MULTIPHASE WIDE GAP BRAZE ALLOYS FOR THE REPAIR OF NICKEL-BASE SUPERALLOY TURBINE COMPONENTS: DEVELOPMENT AND CHARACTERIZATION

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Metallurgical and Materials Engineering).

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ABSTRACT

Gas turbine components made of nickel-base superalloys experience cracking after service in extreme environments. As these cracks can be wide, brazing or fusion welding is typically used to repair them. Properly designed and applied, brazing filler metal will help extend the useful life of damaged turbine components. During repair of defective OEM parts, brazing is also considered, provided that proper filler metals with enhanced ductility and improved resistance to low-cycle fatigue are available. This research strives to develop the brazing technique and alloys to achieve a repair with acceptable mechanical properties. Additionally, the effects of silicon and boron, as fast diffusing and melting point suppressing elements on the braze microstructure and mechanical properties were examined in detail to help guide future alloy development.

Three commercially available “low-temperature” brazing powders were mixed with an additive superalloy powder to prepare a series of filler metals for wide gap brazing used to repair OEM gas turbine components. BNi-2 (Ni-7Cr-4.2Si-3B-3Fe), BNi-5 (Ni-19Cr-10Si) and BNi-9 (Ni-15Cr-3.5B) were mixed with MARM247 (Ni-10W-10Co-8.25Cr-5.5Al-3Ta-1Ti-0.7Mo-0.5Fe-0.015B) at ratios of 40, 50, and 60 wt. pct. creating a total of nine experimental filler alloys. The brazes were applied to a 0.06 inch gap in a René 108™ substrate for mechanical and microstructural analysis.

The wettability and flow of each of the experimental alloys were analyzed to determine the required brazing temperature through isothermal spreadability experiments. Bend testing was performed on brazed joints to determine their mechanical properties and maximum angular deflection. The metallurgical driving factors, such as solidification behavior and compositional effects, were analyzed to correlate the resulting microstructural constituents to the mechanical properties developed through experimentation.

It was found that because of the solid solubility of silicon into nickel, greater amounts of single-phase nickel formed surrounding the additive superalloy powder in the brazes containing silicon when compared with brazes without. This effect is advantageous, as it was found that the increase in the additive powder interaction zones resulted in a beneficial increase in mechanical properties, such as strength and percent strain at failure. Alloys containing boron required a lower processing temperature than alloys containing silicon and are good candidates for use in the process if enough time is given for the boron to diffuse into the parent material and therefore encouraging isothermal solidification, disallowing the formation of mechanically detrimental ternary eutectic boride phases. The BNi-2 alloy, containing both boron and silicon, exhibited the beneficial behaviors of heightened interaction between the liquid braze alloy and the additive powder, in addition to the decreased brazing temperature required.
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DEDICATION

This work is dedicated to my family, including my fiancée, Megan Knudstrup; my parents, Dave and Ellen Nelson; and my little sister, Becca Nelson. Their constant support, love, and encouragement throughout my academic career and through the completion of this research program was invaluable and will never be forgotten.
ACKNOWLEDGEMENTS

I would like to acknowledge the following people for their help and assistance with the completion of my thesis and my graduate work as a whole.

- My advisor, Dr. Stephen Liu, and co-advisor, Dr. Juan Carlos Madeni, for their continued support, technical guidance and generous donation of their time towards the successful development, implementation, and completion of this research program.
- Dr. Srikanth Kottilingam, without whom, this research program would not be possible. His technical expertise and mentoring not only shaped this research program, but also introduced the techniques and intricacies of nickel-base brazing. The financial support provided, thanks to Dr. Kottilingam, also allowed me to complete this research and my Master’s degree.
- My thesis committee including Dr. Stephen Liu, Dr. Juan Carlos Madeni, Dr. David Olson, Dr. Srikanth Kottilingam, for their help in the finalization of this thesis and the time given to review my research.
- GE Power Systems for the financial support for my graduate studies and this research program.
- David Schick, from GE, for the technical assistance used in the development of this research.
- My proofreading team, who helped to give my thesis the polish it deserved: Megan Knudstrup, Ellen Nelson, and Katherine Sebeck.
- Team Industrial Inc. and Nick Mossman for assistance with the radiographic examination of the braze samples and taking the time to teach me the techniques involved with the process.
- Will Garret and Kin-Ling Sham for the work they did refurbishing the vacuum furnace used in this research and for their assistance in training me in its operation and maintenance.
- My officemates, Grant Hudish, Lee Rothleutner, and Seth Griffeths for their companionship, technical expertise, assistance with development of this research and writing of this thesis.
- The students of the Center for Welding, Joining, and Coating Research at the Colorado School of Mines, for the support and discussions held throughout my tenure at CSM.
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CHAPTER 1 INTRODUCTION

A superalloy is defined as a material that can successfully operate at temperatures as high as 25 pct. lower than its melting point, while being able to sustain adequate mechanical strength. [1] Alloys for high temperature applications were originally iron-based and maintained a close composition to modern austenitic stainless steels. As the need for increased operating temperatures, mechanical strength, and corrosion resistance grew, the iron content was replaced by nickel and/or cobalt. Between 1940 and 1970, nickel alloys saw an evolution where their high temperature strength was increased seven-fold (Figure 1.1). [2] Modern superalloys are widely used in the manufacture of gas-turbine engines and land-based turbines for energy generation. The dominance of these superalloys for use in turbine components comes from their ability to withstand and maintain strength in the extreme service temperatures of 1000 to 1200°C for long periods of service, up to 20000 hours. [3]

The material properties desired by turbine manufacturers and designers can be directly related to the microstructure of superalloys, which, like the iron-based predecessors, are comprised of an austenitic face-center cubic (FCC) crystal structure. In addition to this austenitic matrix, nickel-base superalloys have a number of intermetallic strengthening precipitates. The intermetallic compound that is most often promoted and used is the gamma-prime (\( \gamma' \)) phase, with the composition of Ni\(_3\)(Al,Ti) and is also an FCC phase. Gamma-prime particulates present themselves in either a cuboidal morphology (primary \( \gamma' \)), with an average size of 0.6 \( \mu \)m, or a smaller spheroidal morphology (secondary \( \gamma' \)), with an average size of 0.1 \( \mu \)m. [4] Other intermetallic compounds observed in superalloys are carbides, borides, and silicides. These
intermetallic compounds are mostly beneficial to the performance of the superalloys, and prevent dislocation movement and grain boundary sliding at high temperatures. However, they can be detrimental in large quantities, or in undesirable morphologies, such as grain boundary films, often causing material embrittlement. [5]

Figure 1.1: Evolutionary increases in strength through alloy development. [2]

One major disadvantage in using superalloys over advanced steels is the difficulties inherent in joining nickel-base superalloys components through the use of common fusion welding techniques. Traditionally, gas-tungsten arc welding (GTAW) or more advanced welding techniques, such as electron beam or laser welding, have been used for fabrication and repair of turbine components. [1] However, when joining $\gamma'$-strengthened superalloys, heat-affected zone microfissuring and fusion zone cracking (including liquation, ductility dip, and strain age cracking) have been reported to occur. [3] [6] Fusion joints also do not have the thermal and chemical stability necessary to maintain strength in the highly corrosive and high temperature environment experienced by turbine components. [7]
As an alternative to fusion welding, superalloys were joined using a modified diffusion brazing processes. Traditional diffusion bonding has long proved itself to be a useful technique for joining superalloys and other alloy families, such as iron and titanium, as the process involves using brazes of a similar composition to the base material. This braze alloy composition allows for the creation of almost identical microstructural and mechanical properties and removes the concern that differences in thermal expansion could result in a joining defect, as the coefficients of thermal expansion for the substrate alloy and the braze alloy are inherently similar. [8] Unfortunately, the high bonding pressures (3.5 to 35 MPa or 500 to 5000 psi) and temperatures (upwards of 1300 to 1400°C or 2400 to 2600°F) required to create a diffusion bond deform thinner components with complex geometry. The time required to create a diffusion bond is also more dependent on the joint geometry than most non-fusion joining processes and a simple nickel-base superalloy diffusion braze can take anywhere from one to 24 hours to complete. [9] Diffusion bonding is also uneconomical for large-scale production due to the high process tolerances required for surface preparation, fit-up, and long processing time; manufacturing cost also increases due to a higher rejection rate. To successfully join superalloys, a group of researchers from Pratt & Whitney Aircraft developed the modified diffusion brazing technique known as Transient Liquid Phase (TLP) bonding in the late 1960s. [8] As will be examined in section 2.1, the factors vital to the quality of the braze joint are the braze filler metal (composition and flow characteristics), brazing cycle (holding temperature and time), and joint design. The overall process of wide gap brazing (WGB) is a further adaptation of TLP bonding and diffusion brazing. Wide gap brazing was developed to take advantage of the benefits of traditional TLP bonding but for joints with clearances considerably wider than normally feasible for brazing operations. [9] [10]
This ability for wide gap brazing to successfully fill large wide gaps makes it ideal to repair cracks in the turbine components that have failed due to the extreme in-service conditions experienced. While wide gap brazing has been available for the past forty years, it has been used primarily in the refurbishing and repair of in-service turbine components, not to repair OEM parts. When refurbishing components coming out of service and repairing cracks, the damaged areas surrounding the cracks are excised from the bulk component. This procedure is performed to remove any surface impurities that may have formed after the component cracked in-service. The preparation of the repair surface allows for good interaction between the component and the braze repair, creating a high integrity joint. OEM components can fail as a result of cracking during solidification, heat treatment, or other production processes, and a properly designed wide gap braze alloy can be used to salvage components that would otherwise be scrapped, and thereby reducing the rejection rate of the production lines, and overall manufacturing costs. In contrast to the refurbishment of components coming out of service, when repairing OEM components, the braze is applied directly to the crack, with only limited surface preparation including particle ablation and vacuum treating. The difference in preparation originates from the fact that manufacturing defects formed while being processed in a vacuum or other inert atmosphere. Therefore, no impurities will have the opportunity to form on the surface where the braze repair will take place. These differences in the requirements for the braze repair of the OEM and used turbine components need to be acknowledged to adapt the technique for OEM component use.

This thesis research will look into developing and characterizing wide gap brazes for use in the repair of OEM turbine components. This investigation will involve the use of different alloy compositions, encompassing different combinations of commercially available braze powders.
containing boron and silicon, and analyzing them based on brazing parameters, joint metallurgy, mechanical performance, and thermal stability under in-service aging conditions. This experiment will have as a conclusion, general alloy recommendations that will lead to further alloy development and form the foundation to build the body of work and data required to qualify these alloys for use in repairing OEM turbine components.
CHAPTER 2 LITERATURE REVIEW

The process of brazing nickel-base superalloys is very complex, and there has been a great deal of work developing and analyzing different aspects of the systems in the past forty years. This work includes the analysis and development of narrow gap nickel brazing and wide gap brazing along with the examination of joint metallurgy and braze cycles for wide gap brazes.

2.1 Narrow Gap Nickel Brazing

Transient Liquid Phase bonding was initially created as a derivative of high temperature vacuum furnace brazing in an attempt to find an economical solution to create a joint between nickel-base superalloys and fabricate components for high temperature applications. In traditional dissimilar metal brazing, the braze alloy acts as bonding agent, and remains as a discrete alloy layer within the braze joint. [11] Unlike the traditional brazing process, the resulting bond created by TLP processing creates a joint that has nearly identical material properties and microstructure as the parent material. [12] Due to this metallurgical compatibility, the joint is able to withstand the hot, corrosive environment and long-service periods experienced by both jet engine and terrestrial turbine components. [8] Additionally, the use of a simple vacuum or inert gas atmosphere heat treat furnace allows for TLP processing to be performed easily.

In transient liquid phase bonding, a thin (e.g. 0.025 to 0.1mm or 0.001 to 0.004 in.) interlayer of metal comprised of a nearly identical composition to the parent material, but with the addition of a fast diffusing, melting point suppressing element that promotes the joining of the materials, is used. The composition of the interlayer material is chosen so that the melting temperature of the interlayer will be lower than the base material by 400 to 500ºC (750 to 930ºF),
and will therefore not affect the microstructure of the bulk of the solid base material. The bonding temperature is determined to ensure a molten interlayer alloy, with consideration to the parent material, which must not only remain solid but also avoid any disruption of the microstructure, such as solutionizing of strengthening precipitates, [13] nucleation of undesirable phases, [14] and/or grain coarsening. [15] The selected interlayer is placed in between the parent components to be joined, a light compressive force (up to 70 kPa or 10 psi) and an elevated bonding temperature (1090 to 1200°C or 2000 to 2200°F) in a vacuum or inert gas (argon) atmosphere is applied for one to four hours to complete the joining. [8]

Once the interlayer has melted, three distinct process stages occur to complete the TLP bond: substrate dissolution (or erosion), isothermal solidification, and solid-state homogenization. These stages can be seen diagrammatically in Figure 2.1, where the system has been simplified from a ternary (Ni-Cr-X) to a binary system with A as the solid substrate (Ni-Cr) and B as the molten interlayer. [12]

In the substrate dissolution phase, a composition gradient exists between A and B at the solid-liquid interface, which creates a partial dissolution of the solid substrate into the interlayer. This composition gradient provides the chemical driving force for the chemical composition to homogenize across the bond. Since long-range diffusion is not necessary for dissolution and the activation energy is relatively low when compared to interstitial, substitutional, or self-diffusion, [16] the dissolution stage requires only a few minutes at the bonding temperature to complete.

Once the dissolution process is complete, the melting point suppressant diffuses out of the interlayer and into the solid substrate. As the melting point suppressant is lowered within the liquid, the liquidus temperature of the molten interlayer is increased and solidification occurs at the held bonding temperature. In contrast to the substrate dissolution stage, the removal of the
melting point suppressant requires long-range diffusion, and therefore requires prolonged times to fully solidify the liquid interlayer.

![Diagram of the different stages of the TLP bonding process](image)

Figure 2.1: Diagram of the different stages of the TLP bonding process. [12] a) interlayer melts; b) substrate dissolution; c) isothermal solidification; d) isothermal solidification ends; e) solid state homogenization; f) the final condition.
The exact time required for isothermal solidification is highly system specific and is determined by the diffusion coefficient of the melting point suppressant, the amount of the solute (melting point suppressant) that must be removed through diffusion, and the shape of the liquid-solid region of the phase diagram; solute removal can take anywhere from a few minutes to hours when held at the bonding temperature. [12] Once the isothermal solidification stage is complete, the process can be halted and results in a bond with reasonable integrity. However, to take full advantage of the potential of the TLP process, the composition at the bond may be further homogenized by maintaining the bonding temperature after the full solidification of the liquid. This homogenization allows for the composition at the bond line to come into equilibrium with the rest of the base metal and ensures a homogeneous microstructure when cooled. Similar to the isothermal solidification phase, the solid-state homogenization depends on long-range diffusion and can take long holding times to complete. If the composition of the bond is not brought to a point where the solute is in solution at room temperature, undesirable second phase precipitates may form through athermal solidification upon cooling.

As can be seen, the metallurgical concept behind transient liquid phase processing is simple, however, the entire process depends on the proper selection of the interlayer alloy. As stated previously, the interlayer needs to be designed to have a melting temperature below the melting temperature of the solid substrate. The interlayer composition also needs to be complementary to the base metal composition to promote the final homogenization of the microstructure following the completion of the bonding process.

These metallurgical considerations generally lead to the selection of a ternary eutectic with two of the primary base material constituents (e.g. nickel, cobalt and/or chromium) and a third melting point suppressant. Initial experiments performed by Duvall et al. [8] during the
development of the process tested boron, silicon, manganese, molybdenum, and titanium as melting point suppressants. It was found that boron was the most efficient suppressant and created the best bonds. Additionally, alloying elements that create stable intermetallic particles should also be avoided because they will form within the bond line and will not breakdown during the solid-state homogenization stage. [8] Unfortunately, most real world TLP interlayers do not follow the idealized binary eutectic system discussed.

Real world complications involve the solid-state diffusion of constituent elements before the intermetallic compounds reach the liquidus temperatures, which would skew the equilibrium of the system and disrupt the concentration gradients that drive both the substrate dissolution and the isothermal solidification. Another complication is that real world substrates are not semi-infinite, as approximated by models, and thin-walled segments can collect the fast-diffusing species and disrupt the concentration gradients. [12] All of these considerations must be acknowledged in order to successfully achieve a compatible TLP bond.

2.2 Wide Gap Brazing

As stated earlier, the joint design plays a vital role in the creation of a quality braze joint. Lugscheider and Partz [17] determined the maximum joint clearance as 0.1 mm (0.004 in.) and if this is exceeded, the melting point suppressants will be unable to fully diffuse out of the molten braze and into the parent material. The high concentration of melting point suppressant will disrupt the isothermal solidification and leave a liquid phase super-saturated with the solute and will create a detrimental “centerline eutectic” through athermal solidification. In a fabrication scenario, the joint clearances can be carefully controlled and therefore these centerline eutectics can be mitigated through design. When a turbine component cracks due to the adverse conditions
it experiences in-service or due to the manufacturing process, the width of these cracks often exceed the maximum joint clearance by 200 to 500 pct.; these cracks are tortuous and unpredictable, further complicating the repair process.

