, a scan speed of 200 mm/s

(7.87 in./s), a hatch spacing of 70 µm, and a 25 µm layer thickness. These parameters produced a deposit with a density of 99.9% according to light optical observations of sample cross-sections. Tensile specimens with a dog bone geometry were built parallel to the build direction with a cross-section of 5 mm (0.2 in.) and a gauge length of 16 mm (0.63 in.). Representative micrographs showing the microstructure of cast, wrought, and as-built L-PBF specimens are shown in Figure 41. The cast and wrought microstructures are similar to those previously discussed. In contrast to DED builds, the as-built L-PBF samples exhibited a fine martensitic microstructure, as can be identified by the electron backscatter diffraction inverse pole figure map in Figure 41D. This is likely due to the higher cooling rates and more localized melting and reheating associated with L-PBF that prevent tempering of the martensite during the build process. In contrast with DED applications, where cooling rates are on the order of 1×10^3 °C/s $(2 \times 10^3 \text{ °F/s})$, the cooling rate for L-PBF is an order of magnitude higher and has been reported to be in excess of $5 \times 10^5 \text{ °C/s}$ (9 x 10^5 °F/s) [63], [64]. Untempered martensite is an undesirable microstructure in virtually all applications due to its low ductility, reported to be less than 1% elongation in as-built L-PBF samples. X-ray diffraction characterization was conducted on the as-built specimens, where the authors observed a martensitic structure that was not consistent with the previously described β ' martensite. The exact crystal structure was not identified but was closely related to the 18R orthorhombic β_1 ' reported by Nishiyama *et al.* [65] and the P2mm γ_1 ' reported by Duggin *et al.* with a twin relationship between the martensitic laths [46].



Figure 41. SEM characterization of NAB material in the A) Cast, B) Wrought, and C) L-PBF (SLM) as-built condition with D) EBSD inverse pole figure map of the as-built martensitic microstructure [42].

In an attempt to restore ductility, samples were subjected to one hour heat treatments at temperatures of 600 °C (1112 °F), 700 °C (1292 °F), 800 °C (1472 °F) and 900 °C (1652 °F), with representative microstructures shown in Figure 42. The 600 °C (1112 °F) heat treatment successfully tempered the martensitic constituent, resulting in the formation of a very fine α along with a precipitate identified as $\kappa_{\rm V}$. This precipitate is equivalent to the NiAl $\kappa_{\rm III}$ precipitate, but forms intragranularly with a characteristic acicular morphology. The heat treatment with a peak temperature of 700 °C (1292 °F) resulted in similar but coarsened α and κ_V constituents, with discontinuous κ_V precipitates present along prior β grain boundaries. After the 800 °C (1472 °F) heat treatment, further coarsening was observed in addition to the introduction of minor quantities as-quenched martensite, and the acicular morphology of κ_V degenerated into a globular morphology. This shift is consistent with the observations from Shen et al. who noted the morphological transition after a heat treatment at 750 °C (1382 °F) [2]. After heat treating at 900 °C (1652 °F) for one hour, a significant portion of the microstructure transformed back into martensite, decorated with κ_{IV} precipitates and large α grains. As Dharmendra *et al.* observed the κ_{IV} precipitates for lower temperature heat treatments [28], it is likely that the κ_{IV} precipitates are present for all of the heat treatment conditions evaluated by Murray et al. but are too fine to resolve using SEM [42].

Further characterization was done using X-ray diffraction (XRD), with results presented for as-built and heat treated conditions in **Figure 43**. The difficulty in characterizing NAB alloys via diffraction techniques was noted by Murray *et al.* [42] and described in detail by Y. Lv *et al.* [41]. Due to the similar lattice parameters of the α and residual β ' phases, there is significant peak overlap. Due to the difficulty in performing deconvolution on the peaks, the α and β ' constituents are grouped together into a parent α^* phase. The κ phases are similarly difficult to distinguish between, as the Fe₃Al DO₃ κ_{II} and κ_{IV} phases have differences in lattice parameter that fall within the error of the measurement of 5.71 ± 0.06 Å and 5.77 ± 0.06 Å respectively. Although the κ_{III} phase is NiAl with a B2 structure, the lattice parameter is 2.88 ± 0.03 Å, which is half of the Fe₃Al lattice parameter. Therefore, similar to the α and β ' phases, the κ phases cannot be distinguished from one another and are grouped into a single peak according to the (Fe,Ni)Al (110) phase [41].

The microstructural transformations resulted in changes in the tensile properties as shown in **Figure 44**, which includes baseline comparisons to conventional cast and wrought NAB. The ductility of the L-PBF alloys was improved by the heat treatments with peak temperatures of 700 and 800 °C (1292 and 1472 °F), but still fell below the minimum values recorded for castings. Samples subjected to heat treatments of 600 and 900 °C (1112 and 1652 °F) achieved high strength but insufficient ductility, due to the formation of the fine κ_V (likely a misidentified κ_{III}) or the untempered martensitic constituent. The authors did not comment on the reason that one hour heat treatments were used instead of the conventional six hour treatment at 675 °C (1247 °F), but it is possible that more extensive heat treatments could lead to further improvements in ductility. When compared to the wire-arc DED builds, the L-PBF build envelopes are significantly smaller, and exhibit higher tensile and yield strengths but at the expense of ductility.



Figure 42. SEM micrographs identifying microstructures at low and high magnifications for L-PBF samples heat treated for one hour at 600, 700, 800, and 900 °C (1112, 1292, 1472, and 1652 °F) [42].



Figure 43. XRD patterns reported by Murray *et al.* with a cobalt source $(K_{\alpha 1} = 1.7889\text{\AA})$ for the as-built and heat treated conditions with patterns of potential martensitic phases [42].



Figure 44. Tensile properties measured longitudinal to the build direction for heat-treated L-PBF NAB compared to conventional cast and wrought properties [42].

CONCLUSIONS

Although NAB alloys have been well characterized for casting applications, a review of the recent literature indicates that there are significant gaps in knowledge for welding and AM applications. This is in part due to the difficulty associated with microstructural characterization. Material-dependent limitations exist for dilatometry and diffraction techniques, and high resolution TEM is necessary to resolve the fine κ phases and martensitic constituents present in rapidly cooled NAB. Although the microstructural development of NAB alloys is well documented under equilibrium conditions, previous studies have identified unique microstructures associated with the high cooling rates induced by laser-based processing. At the time of reporting, CCT diagrams have not been developed to describe the microstructural evolution during rapid cooling.

NAB alloys are also sensitive to heat treatments, where stress relief coincides with the coarsening of κ phases. Although these heat treatments would benefit from further refinement for laser-based additive manufacturing applications, the conventional heat treatment of 675 °C (1247 °F) for six hours has produced good mechanical properties for NAB material deposited via wire-arc DED. Multiple studies have documented improved strength and ductility for wire-arc DED depositions when compared to the conventional cast or wrought material, where processing conditions resulted in a uniform Widmanstätten α microstructure. Laser wire/powder DED and L-PBF methods have been successfully applied to NAB, where both studies used ASTM C95800

powder provided by Sandvik Osprey Ltd. These conditions resulted in a microstructure consisting of martensitic β ' and/or Widmanstätten α , leading to an improvement in strength at the expense of ductility. Additionally, the laser-based processing techniques have been shown to improve the corrosion resistance of NAB when compared to conventional cast and wrought material. Based on these observations, high-density parts with superior mechanical properties can be readily produced using arc- and laser-based AM techniques. Additional research is needed to understand the influence of thermal history, cooling rates, and heat treatments on the microstructure and properties of welded and additively manufactured NAB alloys.