Gas turbine manufacturers, such as General Electric (GE), developed and patented a number of wide gap brazing (WGB) processes; the process developed by GE is referred to as additive diffusion healing (ADH) or additive diffusion bonding (ADB). [2] [18] WGB processes, as patented by other companies, are M-Fill [19] (Avco Lycoming), Effective structural repair (Howmet) [20] or transient liquid phase infiltration. [21] Despite these varying processes and their names, they all fall under the general process umbrella of wide gap brazing, where a traditional braze alloy is enhanced by an additive material, in some form, with a similar composition to the parent material. The composite brazes vastly decrease the diffusion distance for the melting point suppressant and effectively creates thousands of diffusion joints between the pieces or particles of the additive material within the greater whole.

Despite the increased range of joint designs possible, under the umbrella of “Wide Gap Brazing,” braze alloy design, brazing parameters, and joint clearance are still vital to the creation of a high quality braze joint. Wide gap braze repair has been used to repair and refurbish gas turbine engines for decades with great success that, according to the Federal Aviation Administration, not one failed turbine component has resulted from a faulty WGB joint. [22]

Hoppin and Berry [2] published one of the first investigations detailing Additive Diffusion Bonding (ADB) and what they referred to as an ultra-high strength-bonding alloy in 1970, examining the effects of bonding parameters and alloy design on the mechanical properties of the joint. At the time, this novel process was considered to combine the manufacturing ease of brazing with the high joint-strengths achievable during solid-state diffusion bonding. It was also
noted that up until 1970, braze alloys primarily used expensive precious metals as the melting point suppressant and that minimal braze-substrate interaction was preferred. Additionally, the need for high temperature strength in Ni-base brazes necessitated the precipitation of the $\gamma'$ intermetallic phase, which requires the addition of highly reactive aluminum and titanium. In a process where the braze alloy is fully liquid, the oxides formed by aluminum and titanium would be detrimental to the flow of any traditional braze alloy, and also make it prohibitively difficult to produce pure powder for use as braze alloys; the loss of $\gamma'$ as a strengthening precipitate forced the turbine manufacturers to limit brazing to low-temperature, low-strength applications. The development and use of the ADB technique was the first time the high-temperature strengthening benefits of the $\gamma'$ intermetallic phase could be utilized within a braze.

To verify the ADB technique, Hoppin and Berry [2] performed extensive mechanical tests to ensure that the braze could withstand the designed stresses at the temperatures required. A brazed butt joint comprised of a 40/60 mixture of René 80 and AMS 4782 (BNi-2), and with a relatively narrow joint clearance of 0.25 mm, was tested in tension at the elevated temperatures of 650°C (1200°F) and 870°C (1600°F). The tensile properties of these joints were nearly identical to that of the parent René 80 (Figure 2.2a). During creep rupture tests (Figure 2.2b), it was found that the ADB joints achieved 80 to 90 pct. of the strength of the parent material and strengths considerably greater than those found for the conventional braze alloys AWS 4782 (BNi-5; Ni-19Cr-10Si) and AMS 4786 (BAu6; Au-22Ni-8Pd). In fatigue tests (Figure 2.3) performed at 760°C (1400°F), it was found that the high cycle fatigue life of the ADB joints was approximately 70 pct. of that of the parent material. Overall, Hoppin and Berry declared that this new process could successfully join “difficult-to-weld” nickel-base superalloys and maintain strength at levels 70-90 pct. that of the parent material at elevated temperatures.
Figure 2.2: Top: a) Ultimate Tensile Strength (UTS) and 0.2\% Yield Strength (0.2\%.YS) of the ADB butt joints with a 40/60 mixture of René 80 and BNi-5 with a joint clearance of 0.25 mm.

Bottom: b) Stress rupture properties of activated diffusion bonded joints in René 80 compared with conventional braze joints and the parent material. [2] [22]
2.3 Joint Metallurgy and Microstructures of Nickel Braze Joints

The microstructures of both TLP and wide gap brazes are extremely complicated in nature, as they not only have all of the phases often observed in standard nickel-base superalloys, but the microstructure is also affected by the braze alloy and the parent material if partial dissolution of the base substrate occurs. The coalesced additive powder particles are also affected by the braze alloy. In order to simplify and explain the system, many researchers and engineers identified and named zones based on characteristics such as: phase composition, solidification method, or location. Su, Chou, Wu and Lih identified six joint zones that can exist within a joint consisting solely of the additive superalloy powder and a standard wide gap braze joint, containing both the additive superalloy powder and the low-temperature braze alloy. [23]

These zones were identified based on their location and phase composition, rather than solidification behavior or origin. The zones identified in the joint made with the additive powder were identified as: primary solidification dendrites (1); eutectic/eutectoid structure (2); solid diffusion zone (3); irrigation zones, where there is precipitation in grains and grain boundaries.
(4); short circuit path, where grain boundary precipitation is evident (5); and the unaffected base metal (6). (Figure 2.4a) Many of the same zones were identified in the joints where the additive powder was used in conjunction with the traditional braze alloy. These zones were: the additive powder (1); the filler metal (TLP Zone) (2); the solid diffusion zone (3); irrigation zones (also referred to as the braze/bonding affected zone) (4); short circuit path (5); and the unaffected base metal (6) (Figure 2.4b).

Figure 2.4: Schematic metallographic diagram of wide clearance joints with only the additive superalloy powder in the braze joint (a-left) and additive powder with the addition of the braze filler metal (b-right). [23]

### 2.3.1 Application of TLP Microstructure to Wide Gap Braze Microstructures

As a result of the identification of the zones, microstructures of narrow gap or TLP braze joints can be used as launching points for any analysis of wide gap microstructures using similar composition alloys as the low temperature brazes. This TLP zone, as classified by Su et al., is the material that melted during the brazing cycle and solidified due to isothermal and athermal
solidification around the additive superalloy powders. [23] The TLP zone encompasses both the Isothermal Solidification Zone (ISZ) and the Athermal Solidification Zone (ASZ), which will be discussed in depth later. [24]

Su et al. [23] performed an in-depth analysis on the microstructures of the TLP Zone of activated diffusion braze alloys comprised of Nicrobraz 150 (BNi-9), BRB (Ni-13.5Cr-9.5Co-4Al-2.5B), and D4FB (Ni-14Cr-10Co-3.5Al-2.5Ta-2.7B) with IN738 as both the additive and substrate material. Three major microconstituents were identified in the microstructure of the TLP zone for the ADB braze using the Nicrobraz 150, a blocky phase based on a Cr(B,C) phase, a γ-nickel matrix, and a Ni$_3$B phase that is also found in a eutectic structure with the nickel matrix. These microconstituents can be seen labeled in Figure 2.5. It was also noted that due to the low solubility of boron into nickel, a boride phase is seen precipitating into the additive powder (as seen by arrow labeled “b”).

![Figure 2.5: SEM Micrographs of brazed joint produced by mixture containing 40 wt. pct. BNi-9. Microstructures observed and labeled are: (N) Ni-Ni$_3$B eutectic with the γ-nickel etched; (a) blocky chromium boride phase; (b) Ni$_3$B phase; (AP) additive powder particle. [23]](image-url)
Demo and Ferringo [25] described the additive diffusion brazing (ADB) process as “casting superalloys into a crack using a bonding alloy with a lower melting point.” A simplified schematic of the joint was presented to show the interaction between the bonding alloy and the superalloy particles within a joint. This schematic can help to interpret and predict the resulting microstructures of a wide gap braze and what mechanisms are in effect to create the joint (Figure 2.6). In this schematic, the former particle interfaces are clearly seen, as are the diffusion zones surrounding the unaffected superalloy particle. The particles have also undergone densification through capillary removal of the molten filler metal, as described by Su et al. [23] [26], where the remaining liquid is wicked away from the prior particle sites due to capillary flow, allowing

Figure 2.6: Schematic showing a wide gap braze and the resulting interaction between the low-melting bonding alloy and the superalloy powder. [25]
for the distance between the unmelted particles to decrease. When comparing the microstructural characterizations of the TLP braze using a Ni-Cr-B system by Yuan et al. (Figure 2.7) [27] and the ADB joint in Su et al. (Figure 2.5) [23], it can be confirmed that the microstructure of wide gap brazes can be predicted using the microstructures of joints created by the unaltered commercial braze.

![Diagram of joint microstructures](image)

Figure 2.7: The layer-by-layer SEM images examined after alternate polishing and observing the surface of the joint prepared at 1090°C for 60s. The layers from left to right: 1) unaffected substrate; 2) substrate interface; 3 to 5) isothermally solidified nickel with increasing amounts of chromium boride; 6 to 7) athermally solidified nickel with Ni₃B and Cr borides. [27]

### 2.3.2 Microstructures of Nickel TLP Joints with Boron and Silicon

Yuan, Kim and Kang examined transient-liquid-phase joints made with a duplex stainless steel substrate and a Ni-Cr-B bonding alloy [27] or a Ni-Si-B bonding alloy. [28] The resulting microstructures were analyzed using X-ray microprobe analysis, X-ray Diffraction (XRD), optical and electron microscopy. In both experiments, Yuan et al. examined the effect of time
and temperature on the resulting microstructure of the braze, including the phases present and their morphology when moving from the substrate material into the center of the joint. This layer-by-layer analysis, as referred to and as illustrated in Figure 2.7, is extremely useful when examining the microstructural components in the TLP zones for a wide gap braze type joint using the same types of bonding alloy. The ability to analyze the braze layer-by-layer was accomplished by carefully controlled polishing and is useful to characterize the small braze layers.

In the Ni-Cr-B experiments [27], stainless steel coupons were brazed at 1090°C for 60 to 3600s using a bonding alloy foil with a nominal composition of Ni-15.2Cr-4B. It was found that complete isothermal solidification of the braze alloy at 1090°C will occur within 3600s. If the solidification process is interrupted, the joint will have a layer of isothermally solidified γ-Ni and a centerline eutectic layer comprised of γ-Ni, Ni₃B, and chromium borides. This intermediate sample was examined after holding the joint at the bonding temperature for only 60s and each individual layer was examined metallographically (Figure 2.7).

For the purposes of this characterization, the joint was divided into four regions, I: unaffected steel substrate, II: isothermally solidified material, III: interface between athermally and isothermally solidified materials, and IV: athermally solidified eutectic microstructure. Using x-ray diffraction, region II (Figure 2.7, second layer from left) was comprised of a γ-Ni and nickel borides. Region III was comprised of only γ-Ni, while region IV formed as a complex multiphase eutectic-containing phases such as γ-Ni, chromium borides (CrB, Cr₂B₃, Cr₃B₂, CrB₂, Cr₃B₄, and CrB₄), and nickel boride (Ni₃B) (Figure 2.8). These regions can further be characterized through microhardness traverses from the base metal into the joint. Through this analysis (Figure 2.9), it can be seen that the athermally solidified zone, containing the centerline
eutectic and many intermetallic species, had a hardness of ~550HV and exceeded the average hardness of the other regions by 200 to 250HV. When the joints are held for a sufficiently long period of time, the braze alloy will have the opportunity to undergo isothermal solidification and homogenization, promoting the removal of the detrimental athermally solidified microconstituents through substrate diffusion.

Figure 2.8: Layer-by-layer x-ray diffraction pattern analysis of each layer for a joint with athermal solidification made at 1090°C (1995°F) for 60s. The layers analyzed are: a) I: unaffected steel substrate (layer 1 in Figure 2.7); b) II: isothermally solidified material (layers 3 through 5 in Figure 2.7); c) III: interface between athermally and isothermally solidified materials (layer 6 in Figure 2.7); d) IV: athermally solidified eutectic (layer 7 in Figure 2.7).
Similar to the investigation into the Ni-Cr-B filler metals, the Yuan et al. investigation regarding the Ni-Si-B filler metal joints [28] used a simple duplex stainless steel to test the microstructural response of the filler metal to braze cycles that, ranged from 60s to 300s and temperature between 1060 and 1090°C (1940 and 1995°F). When brazed at the lower temperature and time (1060°C at 60s), it was found that the Ni-Si-B joints maintained the same microstructural regions as the Ni-Cr-B joints: the base metal, the bonding-affected zone, isothermally solidified zone, and the athermally solidified zone.

Using x-ray diffraction, it was found that the isothermally solidified zone was comprised of \( \gamma \)-Ni, BN, and Ni\(_3\)Si, while the athermally-solidified zone contained \( \gamma \)-Ni, Ni\(_3\)B, and Ni\(_3\)Si. When examined using both optical metallographically and energy dispersive spectroscopy (EDS), it was found that the athermally-solidified zone contained boron-enriched \( \gamma \)-Ni, Si-enriched \( \gamma \)-Ni with Ni\(_3\)Si intermetallic compounds and a matrix of Ni\(_3\)B (Figure 2.10). One notable difference

Figure 2.9: Microindentation hardness profiles of Ni-Cr-B alloys as a function of distance from the centerline for the bonds prepared at 1090°C after holding for 60s. [27]
between the athermally-solidified zone in the Ni-Cr-B and the Ni-Si-B systems is the complexity of the centerline eutectic microstructure. It can be seen that there is a high number of brittle intermetallic phases being formed with chromium and boron in the Ni-Cr-B filler alloy.

The joints were characterized using microhardness measurements traverses, using microindentations from the centerline into the base metal, along traverses perpendicular to the
interface (Figure 2.11). Comparing the microhardness results of the Ni-Si-B and the Ni-Cr-B joints, the relative hardness differences between each individual region of the joints is similar for both filler metal compositions

Pouranvari, Ekrami and Kokabi [24] took the analysis performed and the phases identified by Yuan et al. [28] and evaluated the solidification behavior of BNi-3 (Ni-4.5Si-3.2B) in detail. It was found that the solidification of BNi-3 joints could be described in three stages:

I: Formation of Ni-rich γ primary solidification phase (as described by Figure 2.12): γ-Ni in the form of dendrites growing from the solid/liquid interface. The formation of these primary dendrites results in the rejection of boron into the liquid, enriching the composition and leading to stage II.

II: Formation of binary eutectic microstructure consisting of Ni-rich boride and Ni-rich γ solid solution: The rejection of boron into the liquid continues until a eutectic composition is reached. At this point the primary solidification path intersects the eutectic line separating γ and Ni₃B phases. The solidification path then follows the eutectic line as the γ solid solution and nickel boride form simultaneously from the liquid through the eutectic reaction as described by Equation 2.1.

\[ L \rightarrow \text{Ni}_3\text{B} + \gamma \]  

Equation 2.1

III: Formation of ternary eutectic of Ni-Si-B: When analyzed through EDS, it was noted that the boride phase formed in stage II was devoid of silicon, indicating that the silicon was rejected from the eutectic solidification described by Equation 2.1 and led to silicon enrichment in the remaining liquid. Even though the majority of the boron was consumed by the reaction in stage II, some remained in the liquid. The enrichment of both silicon and boron continued until
the liquid composition reached the ternary eutectic point and underwent the ternary reaction described by Equation 2.2.

\[ L \rightarrow \gamma + \text{Ni}_3\text{B} + \text{Ni}_6\text{Si}_2\text{B} \]  
\text{Equation 2.2}

\[ L \rightarrow \gamma + L \rightarrow \text{Ni}_3\text{B} + \gamma + L \rightarrow \gamma + \text{Ni}_3\text{B} + \text{Ni}_6\text{Si}_2\text{B} \]  
\text{Equation 2.3}

Figure 2.12: Ni-Si-B ternary phase diagram at 1100°C used to determine the solidification behavior of BNi-3 with the initial composition indicated by the blue square. Diagram created through Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) modeling by Pouranvari et al. [24]
The solidification reactions and sequence as described by Pouranvari et al. can therefore be summarized and described by Equation 2.3. The definition of the previous solidification sequence and stage III in particular is further supported by the fact that the chemical composition of silicon in the filler alloy (~7.9 at. pct.) is much lower than the solid solubility limit of silicon into nickel indicating that the formation of the \( \text{Ni}_6\text{Si}_2\text{B} \) is due to formation of the boride phase \( \text{Ni}_3\text{B} \) and the resulting rejection and enrichment of Si in the remaining liquid. The analysis completed by this investigation is extremely useful when applied to the formation of wide gap brazes, as it helps to demystify the evolution of the braze microstructure when influenced by the additive superalloy powders.

### 2.3.3 Causes of Porosity in Wide Gap Brazes

Overall, wide gap brazing is an extremely useful process for the repair of cracks in superalloys. Unfortunately, the nature of the process lends itself to inherent problems that can be detrimental to the mechanical properties of the resulting braze, porosity. The root causes of porosity in ADB joints were examined by Su, Chou, Wu, and Lih [23]. In this investigation the commercial filler metals, Nicrobraz 150 (Ni-15Cr-3.5B), BRB (Ni-13.5Cr-9.5Co-4Al-2.5B) and D4FB (Ni-14Cr-10Co-3.5Al-2.5Ta-2.7B) were mixed with IN738 at ratios of 30, 40 and 50 wt. pct.