RECOMMENDATIONS

Insufficient information is available to predict microstructural transformations of NAB alloys when exposed to the high heating and cooling rates associated with arc and laser processing techniques. To date, no CCT diagram has been developed to describe the microstructures of NAB under these conditions. This is in part due to the difficulty associated with measuring the extremely subtle volumetric changes; however, modern measurement devices such as a laser dilatometer coupled with the Gleeble thermo-mechanical simulator or other modern dilatometry systems may be able to identify these reactions. Additionally, the relationship between mechanical properties and the microstructural evolution as a function of temperature and thermal history has not been reported but is needed for accurate computational modeling.

NAB alloys are sensitive to thermal history. Reheating of fusion zone microstructures by subsequent weld passes can cause coarsening of both α and κ phases, dissolution of κ phases, and tempering of martensitic constituents. This reheating can result in a significant range of microstructures and corresponding properties, and controlled Gleeble studies should be conducted to simulate and document the microstructural behavior associated with both arc- and laser-based processes.

There is little published information that characterizes residual stress in NAB alloys, with only a small subset addressing residual stresses induced by fusion welding. Previous studies have indicated that high residual stress can adversely affect the corrosion resistance, showing a higher susceptibility to stress corrosion cracking in association with the high dislocation density at the interface of the κ precipitates. This phenomenon establishes a case for experimental characterization of welding-induced residual stresses along with development of robust ICME tools capable of modeling and predicting residual stress evolution in weldments and additively manufactured NAB components.

Finally, existing heat treatments used for stress relief are optimized for cast and wrought NAB, and do not necessarily apply to additive manufacturing applications. Limited data is available regarding the stress relief treatment of additively manufactured NAB, where localized heating could introduce non-uniform stress fields during deposition. Additional research is needed to compare the microstructure, mechanical properties, and residual stress as a function of heat treatment time and temperature for additive manufacturing applications.

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APPENDIX A: NAB PERFORMANCE REQUIREMENTS

Current NAB applications typically adhere to cast mechanical property requirements specified by ASTM standards. Notably, these include ASTM B824 ("General Requirements for Copper Alloy Castings") [25], ASTM B148 ("Aluminum-Bronze Sand Castings") [66], ASTM B150 ("Aluminum Bronze Rod, Bar, and Shapes") [34], and ASTM B505 ("Copper-Base Alloy Continuous Castings") [24]. Tabulated requirements from ASTM B505 are reproduced below in **Table 8** [24]. ASTM standards were preceded by QQ-C-390 ("Copper Alloy Castings [Including Cast Bar]") [67], in use until 1993, which superseded MIL-B-16033 (BuOrd) ("Bronze, Aluminum: Castings") in 1968 [68]. The high criticality of NAB propellers has led to publication of a component-specific Naval Sea Systems Command (NAVSEA) document that encompasses specific requirements, entitled "Navy Propulsor Sand Cast Nickel-Aluminum-Bronze Specification" [54].

Copper Alloy UNS No.	Tensile Strength, min.		Yield Strength, at 0.5% Extension Under Load, min		Elongation in 4D or 2 in. or 50 mm, min,	Brinell Hardness,
	ksi	MPa	ksi	MPa	%	min
C95500	95	655	42	290	10	
C95500HT ^A	110	758	62	427	8	
C95520HT ^B	125	862	95	655	2	262 [3000 kg]
C95800 ^C	85	586	35	241	18	

 Table 8. Mechanical Performance Specifications for Various Cast NAB

 Alloys [24]

^A Heat treated

^{*B*} Copper Alloy UNS No. C95520 used only in the quench-hardened and tempered (TQ30) condition.

^CAs cast or temper annealed.

This NAVSEA component specification closely mirrors the ASTM standards. The chemistry requirements for C95800 is identical in each. For mechanical testing, NAVSEA identifies one particular option of those given by ASTM B824: separately cast mechanical test bars must be made using a silica sand mold, with a minimum sand thickness of 25.4 mm (1 in.) around the mold cavity [25]. For reference, drawings for one such test specimen is shown below in **Figure 45** and **Figure 46**. Multiple specimens may be cast in a single mold provided the 25.4 mm (1 in.) minimum sand thickness is met. The allowable tolerance on all dimensions is ± 3.2 mm ($\frac{1}{8}$ in.). This approach of testing witness coupons is used to allow evaluation of material performance while preserving the geometry of cast components produced with the same lot of material.