Through the cross sectioning of joints and the use of image analysis techniques of the TLP zone, small randomly distributed pores were discovered within the areas created between the additive particles, along with large irregular voids present in specimens with 30 wt. pct. of the filler metal (Figure 2.13). Su et al. concluded that pore formation stems from two root causes: Kirkendall porosity, where interdiffusion imbalances cause swelling in the additive particles and
deficit of liquid in the TLP zone; and an overspreading of the liquid through capillary flow creating pores at the prior low-temperature filler alloy particle sites. Both the Kirkendall porosity and the filler metal spreading porosity were linked to decreased amounts of the lower filler alloy and are further supported by the area fraction of porosity as calculated through image analysis, and as seen in Figure 2.14.

![Figure 2.13: Optical micrographs of brazed joints with 30 wt. pct. (left), 40 wt. pct. (center), and 50 wt. pct. (right) of the BRB filler metal. [23]](image)

![Figure 2.14: Percentage of porosity as a function of filler metal ratio.](image)
2.4 Effects of Braze Cycles on Nickel Brazes

As described in previous sections, the temperature at which the braze alloy must be held is vital to the formation of a braze with the desired mechanical properties. The microstructural effects of varied braze cycles were examined in multiple papers mentioned previously. These investigations also help to define the temperatures required to create the beneficial microstructural phases and to remove the detrimental phases.

Other than the selection of the interlayer material system, the selection of the braze cycle including the temperature and time controls the resulting microstructure and mechanical properties of the bond. Experiments performed by Duvall et al. examined the mechanical effects of varying bond temperature and times on the joint. [8]

As stated in earlier sections, the longer time and higher temperature allows for increased diffusion of the solute during the isothermal solidification and solid-state homogenization stages of the Transient Liquid Phase bonding process. This increased diffusion allows for the microstructure at the bond line to better mimic the structure and mechanical properties of the parent material. In order to quantify the effect of increase bonding temperature and time, Duvall et al. created a bond using the Ni-based superalloy Udimet 700 at three different temperatures and times: four hours at 2000°F, four hours at 2100°F, and 24 hours at 2125°F. Samples of the unbonded base metal were also exposed to the same thermal history in order to remove any irrelevant thermal effects to the base metal microstructure.

Both the bonded and unbonded samples were analyzed through stress-rupture tests and led to the calculation of joint efficiency, which can be found by dividing the results of the bonded samples with the results of the unbonded samples. The resulting joint efficiency can be seen in Figure 2.15. These experiments also verified the basic assumption that as the TLP bonds...
are held at higher bonding temperatures and longer times, the mechanical properties of the bond approaches those of the pure parent material.

As can be seen, the optimization of the bonding parameters is vital to the successful creation of the transient liquid phase bond. There have been a number of recent research projects from the University of Manitoba to examine alternative bonding parameters and the microstructural and mechanical response of the joint. [30] [29] [31] [32] It has been found that incorrect bonding parameters, where times are too short, or temperatures are too high, do not allow for full isothermal solidification. These incorrectly set bonding parameters ultimately lead to the stranding of a liquid phase within the bond plane, which, upon cooling, will solidify into a eutectic microstructure with a composition similar to the interlayer composition. These generally hard eutectic phases that form along the centerline of the bond are an undesirable constituent since they deteriorate the mechanical properties of the joint. The microstructural and mechanical

Figure 2.15: Joint efficiency in 1400°F/61 ksi stress-rupture tests for bonds between wrought Udimet 700 and cast IN-100 as a function of bonding condition. Joint efficiencies were calculated in reference to Udimet 700 base metal property requirements. [8]
response of a bond as the result of insufficient bonding time is illustrated in Figure 2.16, where the centerline eutectic that forms can clearly be seen.

Figure 2.16: Micrographs showing the effect of insufficient holding time on the centerline eutectic as indicated by the arrows (A-C). Graphs showing average joint microhardness values as the change with increased holding time (D). Joint is comprised of Haynes 282 and BNi-9. [30]

In the event that the bonding temperature is too high, the solidus line on the hypothetical binary eutectic system will be shifted too far toward the base composition side of the diagram that the equilibrium composition required for isothermal solidification may not be achieved. Both the microstructural and mechanical response for a superheated bonding process is identical to the response seen for insufficient bonding time (Figure 2.17). In both cases, the reduction of hardness is indicative of the reduction in the centerline eutectic microconstituent, which is the
ultimate goal when determining the brazing parameters. Therefore, the optimal brazing parameters in Figure 2.16 and Figure 2.17 at 1100°C for 60m and 1130°C for 60m, respectively.

Figure 2.17: Micrographs showing the effects of higher temperatures on the creation of centerline eutectic microconstituents as indicated by the white arrows (A-C). Graphs showing average microhardness values for joint (D). Joint is comprised of Haynes 282 and BNi-9. [30]

To further examine the effect of gap size and solute diffusivity, the following equations from Ghoneim et al. [30] can be used. In Equation 2.4, \( t_r \) represents the time required to complete the isothermal solidification stage of the bonding process, \( h \) represents the gap half-clearance, \( D \) represents the solute diffusivity, and \( \gamma \) is a dimensionless quality found by solving Equation 2.5 numerically. In Equation 2.5, \( C_\alpha \) and \( C_\beta \) represent the solute concentrations, boron for the purpose of this research, in the solid and liquid phases at the migrating solid-liquid interface, respectively, and \( C_m \) is the initial solute concentration in the base material. [30]
where \( C \) is estimated by solving the following equation numerically:

\[
\sqrt{t_f} = \frac{2h}{\gamma \sqrt{D}} 
\]

Equation 2.4

\[
\frac{C_a - C_m}{C_\beta - C_\alpha} = \gamma \sqrt{\pi} \exp(\sqrt{\gamma} (1 + \text{erf}(\gamma)))
\]

Equation 2.5

The model developed show that increased temperature will drastically increase the diffusion coefficient, \( D \), and therefore increase the rate of isothermal solidification. The bonding time required to complete isothermal solidification for a chosen material system, bonding temperature and gap geometry. As can be seen in Figure 2.18A. [30]

![Figure 2.18: A) Numerical simulation plots of half-width of liquid interlayer against holding time for different gap sizes at a constant temperature. B) Numerical simulation plots of the effect of solute diffusivity on deviation from parabolic relationship. Temperature set for both simulations is 1180°C (2150°F) [30]](image)

The resulting model shows a parabolic relationship between the size of the liquified region and the solidification time (Figure 2.18B). This model also explains a phenomenon where isothermal melting can occur if the brazed joint is held at bonding temperatures for too long and
the solute diffusion gradient reverse as predicted by the parabolic relationship. This phenomenon can be clearly seen in the micrographs shown in Figure 2.19. [29]

![Figure 2.19: A) Micrograph of eutectic-free joint prepared at 1180°C for 3h. B) Micrograph of joint prepared at 1180°C for 8h. The arrows point to eutectic microconstituents. [30]](image)

In the investigations by Yuan et al. [27] [28], the effect of time and temperature were also analyzed using microindentation procedures to observe the change in microhardness as the ISZ coarsened. Hardness traverses were performed on joints prepared at the same temperature for 60s with Ni-Cr-B (Figure 2.9) and Ni-Si-B (Figure 2.11), and for 3600s (Ni-Cr-B) and 300s (Ni-Si-B) (Figure 2.20). Looking at the difference in hardness profiles for the varying brazing times, evidence of the coarsening of the softer isothermal solidification zone (ISZ) and the reduction of the athermally-solidified zone (ASZ) is clear. It is also of value to note that the bonding affected zone (BAZ) did not see much of a change in hardness, therefore indicating that homogenization of the melting point suppressants did not result in the precipitation of any hardening intermetallic compounds.
Overall, it is clear that when diffusion of an element is required to promote isothermal solidification of the bonding alloy, the time and temperature of the brazing cycle to create the joint are paramount to the resulting mechanical properties and joint integrity. Since most wide gap brazing cycles are proprietary and not available in literature, microstructural analysis such as this work are often compared with the data gleaned from work dealing with the commercial low-temperature brazes.

Figure 2.20: Microhardness profiles of joints with Ni-Cr-B (top) and Ni-Si-B (bottom) filler alloys at varying brazing temperatures. Adapted from Yuan et al. [27] [28].
CHAPTER 3 EXPERIMENTAL PROCEDURE

The purpose of this thesis research was to develop and characterize experimental alloys for wide gap brazing and to examine the effects of different melting point suppressants on the resulting braze joints. The experimental composite braze alloys were created and their melting temperature and spreading behavior were characterized by isothermal spreadability experiments. The experimental alloys were brazed on two different substrates, type 304 stainless steel, that was used as a low-cost surrogate to initially screen and rank the experimental alloys, and a nickel-base superalloy, René 108™. The brazed joints were characterized mechanically using four-point bending and metallurgically using metallography and failure analysis. The thermal stability of the joints was also tested through aging treatments. The aged samples were characterized using the same methods as the as-brazed specimens. The results were analyzed and ranked using the “Ashby Method for Material Selection in Mechanical Design.” The full experimental methodology and overall procedure can be seen in Figure 3.1.

Figure 3.1: Experimental flow chart for series samples.
3.1 Experimental Braze Alloys

To examine the effects of boron and silicon in varying compositions, the commercially available nickel-base brazes BNi-2, BNi-5, and BNi-9 were selected as the braze alloy or low temperature (LTP) alloys for the wide gap braze. Each of the braze alloys were mixed with an additive powder, consisting of a commercially available nickel-base superalloy powder, MARM247. As stated earlier, the addition of the superalloy powder allows for nickel braze joints to maintain strength levels of 70 to 90 pct. of that of the parent material. At high temperatures, the braze joint requires clearances far beyond the maximum for pure nickel brazes. [2] The commercially available wide gap braze alloy, BRB, was used as a benchmark alloy to compare with the experimental alloys. The compositions for all powders used to create the experimental alloys can be seen in Table 3.1.

Table 3.1: The nominal composition of the commercial brazes and superalloy powders used with their AWS (and internal) designations. All values are in weight percent with the balance of the composition consisting of nickel. [33]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>B</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>Ti</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Mo</th>
<th>Ar</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>MARM247</td>
<td>0.02</td>
<td>0.15</td>
<td>5.40</td>
<td>0.06</td>
<td>1.0</td>
<td>8.7</td>
<td>0.05</td>
<td>10.1</td>
<td>0.7</td>
<td>0.05</td>
<td>10.1</td>
</tr>
<tr>
<td>BNi-2 (CSM-B)</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>4.2</td>
<td>-</td>
<td>7.0</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BNi-5 (CSM-C)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.0</td>
<td>-</td>
<td>19.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BNi-9 (CSM-A)</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>15.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BRB</td>
<td>2.5</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>13.9</td>
<td>-</td>
<td>9.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

These filler alloys were chosen to examine the effects of the melting point suppressants boron (BNi-9 and BNi-2) and silicon (BNi-2 and BNi-5). Since BNi-9 and BNi-5 contain similar
atomic compositions of chromium (14 and 18 at%, respectively), the different effects of boron and silicon can be clearly demonstrated. The BRB, baseline WGB braze alloy, contained all of the elements needed to form a superalloy including aluminum to form the \( \gamma' \) precipitate, boron to reduce the melting temperature, and cobalt to strengthen the \( \gamma \)-Ni phase. As a result of this compositional similarities, its use as a reference is reasonable.

For the initial tests with stainless steel as the substrate, the experimental alloy composition consisted of 30, 50, 70, and 100 wt. pct. of the three commercial brazes, with the balance of MARM247 as the additive powder. The BRB was used in its as-received form. The range of commercial braze alloy composition used for the René 108 samples was narrowed to 40, 50, and 60 wt. pct. following the results of the stainless steel experiments. Each alloy was mixed and then characterized through the use of an isothermal spreadability analysis including calculation of the percent spreading (Equation 3.1) and a spreadability index (Equation 3.2). [23] The variables in Equations 3.1 and 3.2 are defined as the initial area \( (A_0) \), the final area \( (A) \) and the contact angle \( (\theta) \) between the braze droplet and the substrate.

\[
S_\% = \frac{A}{A_0} \quad \text{Equation 3.1}
\]

\[
S_{index} = (A - A_0) \cdot \cos \theta \quad \text{Equation 3.2}
\]

### 3.1.1 Filler Metal Creation

The low-melting temperature alloy, and the additive powder were weighed using an ultra-high precision balance to a tolerance of 0.001g. The powders were then mixed in a small plastic jar for 5 minutes using a vibratory shaker. To verify homogenization, one of the filler metals was analyzed through backscatter electron images (BEI) taken using the scanning electron microscopy (SEM). The relative brightness of the MARM247 powder, because of the heavier
elements was used in the characterization. The two powders were found to mix uniformly. The mixed braze alloy powers were then manually mixed with 10 wt. pct. of a polymer binder in aqueous solution, known commercially as Vitta Braze BinderGel™, and kneaded in a small plastic sample bag. The corner of the plastic bag was then razored off to create a makeshift nozzle through which the wet braze paste could be applied to the test substrate. The bag was then sealed in an airtight plastic sample jar for storage purposes. The braze paste had a shelf life of approximately five weeks before it was unusable for any further experiments.

3.1.2 Isothermal Spreadability

The isothermal spreadability experiments were conducted to define what temperature would be required for the experimental alloys to properly flow and spread on each substrate. This set of tests was performed by taking a prepared sample plate, applied with consistent amounts of each of the experimental braze alloys, then heated in a simplified furnace cycle at varying braze temperatures. Each test was performed in a high vacuum ranging from 10\(^{-4}\) to 10\(^{-6}\) Pa (10\(^{-6}\) to 10\(^{-8}\) torr) to prevent widespread oxidation that would limit the spreading and flow of the experimental alloys.

Initially, flat sample plates of type 304 stainless steel and René 108, \(\frac{3}{8}\) inch thick, were scribed to divide each surface into one inch square sections. The surface of the stainless steel plates were ground to a 600 unidirectional grit surface finish and washed with a 10 vol. pct. Nital solution. The René 108 plates were initially blasted using the NicroGrit™ medium and then vacuum heat treated to 1200ºC (2192ºF) to burn off any impurities present on the surface of the sample that would inhibit wetting and therefore the spreading and the flow of the braze alloy. After preparation and cleaning of the surface was completed, the samples were handled with
gloves and placed into clean sample bags, which limited the exposure to environmental factors that could corrupt the integrity of the surface finish.

For the isothermal spreadability experiments using the stainless steel substrate, experimental alloys containing 30, 50, and 70 wt. pct. of BNi-2, BNi-5, and BNi-9 were tested, along with the benchmark BRB alloy. A dollop of each experimental braze paste, weighing approximately 0.4g, was placed in the center of a designated 1-inch square section on each of the five sample plates. The unmelted droplets were then photographed and the projected area of the droplet on the plane of the plate measured using image analysis. The samples were brazed at 1100, 1150, 1200, 1250, and 1300°C (2012, 2102, 2192, 2282, and 2372°F), respectively. Photographs of the test plate with the sample were taken of the melted droplets and the final areas were measured through image analysis.

The isothermal spreadability experiments using the René 108 substrate were performed in order to verify the temperatures previously determined for the 50 wt. pct. LTP braze alloys and to determine the temperatures for the 40 and 60 wt. pct. LTP alloys, not used during the stainless steel series. The same procedure utilized for the stainless steel substrate tests was followed, but the plates were brazed at 1200, 1225, and 1250°C (2192, 2237, and 2282°F), respectively according to the results from the stainless steel tests and to account for the narrowed composition range of the experimental alloys.

### 3.2 Brazing

The brazing procedure was developed based on the recommendations of similar studies in the literature and industrial practice. While the procedure differs between the nickel-base superalloy and stainless steel, both include the same basic steps. These approaches include the initial machining of the substrate; surface preparation to ensure cleanliness for proper wetting
and contact; a braze cycle; and post-braze examination, visual and radiographic, to verify that the braze alloy flowed and filled the gap properly with limited porosity.

### 3.2.1 Braze Plate Machining

The basic braze plate geometry consisted of a sample of the designated substrate with a groove at a depth equal to the desired final thickness of the bend test specimens. Plates of type 304 stainless steel were obtained and cut into 51 by 102 by 6.4 mm (2 by 4 by ¼ inch) plates, and a 1.5 by 4.8 mm (0.060 by 0.188 inch) groove was cut in the center of the plates using an abrasive saw. Plates of René 108 were initially cut into 25 by 76 by 2.0 mm (1 by 3 by 0.08 inch) samples with a 1.5 by 1.5 mm (0.06 by 0.06 inch) groove machined with Wire Electrical Discharge Machining (Wire EDM) from a stock slab provided by GE Power (Figure 3.2).

![Figure 3.2: Isometric drawing of stainless steel braze plate (left) and René 108 braze plate (right). Drawings made to scale.](image-url)
3.2.2 Surface Preparation

The cleanliness of the substrate surface was paramount to the success of any brazing operation. Impurities, such as oils, oxides, and grime, would disrupt the liquid-solid interface and could prevent the flow of the braze alloy over the substrate and into the joint. The following procedures were implemented to ensure that both the stainless steel and the René 108 substrates were cleaned and ready for brazing.

The machined plates of type 304 stainless steel were washed with a 10 pct. Nital solution and were handled with gloves to prevent the transfer of skin oils to the substrate. The sample plates were allowed to air dry. Once dry, experimental braze alloys were then applied to the machined groove and allowed to dry under a hot air dryer for ten minutes.

For René 108, the wire EDM process left a layer of material affected by the heat and the electrolytic fluid. To remove this layer of affected material and other impurities present on the surface of each sample, the plates were ablated using a NicroBlast™ grit media, which is a spheroidal nickel-chromium powder supplied by the Wall Colomonoy corporation, in a dedicated nickel blasting cabinet. Following the NicroBlast™ cleaning, each sample was then vacuum-heat treated for one hour at 1200°C (2192°F) and a pressure of 10⁻⁶ Pa (10⁻⁸ torr). As with the stainless steel samples, the samples were handled with gloves to prevent the transfer of skin oils following the heat treatment. The experimental braze alloys were then applied to the machined groove and dried under a hot air dryer for ten minutes.

3.2.3 Brazing Operations

The operation used to create the braze joints were performed in a high vacuum furnace set at a pressure of approximately 10⁻⁴ to 10⁻⁶ Pa (10⁻⁶ to 10⁻⁸ torr). A prescribed brazing cycle was then programmed into the furnace controller to execute each necessary brazing segment.
These furnace settings, used to perform the brazing operation, were essential for the spreading of the alloy and the diffusion of the melting point suppressants into the surrounding substrate and the additive superalloy powder. The standard brazing cycle used for wide gap brazing included a pre-heat segment; a braze segment; a diffusion segment; and a controlled-cooling segment returning to room temperature. The braze cycles used for the stainless steel and René 108 joints both included a 60-minute bake-out segment at 150°C (302°F) which was used to remove any residual moisture or impurities present in the vacuum chamber. The temperature of the brazing segment was set by the results of the isothermal spreadability experiments. The set temperatures for the other segments were either set according to standard industrial practices or calculated based on the maximum brazing temperature. The industrial standard set all of the ramp rates used in the cycle. While brazing for both the stainless steel and René 108 samples contained most of these standard features of the brazing cycle, the times and temperatures for each section differed due to the compositions of the braze alloys and the substrates.

3.2.3.1 Stainless Steel Braze Cycle

The simpler stainless steel braze cycle is shown in Figure 3.3. For these joints, the brazing segment was the only segment where the temperature was held for a period of time (30 minutes) and the diffusion segment was assumed to occur during either the brazing hold and/or the slow ramp-up, with a rate of 10°C/min (18°F/min). Following the brazing hold, the furnace was brought back to room temperature with the cooling segment, at a controlled rate of -12°C/min (-21.6°F/min).
The René 108 braze cycle was based off of a template brazing cycle, used as an industrial standard for wide-gap brazing. The long diffusion and aging segments of this braze cycle was to ensure the diffusion of boron and silicon into both the parent material and the additive superalloy powder (Figure 3.4).

Figure 3.4: Sample brazing cycle used for joints with the René 108 substrate. The bake-off segment has been omitted from this figure to simplify the brazing cycle.
In this cycle, the preheat ramp rate of 14°C/min (25°F/min) and first intermediate preheat hold temperature of 538°C (1000°F) were set independently of the brazing temperature. The second intermediate preheat hold temperature, however, was set at 75 pct. of the final brazing temperature. This protracted preheating segment ensured that both the braze alloy and the substrate reached thermal equilibrium before the brazing segment started. Following the second preheat hold, the temperature was ramped up to the designated brazing temperature at a rate of 14°C/min (25°F/min) and held at temperature for ten minutes. The temperature was then lowered below the braze solidus temperature, or approximately 15 pct. lower than the brazing temperature, at a slow rate (-2.75°C/min or -5°F/min) and held for five minutes. The diffusion hold temperature was set 10 pct. lower than the brazing temperature, and was reached following the controlled cooling segment by a ramp rate (14°C/min or 25°F/min), and was held for 120 minutes (two hours). The fast quench segment dropped the furnace temperature to a set 538°C (1000°F) at a rate of -42°C/min (-75°F/min) and the furnace was then brought up to the final aging temperature of 871°C (1600°F) at a rate of 14°C/min (25°F/min). The final aging segment lasted for 240 minutes (4 hours). The samples were then cooled to room temperature at a rate of 28°C/min (50°F/min).

3.2.4 Post-Brazing Examination

Following the furnace brazing operation, each joint was examined both visually and radiographically to ensure that there were no macroscopic cracking, pores, lack of spreading or flow. Visual examination of the sample braze plate was performed and documented by using a Nikon D50 camera with a high-magnification lens and camera stand. The radiographic examination was performed by placing each braze joint on a piece of high resolution D2
radiographic film and exposing it to X-rays for five minutes using a tungsten electrode source and a beryllium filter. Each image was initially examined using a light box. The images were then digitized using a professional Canon film scanner and saved as 16-bit Tiff files with a resolution of 2400 dpi. Quantification of porosity and other imperfections were made using the image thresholding and analysis feature in ImageJ software.

### 3.3 Sample Preparation

For all the mechanical and microstructural characterization activities, a four-point bend test sample bar was used following the specifications for the “Standard Method for Evaluating Braze Joints.” [34] Figure 3.5 and Table 3.2 show the dimensions of the type 304 stainless steel and René 108 specimens. The desired sample length was taken into account with the design of the grooved sample plates, leaving only the thickness and width of the bars to be machined. In order to achieve the desired sample thickness, both the type 304 stainless steel and the René 108 braze plates were ground using a machine shop grinder equipped with an electromagnetic chuck.

![Figure 3.5](image-url)  
**Figure 3.5:** Schematic drawings of four-point bend test bars as specified by AWS. [34]
The grinder removed the excess braze alloy (overfill) from the top of the plate and removed the substrate material under the groove, thus revealing the root of the braze. The stainless steel plates were then sectioned into the desired width through the use of an abrasive chop-saw and the René 108 plates were sectioned using Wire EDM.

Table 3.2: Sample dimensions and test fixture settings as specified. Adapted from AWS C3.2/M/3.2:2008 [34].

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Specimen Length, l (mm [in.])</th>
<th>Specimen Width, W (mm [in.])</th>
<th>Specimen Thickness, D (mm [in.])</th>
<th>Support Span, L (mm [in.])</th>
<th>Loading Span, L/2 (Mm [in.])</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (René 108)</td>
<td>25 [1.0]</td>
<td>2 [0.08]</td>
<td>1.5 [0.06]</td>
<td>20 [0.8]</td>
<td>10 [0.4]</td>
</tr>
<tr>
<td>B (SS 304)</td>
<td>45 [1.8]</td>
<td>4 [0.16]</td>
<td>3.0 [0.13]</td>
<td>40 [1.6]</td>
<td>20 [0.8]</td>
</tr>
</tbody>
</table>

3.4 Aging Experiments

To simulate in-service aging conditions, the experimental braze joints with René 108 substrate were aged using a prescribed treatment defined with temperatures and times often used in the design of turbine components: 754°C (1500°F) and 836°C (1750°F) for 20 and 100 hours.

As the René 108 series bend test bars had a small cross-sectional area (approximately 3 mm²), they were placed into a high vacuum to prevent widespread oxidation. The samples were baked for thirty minutes at 100°C (212 ºF) to ensure that all atmospheric impurities and surface oils were eliminated before the aging treatment began. The temperature was ramped up to the specified aging temperature, either 754°C (1500°F) or 836°C (1750°F), over a thirty-minute period. The samples were then held at the aging temperature for either 20 or 100 hours, and the temperature was brought to room temperature naturally in the vacuum. The atmosphere was not repressurized until the furnace reached room temperature.
3.5 Mechanical Testing

The joints were tested using a standard four-point bending method as specified by the American Welding Society C3 Committee on Brazing and Soldering. [34] Following the AWS specifications, the loading points of the sample test fixture (Figure 3.6) were set according to configuration A for the René 108 joints and configuration B for the stainless steel joints (Table 3.2). The loading point spacing was verified using calipers.

Figure 3.6: The four-point bending fixture used during the mechanical tests.

The four-point bend tests performed for this research were done only at room temperature, rather than at elevated temperatures, which is the standard testing method for braze joints with high service temperatures. Room temperature testing focused only on the relationships between strength, microstructures, and the different filler alloys. Further experimentation can be performed in the future to confirm and correlate the data with high temperature mechanical properties.

The number of specimens tested varied for each substrate and aging treatment series, due to the number of test samples machined from each sample plate. Five specimens were tested for all stainless steel series joints; eight specimens were tested for all René 108 series joints in the
as-brazed condition; and three specimens were tested for all René 108 series joints that underwent an aging treatment. Each individual specimen width and thickness were measured using microcalipers on either end of the joint and in the center; these values were averaged and catalogued for use in the data analysis.

An MTS Test frame was programmed to record the applied load (N), crosshead displacement (mm), and strain (%). The crosshead speed, connected to the upper loading points, was set at $1 \times 10^{-3}$ in./min (0.42 μm/s) for the stainless steel samples and $5 \times 10^{-4}$ in./min (0.21 μm/s) for the René 108 samples. This discrepancy in speed was due to the difference in stiffness of the two substrates and was done to increase the sample acquisition rate of the load cell. Since the René 108 deflects slower than the stainless steel, fewer data points would be obtained before failure if run at the same speed as the stainless steel specimens.

The samples were placed on the lower loading points of the sample fixture and centered on the rollers using a guide. The crosshead was then manually lowered until the load cell recorded a load above 1 N (0.225 lbf). A preprogrammed routine was run loading the test specimen until a characteristic drop in load greater than or equal to 80 pct. of the peak load. Once the drop was observed, the crosshead would be returned to its initial position and the joints that failed were collected for future failure analysis. A simplified schematic can be seen in Figure 3.7.

![Figure 3.7: Mechanical model of bend test set-up.](image-url)
3.6 Analysis of the Bend Test Results

Upon the completion of the four-point bend tests, the characteristic material properties were calculated through equations derived from the ASTM standards and basic trigonometry. The angular deflection (\( \theta \)), ultimate bending strength (\( \sigma_{UBS} \)), failure strength (\( \sigma^* \)), and the elastic modulus (\( E \)) were used to compare the performance of each alloy, and to relate the performance of the joints to the ductility of the experimental braze joints. All the equations used were based off of the values and geometries shown in Figure 3.8. [34]

![Figure 3.8: Schematic drawing of four-point bend test including all values used to calculate material properties, including: load (P), crosshead deflection (\( d_{ext} \)), vertical deflection (\( d_y \)), angular deflection (\( \theta \)), and lower loading point separation (L).][34]

3.6.1 Angular Deflection

Angular deflection was found by assuming that the deformation of the joint occurred linearly creating an obtuse triangle with vertices at each upper loading point of the four-point bend test fixture. The deflection angle (\( \theta \)) was calculated trigonometrically by taking the inverse tangent of the ratio of the crosshead displacement (\( d_{ext} \)) and the distance between the upper and lower loading points (\( L/4 \)) (Equation 3.3). [34]
\[
\theta = \tan^{-1}\left[\frac{d_{ext}}{L/4}\right]
\]
Equation 3.3

### 3.6.2 Stress and Strength

The stress imparted on the center of the braze joint by the test fixture was calculated using an equation taken from the ASTM standard [35] on four-point bending (Equation 3.4), where \( P \) is the load applied by the crosshead, \( L \) is the span between the two lower loading points, \( w \) and \( t \) are the width and thickness of the specimen. A value of stress was calculated for every load data point reported by the test frame and was used to determine the strength values for each experimental joint.

\[
\sigma = \frac{3PL}{4wt^2}
\]
Equation 3.4

Two different values for strength were reported for each bend test; the ultimate bending strength (\( \sigma_{UBS} \)), which was the maximum stress the braze joint endured; and the failure strength (\( \sigma^* \)), which represented the stress where the braze joint either yielded or underwent a brittle failure during elastic deformation. If the joint failed elastically, the failure strength was set equal to the ultimate bending strength. If the joint yielded and failed while undergoing plastic deformation, a 0.2 pct. yield strength was reported as the failure strength. The yield strength was calculated numerically by finding the interception point, the stress-strain data, and a line with elastic moduli as the slope and normalized to place the x-axis intercept at 0.2 pct. strain.
3.6.3 Elastic Modulus

The elastic modulus \((E)\) for each experimental joint was found by calculating the first derivative of the stress-strain data over a strain range of 0.1 to 0.4 pct.. The individual values for the instantaneous derivative were averaged together to find the value for the elastic modulus (Equation 3.5).

\[ E = \frac{1}{n} \sum_{i=0.1}^{n} \left( \frac{\partial \sigma_i}{\partial \varepsilon_i} \right) \]  

Equation 3.5

3.6.4 Alloy Ranking by Mechanical Property Optimization

The experimental brazes were ranked to optimize the material properties critical to the integrity of the joints, failure strength \((\sigma^*)\), and their elastic modulus \((E)\). They were ranked using the “Ashby Method for Materials Selection in Mechanical Design.” The Ashby method used a ranking index and plotted coupling lines derived from a model of the mechanical system. For the purposes of this experiment, a centered distributed load was imparted normal to the surface of a rectangular beam set on two loading points. The boundaries of the distributed load were set as the location of the two upper loading points (not shown) of the bend test fixture (Figure 3.7).

The objective of the ranking was to identify the alloy that exhibits the maximum elastic flexure of the beam, without the beam failing. A material index was determined for each braze by taking the equation for surface strain in bending (Equation 3.6) and the relationship between stress and strain in elastic deformation (Equation 3.7), and using them to solve for stress (Equation 3.8). The derived equation for stress was then solved for the bending radius \((R)\) and stress was substituted for the failure strength of the joint. This rearrangement and substitution formed an equation that indicated the maximum elastic flexure prior to the plastic failure of the
beam. The material index (M) was extracted from this equation and identified because it contained both strength and the elastic modulus to be optimized (Equation 3.9). The equation for the coupling line was found through use of the laws of logarithms and rearrangement into the standard equation of a line (Equation 3.10).

\[ \varepsilon = \frac{t}{2R} \]  
\[ \sigma = E\varepsilon \]  
\[ \sigma = E \frac{t}{2R} \]  
\[ R \geq \frac{1}{2} \left\{ \frac{E}{\sigma^*} \right\} \rightarrow M = \left[ \frac{E}{\sigma^*} \right] \]  
\[ \log(E) = 1 \cdot \log(\sigma^*) + \log(M) \]

Since there were no exponential quantities in the characteristic equation for the material index, the slope of the coupling line was one. These lines were then plotted along with the data on a log-log space, with failure strength on the x-axis and elastic modulus on the y-axis (Figure 3.9), and ranked according to their proximity to the lower-right corner of the graph (indicating high strength, low elastic modulus).

Figure 3.9: Schematic graph showing axes and coupling lines as determined through the Ashby analysis.
3.7 Microstructural Characterization

The microstructure of the as-brazed joints and the microstructural development of both the substrate and the braze joint during aging were essential to the understanding of the thermal stability and the resulting mechanical properties of the joint. To characterize the microstructure, the samples were taken through a set metallographic preparation procedure and analyzed with optical microscopy, scanning electron microscopy, and microhardness tests.

3.7.1 Metallographic Preparation

Despite the different substrates used for the braze joints, the same metallographic procedure was used on both the stainless steel and the René 108 samples because the braze alloy was the primary area of interest. The process used to prepare the metallographic samples was developed using recommendations from multiple sources. [36] [37]

3.7.1.1 Grinding and Polishing

The braze joints were initially cold-mounted in epoxy and taken through a rough grinding sequence of 120, 240, 320, and 600 grit with a LECO automatic grinder. The samples were then polished by hand with a 6 μm on a nylon cloth and 1μm diamond paste on a Lecloth™ with an alcohol extender for both. The final polishing was performed using a colloidal silica solution on Lecloth. All samples were thoroughly washed with detergent and rinsed with water and ethanol. Samples were also cleaned ultrasonically before the 1 μm and colloidal silica polishing sequences.

3.7.1.2 Etching

The samples were etched using glyceregia, a general purpose etch, for heat-resistant alloys. Glyceregia, which is essentially aqua regia with glycerol added, uniformly attacks the γ-
Ni matrix leaving the $\gamma'$ and other intermetallic compounds in relief. The etch was comprised of three parts hydrochloric acid (HCl), three parts glycerin ($C_{3}H_{8}O_{3}$), and one part nitric acid ($HNO_{3}$). The samples were etched by swabbing the surface with a soaked cotton ball for fifteen seconds, rinsed with distilled water and heat dried. This procedure over-etched the base metal, but left the braze, lightly, but adequately etched. The etchant decomposed quickly and needed to be disposed after each use, necessitating that fresh etchant needed to be prepared each time.