Figure 45. Test bar pattern side view (single pattern) [54].



Figure 46. Test bar pattern end view (single pattern) [54].

Test specimens created from the test bars detailed above are required to conform to the small-size test specimen requirements given in ASTM E8/E8M ("Tension Testing of Metallic Materials") with gauge length four times the diameter (6.4 mm [0.25 in.] nominal diameter) [57]. Acceptance criteria for tensile strength, yield strength, and elongation are shown below in **Table 9**. These properties must be achieved by a sample specimen produced with each lot of cast

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material as a form of quality assurance, as destructive testing of each actual component is not possible.

Table 9.	Mechanical Requirements for C95800 Witness Coupons for
	Cast propellers, as Specified by NAVSEA [54]

	Tensile Strength (N/mm ²) [ksi]	Yield Strength 0.5% (N/mm ²) [ksi]	Elongation (%)
Minimum	586 [85]	241 [35]	15

In order to qualify a new mold design or process, a test sample must be extracted from an actual cast part. The specimen is required to achieve the properties listed in **Table 10** for the design or process to be accepted.

Table 10. Mechanical Requirements for Extracted Samples to Qualify
New Propeller Mold Design and/or Process as Specified by
NAVSEA [54]

	Tensile Strength (N/mm ²) [ksi]	Yield Strength 0.5% (N/mm ²) [ksi]	Elongation (%)
Minimum	413 [60]	165 [24]	10

Few records could be located detailing the original material qualification procedures for NAB, but general guidance for development of new NAB alloys and processing procedures requires that they compare favorably to existing ones. A comparison can be drawn to other alloys developed for U.S. Navy use. A discussion of the development of HSLA-80 steel, which was formally introduced for use in structural applications on Naval ships in 1984 as a replacement for HY-80 steel, stated the following: "Certification requires an evaluation of a structural fabrication system which demonstrates that the system will perform in all aspects of structural performance equivalent to or better than the system it replaces" [69].

The NAVSEA technical publication entitled "Material Selection Requirements" (T9074-AX-GIB-010/100), referred to here as Tech Pub 100 for brevity, provides guidance for new material applications. Including "use of an existing material where there is a significant change in metallurgical condition, such as from treatments or shaping applied during the manufacturing process, welding, heat treatment, or changing the form of the material (*e.g.*, forging vs. plate)" [70]. Per Tech Pub 100, any NAB component produced via AM must undergo the materials selection requirements process prior to qualification. The design activity using a new application is required to prepare material selection information (MSI), which is application-dependent and thus not explicitly defined. Nevertheless, the MSI must "[identify] the pertinent material characteristics necessary to meet the performance requirements for the application and intended service conditions, and [demonstrate] using data and experience, that the candidate material and its pertinent characteristics are suitable for the intended application. Reports on material property data, in-service experience, and other pertinent material characteristics may be referred to by the MSI to support justifying the material selection, but need not be included as part of that MSI" [70]. Given these requirements, a favorable comparison of additively manufactured material

performance to the metrics outlined above for NAB propellers is adequate justification for use of new AM processes.

As previously discussed, mechanical property requirements for NAB base material have been specified by ASTM and are listed in **Table 8**. These requirements do not necessarily apply to in-service parts, which undergo further processing. One of the primary manufacturing processes for NAB parts is casting, which has cooling rates dictated by geometry. Thick sections undergo slow cooling and develop coarser microstructures, while small parts or features cool rapidly and develop finer microstructures. This inhomogeneity of microstructures directly affects mechanical and corrosion properties; *i.e.*, the properties of a small cast part are not necessarily comparable to those of a large cast part. Regardless, as covered previously, the accepted quality control method for propellers is to perform mechanical tests on small witness coupons cast at the same time as the components. This does give a measure of control by comparing material between lots, but is not a direct measurement of cast propeller properties. Before use, each casting mold is qualified by extracting samples from within a test casting. These samples undergo mechanical testing and are required to meet the more conservative requirements shown in **Table 10**. A 1983 survey of data by P. Wenschot is discussed below and justifies these qualification requirements [71].