### 3.7.2 Optical Microscopy

Optical microscopy was used to help characterize the microstructure of each experimental braze alloys, and aging treatments. An Olympus PMG3 metallographic microscope equipped with a PaxIt™ microscope camera, was used to observe the microstructure and to record at least ten fields of view (FOV) for all experimental braze joints. Ten individual FOVs are the recommended number for any qualitative metallographic analysis to ensure high accuracy results. [37] The majority of the micrographs recorded were taken with a 200x total magnification (20x objective), and magnifications of 500x and 1000x were used when small intermetallic features, such as precipitated borides, silicides, or a $\gamma'$ eutectic microconstituent, needed to be resolved. Additionally, only the braze microstructures were characterized as the effect of the braze cycle on René 108 base metal was not the focus of this work Depending on the intent, future research can be performed to examine the effects of the brazing procedure on the bulk microstructure and properties of the substrates.
3.7.3 Quantitative Metallography

Manual point counting was used to determine the volume fractions of the individual microconstituents found in the experimental braze joints. The *ASTM Standard E562-11, Standard Test Method for Determining Volume Fraction by Manual Point Counting* [38] was followed. Using the image analysis software, ImageJ, a randomly placed 17x13 grid of 221 points was superimposed on each FOV. Each point was counted if one of the following zones was identified from SEM and EDS analysis: Additive Particle Interaction Zone (APIZ), along with the Matrix Phase and Intermetallic phases, which make up the Athermal Solidification Zone (ASZ). The average value for the volume fraction, the standard deviation, and the 95 pct. confidence interval for each of the microconstituent were calculated automatically on an Excel spreadsheet after the completion of every FOV. The counting continued until all 95 pct. confidence intervals were below one pct. and at least five FOVs had been analyzed for each sample.

In order to quantify the changing microconstituents of the aged sample microstructures, the change in area ($\Delta A$) were calculated by taking the area fractions of each of the quantified microconstituents for the aged samples and finding the difference with the as-brazed samples. The overall change of each individual alloy and aging treatment ($\Delta A_{\text{max}}$) was found as the absolute value of the largest value of $\Delta A$ and then averaged to find the value of $\Delta A_{\text{avg}}$ for an individual alloy or aging treatment. The quantity $\Delta A_{\text{max}}$ acted as an index to quantify the thermal stability of the microstructures during the aging treatments.
3.7.4 Microhardness

Vickers microhardness traverses that were taken on both the stainless steel and the René 108 samples. All microhardness tests were performed using mounted, polished, and etched metallographic samples; indents were made with a 200 gmf load and a ten second dwell time. All joints were tested with three traverses that were made 0.01 inches apart. The joints with the stainless steel substrate were fully traversed with an indent every 0.005 inches, allowing for 12 indents in the braze joint and three indents past the interface into the substrate. Joints with the René 108 substrate were performed 0.01 inches apart starting at the centerline of the joints, with four indents in the braze and three indents past the interface into the substrate. A schematic of the indents taken can be seen in Figure 3.9.

Figure 3.10: Schematic of microhardness traverses performed for stainless steel samples (left) and René 108 samples (right). Drawings are internally to scale, as defined by the dimensions included.

The reported values for braze microhardness were calculated by averaging all of the values taken from the braze and the traverse profiles were taken by averaging the corresponding values by location in the braze. The average hardness values for each microconstituent zone was found by averaging the values of all intents taken each zone.
3.8 Failure Analysis

The failure analyses used during the course of this experimental program were purely qualitative and involved visual inspection of the fracture surface and fractography. After the bend test, each of the failed test bars were characterized through visual inspection. The fracture locations were characterized as either an interface failure, where the fracture occurred along the interface between the braze and the substrate, or a braze failure, where the fracture occurred within the braze alloy itself. Under 10x magnification, the failures were then characterized as intergranular or transgranular. Fractographs were taken of a representative sampling of fracture surfaces with different features and locations. The fractographs were documented using a Nikon D300 with a macro lens mounted on a camera stand with oblique lighting, and using scanning electron microscopy.
CHAPTER 4 RESULTS AND DISCUSSION

This chapter will examine and discuss the results collected throughout this research, including: isothermal spreadability, joint integrity, metallurgical analysis, mechanical properties, failure analysis, and aging effects. These results allow for an in-depth look into the behavior of the constituents of the alloy systems and how they affect the mechanical performance of the joint.

4.1 Isothermal Spreading Analysis

The characterization of braze alloy spreading and the determination of the brazing temperature is essential to the brazing cycle and the successful creation of a braze joint. The spreadability index quantifies the amount of spreading that the alloy undergoes at specific temperatures, and allows for the determination of the brazing temperatures required for each experimental alloy.

During the spreadability experiments, there were four types of droplet morphologies observed: unmelted, non-uniform, uniform, and over-spread. The unmelted droplet had very little powder interaction and the only change from the initial braze droplet was the vaporization of the braze binder, resulting in a solid identical in appearance to the initial condition. A non-uniform morphology showed a droplet with limited powder interaction and spreading, however, the initial droplet remained identifiable in the center of the spread material. In the uniform spreading case, the droplet has completely spread and the initial droplet is no longer identifiable within the mass; this was the desired result and determined the optimum brazing temperatures. For over-spread, the low-temperature powder is drawn out of the droplet mass due to capillary interaction with the substrate and creates a halo of affected material surrounding the braze drop. The LTP halo was also observed to occasionally cause the mass to drifting away from the initial droplet site. A
representative result of each of the morphologies, as seen during the tests, can be seen in Figure 4.1. In this image, the LTP halo can be seen to begin to form surrounding the uniform morphology and the halo encompasses the entire field of view in the over-spread case.

![Figure 4.1](image)

Figure 4.1: A representation of each morphology, as seen during the isothermal spreadability tests using the stainless steel substrates with the droplet boundaries indicated.

### 4.1.1 Spreadability Index

The spreadability index, determined by finding the change in area for each alloy when held at a set temperature, was used to quantify the molten alloy behavior at temperatures. It was found that, in general, as the amount of LTP in the alloy decreased, the amount of spreading for a given temperature decreased. For 70 wt. pct. LTP alloys that exhibited greater amounts of spreading, a critical spreading point existed was reached beyond which droplet spreading remained constant, independent of the brazing temperature. The positive relationship between temperature and composition, along with the critical spreading point for the 70 wt. pct. LTP alloys can be seen in Figure 4.2.
Figure 4.2: Relationship between brazing temperature and the change in area during isothermal spreadability experiments performed with type 304 stainless steel substrate. Droplets are colored based on their morphology, as indicated by the key above the graphs.
The 70 wt. pct. BNi-9, and BNi-5 alloys reached the critical spreading point at 1150°C, and 1250°C, respectively. The critical spreading point for the 70 wt. pct. BNi-2 alloy was not determined, as the range of temperatures tested already exceeded the critical spreading point for this alloy. The critical spreading temperature for the 50 wt. pct. BNi-9 alloy was also reached at 1250°C, as seen by the slight decrease in spreading between the 1250 and 1300°C values. The fact that BNi-9 had the lowest melting point of any of the other commercial braze alloys at 1070°C was probably the contributing factor as to why the 50 wt. pct. BNi-9 alloy is the only alloy, beyond the alloys containing 70 wt. pct. LTP, that reached the critical spreading point. The critical spreading temperature was not reached for most alloys with less that 70 wt. pct. LTP, of the limitations of the furnace and the melting point of the substrate. The BNi-5 alloy was seen to exhibit the most normal behavior, with a linear increase in spreading with temperature and a decrease in initial spreading temperature as the LTP composition is increased. This behavior was due to the fact that the melting point of BNi-5 is the highest of any of the commercially available braze alloys used during this research (1150°C as compared to 1130°C for BNi-2 and 1070°C for BNi9). The greater LTP melting temperature requires an increased amount of heat to melt and spread, therefore forcing the experimental alloy to become more dependent on the brazing temperature. Conversely, BNi-2 and BNi-9 require lower temperatures to spread, resulting in earlier spreading and a larger range in which the alloys can spread.

In all cases the contact angle between the braze alloy and the substrate were negligible, due to the creation of an LTP halo surrounding the alloy, and were therefore not used in the calculation of the spreadability coefficient, traditionally used in this type of analysis and testing. The data resulting from the René 108 isothermal spreadability experiments were not analyzed
quantitatively due to an error in the preparation of the sample plates and the braze temperatures were instead determined based on qualitative observations of the alloy spreading.

4.1.2 Braze Temperature Determination

As stated earlier, the brazing temperature for each alloy was determined through a combination of qualitative observations of the braze droplets following the isothermal spreadability experiments and quantitative analysis of the critical spreading point as established

![Figure 4.3: Isothermal Spreadability results for type 304 stainless steel series samples. The droplets shown represent the brazing temperatures as selected for each alloy.](image-url)
through the spreading index. Qualitatively, the temperatures that were picked were the lowest temperature that the droplets were observed with the uniform spreading morphology, showing good flow, with no visible center mass and a limited LTP halo. Images of the spreadability droplets for each alloy at the chosen temperatures can be seen in Figure 4.3. The 70 wt. pct. BNi-2 alloy presented uniform spreading morphology in a wide temperature range (1100 to 1250°C). The 1150°C was chosen instead of 1100°C because the droplet for 1150°C temperature looked the most intact and the higher temperature agreed with the brazing temperatures set for the 70 wt. pct. BNi-9 and BNi-2 alloys.

![Figure 4.4](image)

Figure 4.4: Determined brazing temperature for experimental WGB alloys used with stainless steel substrate.

For the temperatures determined for stainless steel (Figure 4.4), the brazing temperature \( T_{\text{brz}} \) can be roughly approximated using Equation 4.1, where \( x_{\text{LTP}} \) is the weight fraction of the LTP powder in the alloy and \( T_{\text{m}}^{\text{HTP}} \) is the melting point of the high temperature powder (additive superalloy; HTP) in Celsius. Equation 4.1 was developed empirically for the purposes of this experiment. It should be noted that temperatures above 1250°C (2325°F) exceed the solutionizing
heat treatment temperature of MARM247 and were therefore considered to be detrimental to the microstructure of the base metal. [39] As a result of this substrate temperature limit, the 30 wt. pct. LTP alloys, which required 1300°C (2372°F) to spread, were removed from the experimental matrix for the René 108 experiments.

\[
T_{\text{brazed}} = \frac{-1000}{3} \cdot x_{\text{LTP}} + T_{\text{mHTP}} \quad \text{Equation 4.1}
\]

The brazing temperatures used for alloys with the René 108 substrate (40, 50, and 60 wt. pct. LTP) were set using only qualitative methods (as found in the appendix, Figure A.1 pg. 133), due to experimental errors regarding the sample plates. The experimental matrix of temperatures was also smaller, thus resulting in fewer points to quantitatively analyze. All of the BNi-9 alloys and the 50, 60 wt. pct. BNi-2 alloy were determined to require 1225°C (2237°F), while the 40 wt. pct. BNi-2 and all BNi-5 alloys were brazed at 1250°C (2282°F).

### 4.2 Joint Integrity

To ensure a braze integrity braze joint, each completed braze was examined visually and radiographically. These examinations resulted in visual classifications of brazing issues relating to improper brazing technique and a calculation of internal porosity within each braze joint.

By and large, the brazes that were created experimentally resulted in a sample that exhibited good flow, wetting, and groove fill. However, a number of the brazes were rejected due to visual defects caused by improper brazing technique, including: insufficient brazing temperature, where the braze does not become molten and cracks due to the lack of interaction between the HTP and LTP particles; excessive brazing temperature, where the braze over-spreads and flows out of the intended braze groove; and insufficient braze alloy, where the braze
alloy wets to the sides of the groove, rather than the top surface of the braze plate, creating a concave fillet (Figure 4.5). All of these samples were rejected and proper corrective actions were taken to ensure a good sample could be obtained.

4.2.1 Porosity

As stated in previous sections, porosity is a likely byproduct of the wide gap brazing process, and has proven to be difficult to mitigate. Radiographic examinations of the René 108 series braze joints allowed for the identification and analysis of porosity (Figure 4.6). It was found that as the LTP composition of the braze alloy decreased, the area fraction of porosity detected also decreased (Figure 4.7).

During metallographic analysis, two categories of porosity within the braze matrix were identified: irregular and spherical (Figure 4.8). The irregular porosity indicated that pores were created due to the removal of the braze alloy through capillary action, vacating the prior LTP particle sites, and were also affected by Kirkendall swelling. Larger spherical pores, ranging in

Figure 4.5: Examples of failed braze groove samples and the reasons for rejection. Samples were made with stainless steel and measured four inches long.
size from approximately 1µm-1mm (0.04-40 mils), were most likely caused by entrapped gas. This gas was caused by air entrapped in the paste mixing process, the vaporizing binder, or elements (nickel in particular, as identified by its high vapor-pressure at the brazing temperatures) in the high vacuum atmosphere used during brazing.

Figure 4.6: Radiographs of the best (A: 60 wt% BNI-9), median (B: 60 wt% BNI-2), and worst (C: 30 wt. pct. BNI-5) amounts of porosity (indicated in red). These samples were created with René 108 and are 7.6 cm (3 in) long.

Figure 4.7: Internal porosity as a function of LTP composition within the braze alloy.
Figure 4.8: Micrograph showing a representation of irregular and spherical pores as indicated by the symbols in the legend. The matrix phase appears as a darker grey, whereas the superalloy particles appear lighter. Image taken from an as-polished metallographic sample of the braze alloy with 50 wt. pct. BNi-5 on a type 304 stainless steel substrate; brazed at 1250°C.

The relationship between the braze alloy composition and porosity was likely due to the high amounts of the additive superalloy powder, which limited the mixing and flowability, as the solid particles were suspended in less of the molten braze alloy. In the low LTP alloys, the molten braze was prevented from flowing into the pores, as formed through capillary and Kirkendall porosity. Another possibility, as described by Su et al. [26], indicated that the swelling of the additive superalloy particles would have consumed the liquid, leaving voids, rather than having the liquid mechanically constrained.
In the case of the entrapped gas porosity, the gas was unable to leave the braze due to mechanical inhibitions resulting from the limited amount of liquid within the braze joint to allow for particle mobility. Additionally, traditional shrinkage porosity was another potential cause of pores within the athermally-solidified material. Shrinkage porosity is likely to occur if the composition of the molten braze has a large solidification range, indicating that shrinkage porosity may occur in regions where the composition of the melting point suppressant is depleted in the liquid. This effect is further supported by the experimental trend observed, since the higher LTP alloys have a larger amount of the melting point suppressant in the composition, indicating that it would be more likely that the molten material composition is closer to the eutectic point, limiting the solidification range and therefore shrinkage porosity.

4.3 Metallurgical Analysis

The microstructural analysis of the experimental wide gap braze alloys, combined with published results in literature, allowed for the characterization and generalization of the solidification process. The resulting microstructures described in this document.

4.3.1 Braze Solidification Sequence

To fully understand the microstructures of each braze joint, each stage of the solidification sequence and the corresponding metallurgical driving forces must be understood. Figure 4.9 shows the segment of the René 108 used during this research where the major solidification events occur spanning from the initial heating of the braze to the thermal quench directly following the main brazing segment. The full braze cycle used for the René 108 samples can be seen in Figure 3.4 on page 42. Figure 4.10 shows the five stages of solidification
determined for the purposes of this experiment: 1: Initial Condition (unmelted braze), 2: Melting of LTP, 3: Densification, 4: Isothermal Solidification, and 5: Final (Athermal) Solidification.

Figure 4.9: Time and Temperature diagram of solidification stages during the René 108 braze cycle.

Figure 4.10: Simplified and generalized solidification sequence during the brazing process including, 1: Unmelted, 2: LTP Particles Melt, 3: Densification, 4: Isothermal Solidification, and 5: Final (Athermal) Solidification. The resulting individual microconstituents in stage 5 are examined in-depth in Figure 4.11.
Initially, in stage one, both the low temperature powder (LTP) and additive superalloy (high temperature powder; HTP) are in suspension with the braze binder, which vaporizes at 100°C (212°F); the powdered alloys are considered to be a homogenized mixture. During this stage, the alloys are heated slowly in preparation for the subsequent stages.

In stage two, the brazing temperature is brought above the liquidus temperature for the LTP alloy and a molten matrix is created with the HTP particles in suspension. In stage three, densification occurs where the HTP particles are drawn closer to each other as the liquid matrix moves, through capillary interactions, to fill any voids or unfilled areas left during the stage two. Densification also occurs through coalescing of the HTP particles through particle sintering and local melting due to the Gibbs-Thomson effect. During stage two and three, the melting point suppressants (MPS; boron and/or silicon) begin to diffuse into the HTP particles, thus lowering their composition in the molten LTP matrix.

Stage four begins once the composition of the matrix bordering the HTP particles reaches the liquidus line of the L+Ni region while the system is held at the brazing temperature. This continuous compositional shift allows for a solidification front to form at the surface of the HTP particles and to expand into the molten matrix. The isothermal solidification continues until the bulk melting point suppressant composition is brought below the liquidus line or the system drops below the eutectic temperature. This solidification process also leaves a region of melting point suppressant-lean liquid surrounding the solid-liquid interface.

In stage five, the remaining liquid, saturated with the melting point suppressant when the eutectic temperature is reached, will undergo a rapid athermal solidification creating a ternary eutectic microconstituent between the solidification fronts and melting point suppressant-lean regions. Intermetallic phases comprising of the melting point suppressant will undergo solid-state
precipitation in the center of the original additive particles, as a result of the increased composition. Using a simple diffusion model based on Fick’s First Law to estimate the diffusion distance of the melting point suppressant into a pure nickel substrate during the braze cycles at 1200 and 1250°C, it was found that the boron and silicon, with calculated diffusivities of $2.82 \times 10^{-14} \text{ m}^2/\text{s}$ and $1.18 \times 10^{-26} \text{ m}^2/\text{s}$ respectively, can diffuse a maximum of 14 mm (0.55 in.) and 1.4 mm (0.06 in.) respectively. This diffusion calculation indicates that the MPS has the ability to fully diffuse into, and saturate, the HTP particles during brazing.

Figure 4.10 is a simplified solidification schematic developed through empirical observations made during the course of this research, and was supplemented by partial observations and conclusions made by Su et al. [23] [26], Yuan et al. [27] [28], Pourvarni et al. [24], Demo et al. [25], and Migletti. [3] [22]. This solidification schematic assumes that the initial morphology of additive powder (or HTP) particles remain relatively unaffected by erosion throughout the brazing procedure, where as discussed in section 4.3.2 (pg. 71), this lack of interaction and erosion is distinctly not the case. In reality, the HTP powder particles undergo size and distribution changes through erosion as a result of the diffusing melting point suppressant. This effect can be seen by the fact that the APIZ observed and quantified were larger than the initial MARM247 additive powder particles, which were measured to have an average cross-sectional area of 31 μm². In comparison, the APIZ were found to have an area of approximately $2 \times 10^3$ to $2 \times 10^5$ mm², that can contain over 600 additive particles in one APIZ. The additive particle interaction zones were also found to be contiguous, creating a serpentine pattern across the microstructure of the joint, reinforcing the idea that the additive particles are interacting beyond the simple isothermal solidification. These microstructures will be shown and discussed in more detail in the following sections.
The assumption is also made that the low temperature powder becomes completely molten during the first two segments of the braze cycle and therefore neglects any effects resulting from a semi-liquid LTP matrix, for example, the creation of pores or Kirkendall swelling as discussed in previous sections. Additionally, the melting point suppressants, will already begin to diffuse during the initial heating of the braze joint considering the long time at high temperatures. This diffusion will further increase the interaction between the additive powder particles.

### 4.3.2 Braze Alloy Microstructures

To assist with the characterization and analysis of the braze microstructures; microconstituent zones were identified based on their solidification behavior or particle origin (Figure 4.11). The identified origin zones are the additive powder interaction zone (APIZ) and the filler metal zone (FMZ and referred to as the TLP zone by Su et al. [23]). The transient liquid phase zone (TLPZ) defines the area that is affected by the solute depletion during isothermal solidification and encompasses both the FMZ and the APIZ.

The solidification zones, as classified, are the isothermal solidification zone (ISZ), the athermal solidification zone (ASZ), and the solid diffusion zone (SDZ). It should be noted that there is overlap with zones from both categories, as the APIZ contains the SDZ and the ISZ, the TLPZ and the APIZ overlap to create the ISZ, and the ASZ contains a portion of the TLPZ and the FMZ. These zones are shown schematically in Figure 4.11.

Within these zones, microconstituents have been identified: the eutectic ternary matrix (A), the melting point suppressant-depleted halo (B), the affected superalloy particles (C), and Ni-solution (D); each microconstituent is identifiable in all of the experimental braze alloys. The
parent braze alloy (LTP) heavily influences microconstituents contained within the ASZ, and the microstructural characterization and analysis are therefore based on the identification of phases created and affected by the melting point suppressant: boron (BNi-9 and BNi-2) and silicon (BNi-5 and BNi-2).

The full microstructure of a René 108-series braze joint is in Figure 4.12, where each of the identified zones and individual microconstituents can be seen. In this joint, the isothermal solidification zone can be seen surrounding the braze groove, where the diffusion of the melting point suppressant into the substrate allowed for the solidification of the solid nickel phase (red inset). The extent of the coalescence of the additive powder particles, as discussed earlier, can also be observed to have formed into the large irregular APIZ areas that measured 0.5 mm across in places. The characteristic eutectic solidification pattern of the athermal solidification zone can be clearly seen throughout the overall joint and magnified in the blue inset.

Figure 4.11: Microstructural zones (right top) and the phases (right bottom) as based on the solidification stages (Figure 4.10). The corresponding zones as shown on an optical micrograph (left) of the braze alloy containing 50 wt. pct. BNi-9 and René 108 substrate.
Figure 4.12: Optical micrograph showing full as-brazed 50 wt. pct. BNi-9 microstructure and specific magnified regions as identified by the inset squares. Individual microconstituents and zones are identified with numbers according to the key.
A layer of intermetallic compounds can be seen close to substrate reaction layer; they can also be unmelted impurities present on the groove surface and remained within the braze as the molten alloy eroded the substrate. These phases are indicated in Figure 4.12 by a red arrow in the red inset. These compounds were not characterized, but this layer is believed to represent the previous braze groove dimensions. The joint interface is sloped away from the center as a result of the interaction with overfill alloy present above the braze joint and removed during machining.

### 4.3.2.1 BNi-9-based Braze Alloy Microstructures

The BNi-9 alloy is composed nominally of 3.5 wt. pct. (16.18 at. pct.) boron, 15 wt. pct. (14.42 at%) chromium, and nickel makes up the balance of the composition (81.5 wt%. or 69.40 at%). The diffusion of boron into the additive powder and the erosion of the additive powder into the molten liquid in stage 3 of solidification controls the microstructures of the BNi-9-series braze alloys. This assumption was confirmed through the use of energy dispersive spectroscopy.

Unfortunately, due to the low atomic weight of boron, no x-rays were collected indicating its presence and the individual spectra were not quantified. Despite this limitation, it was found that the ternary eutectic matrix (M) was composed of nickel (1), Ni₃B (2) and a chromium boride, most likely Cr₂B₃ (labeled as 3 or IM) (Figure 4.13; Table 4.1).

The APIZ (A) comprised of nickel with elements from the erosion of the HTP particles (W, Al, Ti and Co). Intermetallic compounds (IA) resulting from the solid diffusion of boron, dispersed through the APIZ, were most likely nickel borides, however it could not be confirmed, since boron was undetectable and the precipitate phases are smaller than the x-ray interaction volume.
Table 4.1: Chemical compositions (at. pct.) of microconstituent zones for braze containing 50 wt. pct. BNi-9 as identified in Figure 4.13

<table>
<thead>
<tr>
<th>Element</th>
<th>Matrix (M)</th>
<th>APIZ (A)</th>
<th>Matrix IM (IM)</th>
<th>APIZ IM (IA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.75</td>
<td>4.41</td>
<td>0.01</td>
<td>6.23</td>
</tr>
<tr>
<td>W</td>
<td>1.10</td>
<td>1.35</td>
<td>1.67</td>
<td>1.53</td>
</tr>
<tr>
<td>Ti</td>
<td>1.19</td>
<td>1.45</td>
<td>0.37</td>
<td>0.38</td>
</tr>
<tr>
<td>Cr</td>
<td>18.14</td>
<td>6.19</td>
<td>91.74</td>
<td>10.70</td>
</tr>
<tr>
<td>Co</td>
<td>5.99</td>
<td>6.38</td>
<td>2.25</td>
<td>6.19</td>
</tr>
<tr>
<td>Ni</td>
<td>69.82</td>
<td>80.22</td>
<td>5.61</td>
<td>74.97</td>
</tr>
</tbody>
</table>

Figure 4.13: Scanning electron microscope analysis of the braze containing 50 wt. pct. BNi-9 with the René 108 substrate was brazed at 1225°C (2237°F). Letters indicates analyzed bulk phases and numbers indicates phases comprising the ternary eutectic.

4.3.2.2 BNi-2-based Braze Alloy Microstructures

The nominal composition of BNi-2 is 4.2 wt. pct. (7.38 at%) silicon, 7 wt. pct. (6.64 at%) chromium, 3 wt. pct. (13.7 at%) boron, 3 wt. pct. (2.65 at%) iron, and the balance of the
composition of nickel (82.8 wt. pct. or 69.62 at. pct.). The BNi-2-based alloy microstructures were the most complex of all of the alloys used, due to the existence of two melting point suppressants (boron and silicon) and the addition of iron. Like the BNi-9 based alloys, the microstructures were controlled by the diffusion of the melting point suppressants; promoting isothermal solidification and the coarsening of the APIZ, and forming intermetallic compounds in the ternary eutectic matrix during athermal solidification. Once again, the composition of boron in the braze alloy eluded detection or quantification due to the low atomic weight and the limitations of the EDS system used.

The microconstituents and phases of the BNi-2-based alloys were identified by morphology and confirmed through EDS analysis (Figure 4.14; Table 4.2). The ternary eutectic matrix (M) was found to contain nickel (1), Ni3(Si, B) (2) and two species of intermetallic compounds, chromium silicide (3 or IM) and a chromium boride (4 or IM-2). The isothermally solidified APIZ contains the nickel phase (A) and an intermetallic precipitate (IA). No definitive identification of the intermetallic species can be made due to the size of the particle in relation to the interaction volume and the inability to detect boron. It is also clear that erosion of the

<table>
<thead>
<tr>
<th>Element</th>
<th>Matrix (M)</th>
<th>APIZ (A)</th>
<th>Matrix IM (IM)</th>
<th>Matrix IM Dark (IM-2)</th>
<th>APIZ IM (IA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.86</td>
<td>7.16</td>
<td>0.28</td>
<td>0.35</td>
<td>6.27</td>
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<tr>
<td>Si</td>
<td>7.35</td>
<td>6.48</td>
<td>34.82</td>
<td>2.54</td>
<td>11.25</td>
</tr>
<tr>
<td>Ti</td>
<td>1.65</td>
<td>6.41</td>
<td>0.35</td>
<td>0.37</td>
<td>0.27</td>
</tr>
<tr>
<td>Cr</td>
<td>3.55</td>
<td>7.07</td>
<td>47.70</td>
<td>87.15</td>
<td>9.40</td>
</tr>
<tr>
<td>Fe</td>
<td>1.01</td>
<td>2.15</td>
<td>1.14</td>
<td>1.73</td>
<td>2.04</td>
</tr>
<tr>
<td>Co</td>
<td>6.00</td>
<td>5.60</td>
<td>3.57</td>
<td>2.25</td>
<td>5.77</td>
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<tr>
<td>Ni</td>
<td>76.58</td>
<td>71.13</td>
<td>12.12</td>
<td>5.61</td>
<td>64.99</td>
</tr>
</tbody>
</table>
additive superalloy particles into the liquid phase during brazing occurs, as shown by the presence of titanium, aluminum and cobalt across the bulk of the braze alloy.

4.3.2.3 BNi-5-based Braze Alloy Microstructures

The nominal composition of the BNi-5 is 10 wt. pct. (18.44 at%) silicon, 19 wt. pct. (18.92 at%) chromium and nickel (71 wt% or 62.6 at%). For BNi-5-based braze alloys, silicon is the melting point suppressant, which therefore controls the isothermal solidification and the ternary eutectic matrix that results from the athermal solidification. It was found that the ternary eutectic matrix (M) (Figure 4.15; Table 4.3) was comprised of a nickel silicide (1), a nickel solid solution (2), and two types of intermetallic compounds: a chromium silicide (IM or 3) and nickel silicide (IM-2 or 4). The APIZ was comprised of a nickel solid solution (A) with nickel silicide precipitated with a needle-type morphology (IM-2).

Figure 4.14: Scanning electron microscope analysis of the braze containing 50 wt. pct. BNi-2 with the René 108 substrate was brazed at 1225°C (2237°F). Letters indicates analyzed bulk phases and numbers indicates phases comprising the ternary eutectic.
As with the BNi-9 and BNi-2 alloys, there is clear evidence of superalloy erosion during the brazing process, however the chemical composition for the BNi-5-based alloy is much more homogenized than the other two. This more unified composition is probably the result of either higher brazing temperature required for the BNi-5 alloys or the greater solid solubility of silicon in nickel in comparison to boron into nickel.

![Figure 4.15: Scanning electron microscope analysis of the braze containing 50 wt. pct. BNi-5 with the René 108 substrate was brazed at 1250°C (2282°F). Letters indicates analyzed bulk phases and numbers indicates phases comprising the ternary eutectic.](image)

Table 4.3: Chemical compositions (at. pct. of microconstituent zones for braze containing 50 wt. pct. BNi-5 as seen in Figure 4.15.

<table>
<thead>
<tr>
<th>Element</th>
<th>Matrix (M)</th>
<th>APIZ (A)</th>
<th>Matrix IM (IM)</th>
<th>Matrix IM (IM-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>9.66</td>
<td>7.41</td>
<td>3.96</td>
<td>7.37</td>
</tr>
<tr>
<td>Si</td>
<td>14.11</td>
<td>14.14</td>
<td>11.55</td>
<td>16.58</td>
</tr>
<tr>
<td>Ti</td>
<td>0.76</td>
<td>0.70</td>
<td>0.42</td>
<td>0.88</td>
</tr>
<tr>
<td>Cr</td>
<td>4.43</td>
<td>7.12</td>
<td>14.50</td>
<td>4.24</td>
</tr>
<tr>
<td>Co</td>
<td>3.46</td>
<td>3.53</td>
<td>5.82</td>
<td>3.33</td>
</tr>
<tr>
<td>Ni</td>
<td>67.58</td>
<td>67.09</td>
<td>60.76</td>
<td>67.60</td>
</tr>
</tbody>
</table>
4.3.3 Microstructural Phase Trends

The solidification zones and microconstituents identified, evolve with the increase of amount of LTP present in the braze powder. The trends, as calculated through extensive point counting of the joint microstructures of the René 108-series, reveal how the microstructure of each alloy series is affected by the amount of filler metal used. This analysis will also be used to relate mechanical properties and resulting failure types to the microconstituents and solidification zones.

Figures 4.16, 4.17, and 4.18, show the joint microstructures and the evolution of the microconstituents and solidification zones of the BNi-9, BNi-2 and BNi-5 series alloys respectively. In general, as the amount of initial additive powder/HTP composition increases, the amount of additive powder interaction zones increase. Additionally, the amounts of the ternary eutectic matrix and the intermetallic compounds increase as the initial LTP composition increases.

This effect can be seen further by the graphs showing the evolution of the isothermal solidification zone (ISZ; equivalent to the APIZ) and the athermal solidification zone (ASZ; the ternary eutectic matrix and the intermetallic compounds), where the ISZ area decreases and the ASZ area increases for all three filler metals as the LTP composition increases. These general trends make metallurgical sense as the larger amounts of molten filler metal results in an excess of diffusing species, leading to a higher amount of liquid that athermally solidifies into the ternary eutectic matrix and the intermetallic compounds.
Figure 4.16: Optical micrographs of BNi-9 series braze alloys with: 40 wt. pct. (A), 50 wt. pct. (B) and 60 wt. pct. (C) BNi-9. Microconstituents are identified as: APIZ (1); Ternary Eutectic Matrix (2); and Intermettalic Phases (3). Bottom: Microstructural phases (D) and solidification zones (E) by the LTP composition.
Figure 4.17: Optical micrographs of BNi-2 series braze alloys with: 40 wt. pct. (A), 50 wt. pct. (B) and 60 wt. pct. (C) BNi-2. Microconstituents are identified as: APIZ (1); Ternary Eutectic Matrix (2); and Intermettalic Phases (3). Bottom: Microstructural phases (D) and solidification zones (E) by the LTP composition.
Figure 4.18 Optical micrographs of BNi-5 series braze alloys with: 40 wt. pct. (A), 50 wt. pct. (B) and 60 wt. pct. (C) BNi-5. Microconstituents are identified as: APIZ (1); Ternary Eutectic Matrix (2); and Intermettalic Phases (3). Bottom: Microstructural phases (D) and solidification zones (E) by the LTP composition.
When examining at the microconstituents of the athermal solidification zone, unlike the APIZ, a unified trend does not exist. As the LTP composition increases, the intermetallic microconstituent zones grows between the 50 and 60 wt. pct. alloys, but remains somewhat unchanged between 40 and 50 wt. pct. in the BNi-9 alloys; increases uniformly in the BNi-2 series alloys, but remains relatively constant across all compositions in the BNi-5 alloys. For the matrix microconstituent, the BNi-9 alloys show a large amount of the microconstituent for the 50 wt. pct. LTP composition, but lower amounts for the 40 and 60 wt. pct. LTP alloys. This effect is most likely due to the increased growth of the APIZ in the 40 wt. pct. alloy and the high boron content available to allow for the formation of stable chromium borides in the 60 wt. pct. alloy.