Wenschot collected experimental data on NAB castings of varying size and shape in order to investigate the correlation between section thickness and both mechanical and corrosion fatigue properties. Condenser tube plates and small propellers were used for section thicknesses between 10 - 40 mm (0.39 - 1.6 in.), test bars provided section thicknesses of 25 mm (0.98 in.), and experimental propeller blades were the source of 90 mm (3.54 in.) and 250 mm (9.84 in.) thick samples, with samples extracted from both the edge and center of the casting. Full datasets are provided in the source paper, with selections tabulated below [71]. Data illustrating cast section thickness and corresponding properties are presented in Table 11. Data illustrating the differences between properties measured at different locations within a single propeller blade casting are presented in Table 12. General trends emerged in the data: as section thickness increased and thus cooling rate decreased, mechanical properties tended to degrade. Specifically, tensile strength, yield stress, elongation, hardness, and corrosion fatigue all decreased as thickness increased. Properties measured for relatively thin parts exceeded the NAVSEA minimum material requirements listed in Table 9, but as section thickness increased above 75 mm (2.95 in.), the properties dropped below acceptable values. However, in all cases, measured mechanical properties meet the NAVSEA qualification requirements for extracted samples shown in Table 10. Wenschot's report [71] predated the current NAVSEA propeller specification [54], and may well have been the basis for the selected values, but the relationship between the two is unknown to the authors of this report.

In addition to mechanical properties, corrosion fatigue is an important consideration for propellers. A recent analysis by Hoerbert *et al.* examined data for C95800 in seawater using ALTA 9 software to produce S-N curves [72]. Multiple stressors were examined, but the only one found to make an appreciable difference in performance predictions was surface roughness. S-N curves produced for both rough (1.6 μ m [63 μ in.] and smooth 0.41 μ m [16 μ in]) finishes are shown in **Figure 47**.

		Average values of properties							
Range of cast section thicknesses, mm	Number of castings	Tensile strength R _m , N/mm ²	0.2% proof- stress R _{P0.2} , N/mm ²	Elongation A ₅ , %	Brinell hardness H _B , kgf/mm ²	$\begin{array}{c} Corrosion \\ fatigue life at \\ S_a = 127.5 \\ N/mm^2 \\ N_f^*10^6 \ , \ rev. \end{array}$			
20-30	33	679	262	22.3	163	100			
30-60	4	636	252	18.3	160	90.3			
60-75	3	613	241	18.9	160	-			
75-110	4	589	230	19.3	149	-			
150-160	3	582	210	20.7	136	-			
250-280	12	503	201	14.0	129	33.3			
280-320	5	511	199	15.0	128	33.9			
320-360	12	487	196	13.8	131	29.8			
360-380	17	496	197	15.0	128	29.0			
380-420	8	478	195	15.6	126	22.9			
420-450	16	489	189	15.9	129	26.3			

Table 11. Tabulated Comparison Between Cast Section Thickness and Properties [71]

Table 12. Mechanical Properties Comparison Between Different Regionsof a Single Propeller Blade Casting [71]

Locatio n r/R	Section Thicknes	Tensil	e strength N/mm ²	0.2 Rp	2% pro stress 0.2, N/m	of- m ²	Elongation A5, %			
	s (mm)	S*	C*	P *	S	С	Р	S	С	Р
		-	564	566	-	226	210	-	23.0	21.4
0.3 - 0.4	250	534	552	563	187	220	200	13.4	15.8	22.0
		549	542	524	210	205	195	15.2	14.6	15.0
		557	547	566	215	210	200	18.2	15.6	21.0
		580	581	589	236	215	242	18.6	16.8	16.0
0.7 - 0.8	00	584	587	589	236	228	235	18.8	18.8	14.4
	90	632	595	-	243	231	-	24.4	19.2	-
		545	589	529	223	220	225	12.6	18.2	12.5

*S = suction side, C = center, P = pressure side



Figure 47. S-N curves generated with ALTA 9 for both rough (1.6 μm [63 μin.]) and smooth (0.41 μm [16 μin]) surface finishes [72].

Fatigue data was collected by Prager in 1979 for several materials relevant to propellers, namely manganese bronze, NAB, and manganese-NAB [73]. The exact compositions of the NAB samples were not provided, naming them only as "ABS Type 4" with listed composition ranges similar to, but not identical to, modern alloys. Nevertheless, the values lend credibility to the work done by Hoerbert *et al.* discussed previously. A selection of values are listed below in **Table 13**, and it is noted that a large dataset (including behavior under different environments) is included in the source paper, but is out of scope for this discussion [73].

Alloy	Corrosion-Fatigue Str Life, MPa	Test Environment				
	10 ⁷ Cycles	10 ⁸ Cycles				
Ni-Al Bronze	138 [20.0]	83 [12.0]	Severn River Water			
	138 [20.0]	86 [12.5]	Seawater			
	223 [32.3]	131 [19.0]	3% NaCl Solution			
	-	117 [17.0]	Seawater			

Table 13.	Corrosion-	Fatigue	Strength	for NAB	Adapted	from	[73]
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APPENDIX B: WELDING GUIDANCE REQUIREMENTS

The intent of this appendix is to summarize the current commercial and military specifications, handbooks, and technical publications that provide guidance on welding process variable selection and performance requirements for arc welding of NAB. Many of these crossreference one another, and an effort has been made to outline the relationships between guidance documents in common use. While this guidance may not be directly applicable to for additive applications, it can provide insight into historical use of this alloy family in a welding context. Limited discussion of experimental work is present where guidance was not found in specifications.

A commonly referenced commercial specification for NAB welding electrodes is AWS A5.7 ("Specification for Copper and Copper-Alloy Bare Welding Rods and Electrodes") [35]. The only requirement listed in AWS 5.7 is chemical composition. A corollary military specification, MIL-E-23765/3A ("Electrodes and Rods – Welding, Bare, Solid – Copper Alloy") [74], describes two alloys with identical requirements for composition. The two electrodes of interest, designated by AWS A5.7[35] as ERCuNiAl (C63280) and ERCuMnNiAl (C63380), are designated by MIL-E-23765/3A [74] as MIL-CuNiAl and MIL-CuMnNiAl, respectively. Table I of MIL-E-23765/3A is reproduced below in Table 14 and includes chemical composition for the two alloys of interest [74].

Туре	Соптол пате	Copper including silver	Zinc	Tin	Manga- nese	Iron	Sili- con	Nickel includ- ing cobalt	Phos- phorus	Alumi- num	Lead	Total other elements
MIL-CuS1	Copper-silicon alloy (silicon bronze)	Remainder	*	<u>3/</u> 1.50	<u>3/</u> 1.50	0.50	2.80- 4.00	*	*	0.010*	0.020*	0.50
MIL-CuSn-C	Copper-tin alloy (phosphor bronze)	Remainder	*	7.00- 9.00	*	*	*	*	0.10- 0.35	•010*	•020*	• 50
MIL-CuA1-A2	Copper-aluminum alloy (aluminum bronze)	Remainder	0.020			0.75-	0.10			9.0- 11.0	•020	•50
MIL-CuMnNiA1	Copper-manganese- nickel-aluminum alloy (manganese, nickel, aluminum bronze)	Remainder	*	*	11.0 14.0	2.00- 4.00	*	1.50- 3.00	*	7.00- 8.50	•020	.50
MIL-CuNiA1	Copper-nickel- aluminum alloy (nickel, aluminum bronze)	Remainder	*	*	0.60 3.50	3.00- 5.00	*	4.00- 5.50	*	8.50- 9.50	.020	• 50

Table 14. Chemical Composition of NAB Wire (wt. %) [74]

 $\frac{1}{2}$ Analysis shall be made for the elements indicated by an asterisk (*) and those for which specific values are shown in this table. If, however, the presence of other elements is indicated in the course of routine analysis, further analysis shall be made to determine their content. The total of these other elements and the elements indicated by an asterisk (*) shall not be present in excess of the limits specified for the "total other elements" in the last column in the table.