In the alloys with the silicon melting point suppressant (BNi-2 and BNi-5), there is an increase in the amount of the matrix microconstituent between the 40 and 50 wt. pct. alloys and little change between the 50 and 60 wt. pct. alloys. This effect is most likely due to the growth of the APIZ, with the solid solubility limit of silicon (~17 at% Si) into nickel controlling the rate of silicon depletion in the molten liquid, and the increased creation of intermetallic compounds consuming the matrix material.

With the exception of the 60 wt. pct. BNi-9 alloy, the additive particle interaction zone (APIZ) comprised the majority of the microstructure. The difference between the initial additive particle composition and the resulting APIZ area fraction indicates the amount of interaction, or isothermal solidification, that occurred during the brazing process (ΔAPIZ). For the alloys containing boron, a distinct increase can be noted in the ΔAPIZ when the composition of additive powder/HTP increases (Figure 4.19). This observation indicates that the presence of boron in the braze inhibits the growth of the APIZ during brazing, potentially due to the low solid solubility of boron into Ni (<2 at% B).
The growth of the APIZ increases with the addition of silicon as a melting point suppressant and a distinct trend can be seen when the silicon composition of the system (as calculated by the rule of mixtures) is compared with $\Delta$APIZ for the systems containing silicon (Figure 4.20). This effect is most likely due to the increased solid solubility of silicon into nickel (~17 at% or 9 wt% Si), which promotes the isothermal solidification. Isothermal solidification would require less depletion of the silicon in the molten filler metal at the solid-liquid interface, as compared to the boron system. No trend existed between boron and the creation or promotion of any of the quantified microconstituents.

Figure 4.19: A: The change in additive particle interaction zone during brazing, as calculated by taking the difference of the initial fraction of additive powder and the resulting APIZ fraction, by the LTP Composition.
Figure 4.20: The change in APIZ by the total silicon composition, as calculated through the rule of mixtures from the reported compositions of the as-received powders from certification testing, and logarithmic trend line for alloys with silicon as the melting point suppressant (BNi-2 and BNi-5).

4.3.4 Comparing René 108 and Stainless Steel Microstructures

The microstructures, as observed with the type 304 stainless steel substrate, exhibited similar microstructural trends as the microstructures from the René 108, with a few distinct differences: grain boundary intermetallic compounds precipitating on the substrate side of the interface, and more distinct microstructural trends as a result of the larger LTP composition range examined. This Section will merely reinforce the metallurgical analysis as performed with the René 108 samples.
The microstructures for the BNi-9 and BNi-2-series alloys showed the same trend of increased additive particle interaction zones with the decreased amounts of low temperature powder composition. The alloys with 30 wt. pct. LTP showed little to no evidence of the ternary eutectic matrix, and the only intermetallic compounds present were either due to solid-solution precipitation in the SDZ or entrapped between growing ISZ interfaces. The 70 wt. pct. LTP alloys showed very large amounts of the ternary eutectic matrix and very large intermetallic compounds. The micrographs for BNi-9-series stainless steel samples (Figure A.2, on page 134 and BNi-2-series samples (Figure A.3, on page 135) can be found in the appendix. Similar to the René 108 samples, there was very little difference observed for the different LTP compositions of the BNi-5 alloys as the higher silicon content encourages isothermal solidification, resulting in more uniform microstructures and mechanical properties. The BNi-5-series micrographs can also be found in the appendix (Figure A.4, pg. 136). These qualitative observations clearly support the conclusions reached quantitatively with the samples created with the René 108 substrate.

Despite all the microstructural similarities between the bulk braze microstructures of the type 304 stainless steel and the René 108 joints, the stainless steel samples presented a distinct \( \sigma \)-phase \((\text{Fe, Cr})\) intermetallic unique to iron-based substrates (Figure 4.21). During brazing, a large composition gradient exists for nickel, chromium, and the melting point suppressants (B or Si). The chromium and the melting point suppressant diffuse into the substrate as iron diffuses into the braze. The formation of the \( \sigma \)-phase intermetallic compounds in the substrate grain boundaries show that the chromium from the braze alloy takes a short circuit diffusion path, as described by Su et al. [23] The formation of this phase has been found to be detrimental to Ni-Cr brazes when applied to an iron-base substrate and should be limited. No further investigation was done into this phase.
It should be noted that the erosion of the substrate by the base metal results in an increase in iron and carbon content in the braze alloys. This substrate erosion results in a shift from borides/silicides to include carbides as the constituent intermetallic compounds and the addition of iron as a solute element throughout the microstructure. The effects of the change in microstructural morphology in the stainless steel joint are not examined in this research.

Figure 4.21: Full braze gap from interface to interface of 70 wt. pct. BNi-9 alloy with stainless steel substrate (left). Examination of grain boundary intermetallic compounds precipitating into the stainless steel substrate with a secondary electron image (inset right).

### 4.4 Mechanical Properties

The mechanical properties of the experimental braze joints are one of the most important pieces of information to be collected and analyzed throughout this experimental program. Both
the stainless steel and René 108 series braze joints were tested to determine the strength (failure strength, $\sigma^*$, and ultimate bending strength, $\sigma_{UBS}$), strain and deflection at failure, and elastic modulus. The results obtained were ranked using the Ashby Analysis.

### 4.4.1 Stress-Strain Curve Analysis

During mechanical testing, it was found that the tests could be categorized into three types of results: brittle failure, ductile failure, and extended ductile failure. Each category led to different treatment of the mechanical data collection, specifically in regards to the joint strength. In brittle failure, the joints failed prior to or shortly after yielding. Joints categorized as a ductile failure underwent yielding and plastic deformation prior to failure.

Examples for the bend curves and the data treatment can be seen in Figure 4.22. Joints failing in the extended ductile failure category experienced secondary elastic deformation.

![Stress-Strain Curve Analysis](image)

Figure 4.22: Example bend curves showing brittle and ductile behavior with mechanical properties.
behavior, most likely due to the elastic deformation of the surrounding base material simultaneous to the plastic deformation of the braze alloy, before yielding. Examples of these behaviors can be seen in Figure 4.23.

Since this secondary deformation is directly related to the strength and elastic modulus of the substrate material, this secondary elastic deformation presents itself differently for each substrate. In the stainless steel samples, a secondary yielding occurred concurrently or shortly following the initial yielding of the braze alloy. Through a simple comparison of the reported yield strengths of these materials, it was most likely that the type 304 stainless steel substrate would be the first to yield, followed by the yielding of the braze, however, no data was collected to confirm or refute this conjecture. For the René 108 samples (Figure 4.22), the secondary deformation was only observed at extremely high bending stresses (>5000 MPa).

Figure 4.23: Extended Ductile Failure examples for stainless steel and René 108. Yielding behavior in the stainless steel samples (left). Secondary elastic deformation observed in the René 108 series joints (right).
The type 304 stainless steel specimen bend curves predominantly included both primary and secondary yielding and therefore fell into the extended ductile failure category. None of the stainless steel samples failed during elastic deformation, placing all of them into the ductile failure category. As-brazed samples with the René 108 substrate failed primarily in the brittle category (78%), with 22 pct. failing during plastic deformation. The only as-brazed René 108 braze alloys that failed while undergoing plastic deformation were 40 and 50 wt. pct. BNI-2 and the baseline BRB alloy, indicating that these alloys were good candidates for use. The only alloys that failed with the secondary elastic deformation (extended ductile failure) were the 40 wt. pct. BNI-2 alloys after aging treatments.

4.4.2 Strength

For the purposes of this research, two types of strength were calculated and reported, the ultimate bending strength ($\sigma_{UBS}$) and the failure strength ($\sigma^*$). As the name would indicate, the value of $\sigma^*$ represents the strength at which the braze fails, either catastrophically for brittle failures, or through plastic yielding (0.2 pct. offset yield strength) for the ductile and extended ductile failures. Both values of strength calculated for the samples with the René 108 and are reported. However, due to the unknown nature of the secondary yielding in the type 304 stainless steel samples, only $\sigma_{UBS}$ was reported for the stainless steel samples. For examples of how the values of strength were determined, see Figure 4.22.

For the type 304 stainless steel series joints, the strength decreased as the LTP composition increased. This trend indicates that the addition of the LTP is detrimental to joint strength, most likely due to the increased brittle intermetallic compounds in both the braze joint
and the base metal interface (\(\sigma\) phase, Fe, Cr) as formed from the increased boron or silicon composition.

Table 4.4: Ultimate Bending Strength for each alloy composition, as seen in Figure 4.24. Error reported is one standard deviation from the average.

<table>
<thead>
<tr>
<th>Braze Alloys</th>
<th>BNi-9</th>
<th>BNi-2</th>
<th>BNi-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt. pct. LTP</td>
<td>1115.5 ± 105 MPa</td>
<td>1003.2 ± 278 MPa</td>
<td>886.1 ± 147 MPa</td>
</tr>
<tr>
<td>50 wt. pct. LTP</td>
<td>547.8 ± 11 MPa</td>
<td>986.4 ± 43 MPa</td>
<td>646.3 ± 61 MPa</td>
</tr>
<tr>
<td>70 wt. pct. LTP</td>
<td>449.1 ± 32 MPa</td>
<td>618.5 ± 16 MPa</td>
<td>609.1 ± 45 MPa</td>
</tr>
</tbody>
</table>

Figure 4.24: Ultimate Bending Strength by LTP composition and alloy series for the samples with the type 304 stainless steel substrate samples. Errors represented by shaded areas.

For the samples with the René 108 substrate, both the BNi-9 and BNi-2 data shows similar trends when compared with the stainless steel tests, with both the ultimate bending strength and the failure strength decreasing with increased LTP composition (Figure 4.25; Table
4.5. The smaller reduction in ultimate bending strength with the BNi-5 series alloys stems from the limited change in the constituent phases as the LTP composition changes, as described in earlier sections. The effects of microstructure on mechanical properties will be examined in-depth in section 4.4.5 (pg 100). Due to the existence of solidification cracking, as observed through metallography, the values of strength calculated for the 40 wt. pct. BNi-9 alloy and the 50 wt. pct. BNi-5 alloys were invalid and have been removed from consideration for all mechanical testing, which will be discussed in Section 4.7 (pg 115).

Figure 4.25: Ultimate Bending Strength (top) and Failure Strength (bottom) by LTP Composition. Scatter (one standard deviation) represented by shaded areas.
Table 4.5: Average values for Ultimate Bending Strength and Failure Strength for Braze Joints with René 108 substrate as seen in Figure 4.25. Error shown is one standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>BNi-9</th>
<th>BNi-2</th>
<th>BNi-5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_{UBS}$ (MPa)</td>
<td>$\sigma^*$ (MPa)</td>
<td>$\sigma_{UBS}$ (MPa)</td>
</tr>
<tr>
<td>40 wt%</td>
<td>338.52 ± 139</td>
<td>338.52 ± 139</td>
<td>1334.0 ± 385</td>
</tr>
<tr>
<td>50 wt%</td>
<td>784.7 ± 379</td>
<td>776.7 ± 367</td>
<td>806.3 ± 206</td>
</tr>
<tr>
<td>60 wt%</td>
<td>447.8 ± 195</td>
<td>442.4 ± 201</td>
<td>721.4 ± 149</td>
</tr>
</tbody>
</table>

To further assist with the analysis of the experimental braze alloys, the data obtained can be compared to the benchmark alloy tested, BRB. The values of strength experimentally determined and calculated for BRB for this research can be seen in Table 4.6. The 30 wt. pct. LTP alloys for the BNi-9, BNi-2, and BNi-5 series alloys, and 50 wt. pct. BNi-2 alloy with the stainless steel substrate exceeded the equivalent ultimate bending strength of BRB and stainless steel by 41 pct., 34 pct., 26 pct., and 33 pct. respectively. For the René 108 substrate joints, only the 40 wt. pct. BNi-2 alloy exceeded the value of $\sigma_{UBS}$ calculated for BRB and René 108 (by 23%).

Table 4.6: Average strength values found for joints made with pure BRB braze alloy.

*All values in MPa*

<table>
<thead>
<tr>
<th>Type 304 Stainless Steel</th>
<th>René 108</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{UBS}$</td>
<td>$\sigma_{UBS}$</td>
</tr>
<tr>
<td>659.8 ± 19.7</td>
<td>1026.7 ± 176.4</td>
</tr>
</tbody>
</table>
Traditionally, braze strength values are also compared to the strength of the parent material with brazes with yield strengths in the range of 70 to 90 pct. of the parent material being deemed acceptable. [3] Using 859.8 MPa as the 0.2% offset yield strength of René 108, the following braze alloys had failure strength that met or exceeded the criterion for acceptable strength: 40 wt. pct. BNi-2 (142.2% of the parent yield strength); 40 wt. pct. BNi-5 (115.8%); 60 wt. pct. BNi-5 (109.8 wt%); 50 wt. pct. BNi-2 (92.6 %); 50 wt. pct. BNi-9 (90.3 %); and 60 wt. pct. BNi-2 (89.3%).

4.4.3 Strain and Angular Deflection

Since both maximum strain, as defined as the strain that corresponds to the ultimate bending strength (Figure 4.22), and maximum angular deflection are calculated from the crosshead deflection as reported by the load frame, they are directly related to each other. To further reinforce this relationship between strain and angular deflection, when the experimental values are plotted against each other, a clear linear trend is seen (Figure 4.26). Increasing strain in a braze joint is also accompanied by a linearly proportional increase in angular deflection. In the following Section the value of strain will be reported primarily, and the value of deflection will be reported as a secondary value, if reported at all.

![Graph](image)

Figure 4.26: Experimentally determined strain and deflection for both substrates with trend line.
For the stainless steel samples, much like the values for ultimate bending strength, a negative relationship existed between maximum strain and the LTP composition for the BNi-9 and BNi-2 series alloy (Figure 4.27; Table 4.7). This relationship once again points to limiting the amount of LTP added to the braze alloy, as the additional athermally solidified microconstituents and degraded APIZ deteriorates the ductility of the braze joints.

Table 4.7: Average maximum strain for each braze composition with stainless steel substrate as seen in Figure 4.27. Error reported is one standard deviation.

<table>
<thead>
<tr>
<th>Braze Alloys</th>
<th>BNi-9</th>
<th>BNi-2</th>
<th>BNi-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt% LTP</td>
<td>16.1% ± 2.2%</td>
<td>12.8% ± 6.3%</td>
<td>13.8% ± 2.7%</td>
</tr>
<tr>
<td>50 wt% LTP</td>
<td>2.3% ± 0.2%</td>
<td>9.8% ± 1.2%</td>
<td>13.6% ± 2.7%</td>
</tr>
<tr>
<td>70 wt% LTP</td>
<td>1.0% ± 0.2%</td>
<td>3.1% ± 0.8%</td>
<td>10.9% ± 2.9%</td>
</tr>
</tbody>
</table>

Figure 4.27: Maximum strain by LTP composition and alloy series for the samples with type 304 stainless steel substrate.
A similar trend can be seen in the samples using the René 108 samples, with the maximum strain decreasing as the LTP composition of the filler metal increases. As previously stated, this trend is most likely due to the brittle nature of the athermally solidified zone (ASZ), which contains the ternary eutectic matrix and intermetallic compounds. As with the values for joint strength, the BNi-5 series alloys displayed little to no change in maximum strain as the LTP composition increases (Figure 4.28; Table 4.8).

![Figure 4.28: Maximum strain by LTP composition and alloy series for the samples with René 108 substrate.](image)

**Table 4.8:** Average maximum strain for each braze composition with René 108 substrate as seen in Figure 4.28. Error reported is one standard deviation.

<table>
<thead>
<tr>
<th>Braze Alloys</th>
<th>BNi-9</th>
<th>BNi-2</th>
<th>BNi-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 wt% LTP</td>
<td>0.74% ± 1.3%</td>
<td>0.99% ± 0.46%</td>
<td>0.60% ± 0.13%</td>
</tr>
<tr>
<td>50 wt% LTP</td>
<td>0.55 ± 0.23%</td>
<td>0.54% ± 0.15%</td>
<td>0.34% ± 0.06%</td>
</tr>
<tr>
<td>60 wt% LTP</td>
<td>0.29% ± 0.13%</td>
<td>0.46% ± 0.06%</td>
<td>0.60% ± 0.09%</td>
</tr>
</tbody>
</table>
When tested, the BRB with a stainless steel joint resulted in a maximum strain of 16.0 pct. (78.2°), which performed better than any other alloy in the stainless steel substrate series. For the BRB and René 108 joint, a maximum strain of 0.56 pct. (3.23°) was calculated and was exceeded by the 40 wt. pct. BNi-2, 40 wt. pct. and 60 wt. pct. BNi-5 alloys by 44 pct., 7 pct. and 7 pct. respectively. When the maximum strain is plotted against the ultimate bending strength, a distinct linear trend can be seen for both the stainless steel and the René 108 series samples (Figure 4.29).