 $\frac{2}{2}$. Unless otherwise specified, single values are maximum.

 $\frac{3}{2}$ One or both of these elements may be present within the limits specified.

In order to meet the MIL-E-23765/3A specification, an all-weld metal (AWM) NAB specimen is required to achieve a minimum room temperature tensile strength of 586 MPa (85 ksi) [74]. AWS 5.7 does not require tensile testing, but for informational purposes lists a minimum UTS of 480 MPa (72 ksi) [35]. UTS requirements specified by MIL-E-23765/3A [74] apply to single bead gas metal arc (GMA) or gas tungsten arc (GTA) weldments, while the

number provided in AWS 5.7 [35] applies to GTA weldments only. MIL-E-23765/3A [74] constrains welding conditions further by imposing a maximum preheat and interpass temperature of 232 °C (450 °F) when depositing material for mechanical testing. In addition to tensile test requirements, MIL-E-23765/3A requires that two transverse side bend tests be performed such that the convex surface of the specimen after bending has no visual cracks exceeding 3.2 mm (1/8 in.) [77].

NAVSEA requirements for NAB weldments are discussed in the NAVSEA Technical Publications entitled "Requirements for Weld and Braze Procedure and Performance Qualification" (S9074-AQ-GIB-010/248) [75], referred in this appendix as Tech Pub 248 for brevity, and "Requirements for Fabrication Welding and Inspection Cast Inspect and Repair" (TP-S9074-AR-GIB-010-278), referred to here as Tech Pub 278 [76]. Tech Pub 248 uses Table I, "Grouping of base materials (welding)," to designate letter numbers that describe broader alloy families. NAB base materials in general are designated as letter number S-36A. Certain alloys (*e.g.*, C95800) discussed previously in this report are not directly called out in this table, but fall under the MIL-B-24480, "Bronze Nickel-Aluminum Castings for Seawater Service" [77]. Cast materials defined in MIL-B-24480 are explicitly called out in Table I of Tech Pub 248 and are considered to be S-36A base materials.

Tech Pub 278 provides guidance on welding conditions for S-36A base material (which encompasses NAB alloys of interest) [76]. It stipulates that preheat is not mandatory, though preheat and interpass temperatures are considered to be essential elements for a welding procedure. Additional information is given in Section 6.4.5, which notes that "…in accordance with MIL-B-24480, …a post-weld temper anneal heat treatment is required if the weld is made on any surface exposed to seawater or where the heat affected zone extends to within 1/4 inch of this surface. Post-weld heat treatment is not required for non-seawater applications. When required, temper annealing shall consist of holding the casting at 1250 ± 25 °F for 6 hours minimum, followed by air cooling." It is further noted that this requirement for temper annealing is occasionally exempted for specific components, as is the case for weld repair of certain propellers [54].

Tech Pub 248 lists filler materials in Table II ("Grouping of filler materials [welding]") [75]. Nickel-aluminum bronze bare electrodes and rods are designated as group A-37B, and include two particular filler materials: MIL-CuNiAl and MIL-CuMnNiAl, as defined by MIL-E-23765/3A [74]. Certain cases for joining dissimilar metals call for use of electrodes from other groups. In those cases, "if the S-36A material is to be post-weld temper annealed, A-37B filler materials shall be used."

For efficient and high quality joining of NAB alloys, The Welding Institute (TWI) recommends use of gas tungsten arc welding (GTAW) or gas metal arc welding (GMAW). Both processes limit absorption of oxygen into the weld pool from the atmosphere by using gas shielding and disperse surface oxide with the arc. NAB alloys readily form an alumina surface oxide that aids corrosion resistance in finished components but must be removed prior to welding to prevent inclusions. In general, GMAW is associated with lower quality welds but allows higher deposition rates than GTAW. Shielded metal arc welding (SMAW) is acceptable for joining but is typically not used in shipyard applications due to slow deposition rates and the risk of surface oxide and/or slag entrapment [78]. Typically, for joining a particular base material composition, matching filler metals are used, per AWS A5.6 ("Specification for Covered Copper

and Copper-Alloy Arc Welding Electrodes") [79] and AWS A5.7 ("Specification for Copper and Copper-Alloy Bare Welding Rods and Electrodes") [35].

General shielding gas recommendations for welding copper include argon, helium, or a mixture of both. The AWS Welding Handbook Vol. 5 [39] offers the following guidance for shielding gas selection: "For GTAW of copper alloys up to 1.5 mm (0.06 in.) thick; helium is preferred for welding sections greater than 1.5 mm (0.06 in.) thick. Compared to argon, helium produces deeper weld-bead penetration or permits higher travel speed, or both, at the same welding current. **Figure 48** illustrates the differences in weld-bead penetration in copper when using argon and helium shielding gases. Helium produces a cleaner, more fluid weld pool with considerably less risk of oxide entrapment. Mixtures of argon and helium result in intermediate welding characteristics. A mixture of 75% helium and 25% argon produces a good balance between the enhanced weld penetration of helium, and the easier arc starting and better arc stability of argon" [39]. **Figure 49** illustrates the interrelationship between plate thickness, shielding gas, weld procedure, and recommended preheat temperature for copper alloys in general [39].



Figure 48. Effect of shielding gas and preheat temperature on weld bead penetration in copper when gas tungsten arc welded with 300 A dc at a travel speed of 3.4 mm/sec (8 in./min) [39].



and Metal Thickness on Preheat Requirements for Welding Copper Figure 49. Correlation of process, shielding gas, and metal thickness with

preheat requirements for arc welding copper [39].

No record of nitrogen shielding gas was found for arc welding NAB. In general, nitrogen shielding is restricted to laser welding processes, which have not historically been employed to the same extent as arc welding for joining NAB. The use of nitrogen as shielding for GMAW and GTAW of pure copper was investigated in a 1974 study by Littleton et al. [80]. Extreme porosity was observed in all tests, with porosity decreasing slightly with increased travel speed. Welds made with a mixture of argon and as little as 0.1% nitrogen were described as producing appreciable porosity for the two tested travel speeds (2 and 6 mm/s [0.08 and 0.24 in./s]). Introduction of denitriders to the weld metal via filler materials was extremely effective in mitigating porosity. Littleton et al. showed that filler material containing both 0.20% wt. aluminum and 0.1 wt. % titanium produced GMA weldments with no porosity, independent of travel speed [80]. NAB alloys have no titanium alloying additions, but are typically composed of approximately 10 wt. % aluminum. This suggests that nitrogen porosity would be avoided thanks to aluminum acting as a denitriding agent. Low aluminum content (below 9%) in NAB is associated with the stabilization of α phase at high temperatures, shrinking the single phase β regime. This phase is targeted for solution treatment and thus a low aluminum content may render typical heat treatments ineffective and compromise mechanical properties of a final product [12]. Further, the effect of introducing aluminum nitrides to NAB is unknown. The potential for nitrogen shielding to cause excessive porosity or disrupt β phase formation makes it a poor candidate.

A myriad of welding parameters can affect weld bead characteristics. One study by Sriintharasut *et al.* investigated the effects of heat input and welding current waveform (*i.e.*, standard or pulsed) when using GMAW to join NAB plate [81]. Though the material is listed as UNS No. C95800, the nickel, iron, and manganese contents are too low to meet that specification [24]. Three heat inputs were investigated: 535, 704, and 870 J/mm (13.6, 17.9, and 22.1 kJ/in.). These heat inputs were targeted for each of the two welding current modes. For both cases, a higher heat input corresponded to wider and deeper weld bead profiles, as expected. The depth to width ratio and the dilution ratio both increased with heat input as well. For each heat input, the standard current produced wider beads, while the pulsed current resulted in deeper penetration.

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