Figure 4.29: Ultimate bending stress as it depends on the maximum strain of stainless steel (top) and René 108 (bottom) series braze joints.
When examining the figures representing the ultimate bending strength and maximum strain at failure, it can be seen that the slope of the assumed trend is inverted when compared to a conventional strength and ductility relationship, where as material strength increases ductility decreases. During this research, the joints did not all fail in the same region of the stress-strain curve. As discussed in Section 4.4.1, some of the joints failed during elastic deformation, shortly after yielding, or in the fully plastic region. This discrepancy led to the abnormal relationship.

4.4.4 Elastic Modulus

The elastic modulus is an essential material property when analyzing the resulting braze joints. While the amount of scatter present in this data is large, a general negative trend with LTP addition, similar to the trend seen for strength and strain, can be seen for BNi-9 and BNi-5. Once again, no trend existed for the BNi-5-series joints due to the relatively small changes in microstructures observed over different LTP compositions (Figure 4.30; Table 4.9).

Table 4.9: Elastic Modulus by LTP composition for René 108 substrate samples. Error reported is one standard deviation.

<table>
<thead>
<tr>
<th>Braze Alloys</th>
<th>BNi-9</th>
<th>BNi-2</th>
<th>BNi-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 wt. pct. LTP</td>
<td>139.2 ± 18.2 GPa</td>
<td>200.8 ± 11.1 GPa</td>
<td>174.6 ± 16.7 GPa</td>
</tr>
<tr>
<td>50 wt. pct. LTP</td>
<td>174.0 ± 33.4 GPa</td>
<td>176.0 ± 24.4 GPa</td>
<td>123.5 ± 49.5 GPa</td>
</tr>
<tr>
<td>60 wt. pct. LTP</td>
<td>148.7 ± 29.2 GPa</td>
<td>166.5 ± 17.1 GPa</td>
<td>155.2 ± 61.1 GPa</td>
</tr>
</tbody>
</table>
Figure 4.30: Elastic Modulus by LTP composition and alloy series for the samples with René 108 substrate.

Similar trends existed between the elastic modulus and LTP composition with the type 304 stainless steel samples; however, due to the uncertainty in regards to the secondary yielding behavior, the values will be used for the Ashby Analysis (Section 4.4.6) but will not be analyzed on their own.
4.4.5 Mechanical Property and Microstructural Relationships

When the mechanical properties are compared with the microstructures quantified, a clear trend becomes evident. The greater the extent of isothermal solidification, the larger the additive particle interaction zones, and the better the joint performance. Conversely, larger amounts of intermetallic compounds observed in the matrix phases of the braze joint generally result in worse joints performance.

These trends can be clearly seen in Figures 4.31 and 4.32. This relationship further reinforces all the trends identified previously between mechanical properties and the LTP composition of the braze alloys. For BNi-9 and BNi-2, the amount of APIZ present decreases as the LTP composition increases, and the strength and maximum strain decreases accordingly. For BNi-5, the amount of APIZ does not change with the LTP composition, and therefore the mechanical performance is stable between all of the tested compositions.

For this analysis, the intermetallic microconstituent fraction was used instead of the athermal solidification zone. This procedure was followed because the microconstituent zone fraction reported as the athermal solidification zone was calculated by adding the values for intermetallic and matrix phase together, representing the inverse of the additive particle interaction zone. As a result of this, any trend shown using the additive particle interaction zone and athermal solidification zone would only be the inverse of each other, rather than two unique trends. Therefore, the trends found between the intermetallic microconstituent fraction and the strength and maximum strain, as plotted in Figures 4.31 and 4.32, are separate from the trends seen with the additive particle interaction zone and further reinforces the conclusion that the evolution of these microconstituent zones have a direct effect on the resulting mechanical properties of the braze joints.
Figure 4.31: Failure strength as it relates to the amount of microconstituents present in the René 108 braze joints.

Figure 4.32: Maximum strain as it relates to the amount of microconstituents present in the René 108 brazes joints.
4.4.6 Ashby Ranking and Experimental Scope Adjustment

To rank the alloys according to mechanical performance, the “Ashby Method for Materials Selection in Mechanical Design” was used. For the stainless steel samples, the resulting ranking was used to narrow the experimental matrix for use with the René 108 substrate. The rankings were then used to help finalize alloy recommendations for the experimental program and to direct further research programs.

In the stainless steel joints (Figure 4.33; Table 4.10), the ranking showed that the 30 wt. pct. LTP alloys outperformed the other compositions in their series, with the exception of the 50 wt. pct. BNi-2 alloy. Prior to beginning of experimentation, the 70 wt. pct. LTP alloys were hypothesized to outperform the other alloys in regards to the maximum deflection reached prior to failure; however, 70 wt. pct. LTP alloys performed poorly mechanically and were, in general, ranked the lowest in their respective alloy series. This analysis led to narrowing the experimental matrix, moving the lower bound from 70 wt. pct. to 60 wt. pct. Additionally, despite the exemplary mechanical performance, the 30 wt. pct. alloys were rejected due to the required brazing temperature exceeding the solutionizing temperature of René 108.

<table>
<thead>
<tr>
<th>ASHBY RANK</th>
<th>ALLOY</th>
<th>ASHBY RANK</th>
<th>ALLOY</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30 wt% BNi-9</td>
<td>5</td>
<td>50 wt% BNi-5</td>
</tr>
<tr>
<td>2</td>
<td>30 wt% BNi-2</td>
<td>6</td>
<td>70 wt% BNi-2</td>
</tr>
<tr>
<td>3</td>
<td>50 wt% BNi-2</td>
<td>7</td>
<td>70 wt% BNi-5</td>
</tr>
<tr>
<td>4</td>
<td>30 wt% BNi-5</td>
<td>8</td>
<td>50 wt% BNi-9</td>
</tr>
<tr>
<td>–</td>
<td>BRB</td>
<td>9</td>
<td>70 wt% BNi-9</td>
</tr>
</tbody>
</table>

Table 4.10: Ashby Ranking for stainless steel joints
Figure 4.33: Ashby Ranking chart for stainless steel joints with elastic modulus by ultimate bending strength. Ashby coupling lines are plotted with a slope of 1.

Figure 4.34: Ashby Ranking chart for René 108 joints with elastic modulus by failure strength. Ashby coupling lines are plotted with a slope of 1.
For the René 108 joints (Figure 4.34; Table 4.11), it was found that the 40 wt. pct. BNi-2 alloy outperformed all the other alloys mechanically. The 40 wt. pct. and 60 wt. pct. BNi-5 alloy also exceeded the benchmark alloy, BRB, in the ranking. If not for the cracking observed in the 40 wt. pct. BNi-9 and 50 wt. pct. BNi-2 samples, these alloys would have most likely also overtaken the benchmark alloy. This ranking was used to help to reach a final conclusion on alloy performance.

The Ashby Analysis for both the stainless steel and the René 108 series samples agree with the rankings developed by simply ordering the alloys by ultimate bending strength. The Ashby rankings determined also agrees with the strain rankings for the René 108 series samples, but not for the stainless steel series. In the stainless steel samples, the BNi-5 braze alloys outperform their Ashby ranking positions rising from fourth, fifth, and seventh (for 30, 50 and 70 wt. pct. BNi-5 alloys) best in the Ashby rankings to second, third and fifth best in the maximum strain rankings. This change in ranking is most likely because the Ni₃Si matrix is more ductile than the boron-based matrix (Ni₃B) as found by Schulson et al. [40] The rankings by material properties were determined by the ultimate bending strength and maximum strain relationship as seen in Figure 4.29.
4.5 Failure Analysis

To fully understand the mechanical properties and performance of these braze alloys, the fracture surfaces were analyzed in depth and related to the mechanical properties of the braze joints.

4.5.1 Fracture Modes

All the failed bend test samples for the René 108 exhibited brittle fractures with no ductile failure evident. Three major fracture modes were observed for the failed bend test samples: transgranular, transgranular fracture with some intergranular facets (referred to as mixed), and intergranular fracture.

The vast majority of failure occurred as an intergranular fracture, with 57 pct. of the samples (112 out of 196 samples) failing with the rough, reflective fracture surface (Figure 4.35). Under high magnification, the clear faceted fracture surface can be seen with the intermetallic compounds (red arrow) on the surface of the facets. A cursory chemical analysis of the “dull grey phase” that comprises the majority of the fracture surface revealed that failure occurred at the interface of the isothermal solidification and athermal solidification zones. The mechanical properties of the specimens failing in this mode had an average $\sigma^*$ of 883 MPa, $\sigma_{UBS}$ of 915 MPa, maximum strain of 0.66 pct. (3.5°), and an elastic modulus of 185 GPa.
A mixed-fracture mode was observed in 18 pct. of the samples (35 out of 196 samples) with a dominant transgranular failure mode, with evidence of a few intergranular facets (Figure 4.36). Under high magnification, a flat, dull, transgranular fracture, travelling through the ternary eutectic matrix is seen with intergranular facets around the larger intermetallic compounds (red arrow) that exist within the athermal solidification zone. On average, the specimens failing with this fracture mode performed the best mechanically when compared to the other modes. These specimens had an average $\sigma^*$ of 1042 MPa, $\sigma_{UBS}$ of 1318 MPa, maximum strain of 0.87 pct. (5.0°), and an elastic modulus of 193 GPa.

The pure transgranular fracture was linked with samples that failed due to pre-existing cracks, with 25 pct. of the samples (50 out of 196 samples) failing with the characteristic flat, dull fracture surface (Figure 4.37). Despite the fact that these tests were found to be mechanically deficient, the specimens had an average failure strength/ultimate bending strength...
of 570 MPa, a maximum strain of 0.4 pct. (2.2°), and an elastic modulus of 160 GPa were observed.

For the BNi-9 and BNi-2-series alloys, the increased amounts of LTP promotes the intergranular fracture mode and the mixed fracture mode is more common with the low-LTP alloys (Figure 4.38). As usual, no obvious trend exists between LTP composition and the fracture mode of the BNi-5-series alloy. The alloys predominantly failing with transgranular failure (40 wt. pct. BNi-9 and 50 wt. pct. BNi-5) are due to the pre-existing cracks that have been observed through metallographic methods. These cracks will be described in-depth in following sections. Overall, when compared to the quantified amounts of microconstituents, there is an indication that the intergranular failure mode is linked to the size of the ASZ and, therefore, the promotion of the ISZ is beneficial to the mechanical performance of the braze joints. Since the fracture mode of each individual sample was identified qualitatively through visual examination, a larger number of samples need to be more precisely analyzed to confirm or quantify the trend.

![SEM fractographs](image)

Figure 4.36: SEM fractographs of the mixed fracture mode with a high magnification (left) and a low magnification secondary electron image (right) showing the entire fracture surface. Sample shown is as-brazed 50 wt. pct. BNi-9 with René 108 substrate.
Figure 4.37: SEM fractographs with a high magnification (left) and a low magnification secondary electron image (right) showing the entire fracture surface. Sample shown is as-brazed 40 wt. pct. BNi-9 with René 108 substrate.

Figure 4.38: Percentage of failure mode occurrence by LTP composition.
4.5.2 Other Fracture Features: Porosity, Location, and Abnormal Failures

While observing and cataloging the fracture modes, other fracture features, such as porosity visible on the fracture surface and the location of the failure within the braze were also catalogued. It was found that 89 pct. of the René 108 specimens failed without visible porosity on the surface, 4 pct. failed with pores smaller than 0.5 mm, and 7 pct. failed with pores larger than 0.5 mm. The amount of joints that failed with porosity on the surface are well within the acceptable rejection rates for porosity in wide gap braze joints. [40]

In terms of fracture location, all the brazes failed within the braze alloy itself, with no failures occurring directly on the braze-substrate interface. However, 67 pct. of the René 108 specimens failed near the interface, including 96 pct. of samples that failed according to transgranular fracture and 74 pct. of samples that failed with the mixed-fracture mode. These interface-adjacent fractures most likely fractured in the athermally solidified zone that borders the solid nickel that solidified isothermally away from the base metal. Specimens that failed in the intergranular mode failed evenly within the braze and the interface, however, 82 pct. of the inter-braze failures that occurred did so in the intergranular mode. Joints with either the interface-adjacent or the inter-braze failure location did not, on average, perform mechanically better than the other, beyond the mechanical differences inherent with the failure modes (as stated earlier).

In the vast majority of specimens tested, the failure occurred in a direction parallel to the loading axis. For some rare cases (3%; 5 out of 196 specimens), the failure travelled through the bulk (90%) of the sample, perpendicular to the loading axis, before changing direction to follow the isothermally solidified layer material as affected by the root of the substrate groove that was present when the braze was created. The reduced cross-sectional area (in the plane parallel to the...
loading direction) then succumbed to the shear stresses and catastrophically failed (Figure 4.39). An insufficient number of samples failed in this method to allow for any conclusions regarding the cause or effect of this abnormal failure path.

![Figure 4.39: SEM fractograph of 50 wt. pct. as-braze BNi-9 sample with René 108. Shown with schematic of abnormal failure path with cross-section oriented normal to the fracture surface.](image)

### 4.6 Aging Effects

To ensure that the braze alloys will be able to withstand the temperatures and times required for the repair of turbine components, the samples were aged with four different treatments, and the microstructural and mechanical effects were observed and quantified.

Overall, the closer the alloys were to microstructural equilibrium, the more stable they were during aging. All of the microstructural and mechanical changes can be linked to the diffusion of the melting point suppressants from the athermally solidified zones into the isothermally solidified nickel and the additive powder particles. One effect of diffusion is the coarsening of the intermetallic compounds in the solid diffusion zone (SDZ) and overall growth of the zone. As discussed in Section 4.3, the SDZ is created by the increased amounts of the
melting point suppressants that concentrate in the center of the prior additive particle sites and then precipitate internal APIZ intermetallic compounds, as seen in the microstructures shown in Figures 4.15, 4.16, and 4.17. The coarsening of the SDZ intermetallic compounds is therefore caused by the melting point suppressants diffusing from the athermally-solidified microstructures (Figure 4.40). Another effect that is seen is the coarsening of the isothermally solidified zones, which have been observed in alloys with a large amount of the ternary eutectic matrix microconstituents. In the vast majority of cases, the matrix phase is being sacrificed for the growth of the APIZ and the internal intermetallic compounds. As described in Section 3.7.3 (pg. 54), the microstructural stability index is defined as the overall change of all microconstituent zones observed for a specific alloy.

As-Brazed

Figure 4.40: Aged microstructures of 60 wt. pct. BNi-9 alloy treated at 836 °C (1750°F). Arrows indicate coarsening SDZ.
Figure 4.41: The microstructural stability index averaged for each individual alloy over all of the aging treatments. Margin of error is ±3 pct.

Comparing the microstructural stability of each of the alloys, regardless of aging treatment, it can be seen that the BNi-9 alloy is the least stable, with BNi-2 mostly stable and BNi-5 stable within the margin or error. This effect is most likely due to the diffusivity of boron in comparison to silicon, where the boron contained within the ternary eutectic matrix will be much more likely to diffuse into the isothermally-solidified additive particle interaction zone faster. Therefore, the conclusion can be reached that the addition of boron is the cause of the microstructural stability of the alloys. These trends and values can be seen in Figure 4.41, where the overall stability of the boron containing alloys (BNi-9 and BNi-2) is also dependent on the LTP composition of the alloys, with the microstructural instability increasing as the LTP composition is increased. The reason for this increase is also the result of the increased amount of the athermally-solidified melting point suppressant (silicon and boron) present in the sample.
When examining at individual aging treatments and their overall effect on each individual alloy (Figure 4.42), the alloys treated at 100 hours had a greater amount of microstructural change than the alloys treated at the same temperatures and twenty hours. This effect makes metallurgical sense, as the increased time allows for greater amounts of diffusion to occur within
the microstructure. The higher temperature aging treatments result in a smaller amount of microstructural changes on average, which indicates that the higher temperature allows for the composition to homogenize across all of the microconstituents, resulting in a relatively stable microstructure. Further analysis of these treatments can be performed and the assumptions made in this section can be confirmed through use of thermodynamic modeling. All of the individual phase changes for BNi-9 (Table A.1), BNi-2 (Table A.2), and BNi-5 (Table A.3) are on page 154 in the Appendix.

For the alloys treated at 754°C (1500°F), despite the microstructural changes occurring, the mechanical response discovered is minor and within the margin of error for the mechanical testing. However, a distinct mechanical response can be seen for the alloys treated at 836°C (1750°F), where the failure strength and maximum strain increased by an average of 20 pct. and 15 pct. respectively for both the 20 and 100-hour treatments. This effect can be seen in Figure 4.43, where improvements in the mechanical properties of the aged samples can be seen. The most dramatic change is evident in the 40 wt. pct. BNi-2 alloy, where the 100-hour aged sample increased the maximum strain and ultimate bending strength two-fold.

Overall, the relevant mechanical responses observed as a result of the aging treatment are positive, and do not degrade the mechanical integrity of the braze joint. This response to the aging treatment indicates that in the prescribed brazing cycle for the René 108 joints, the “aging” segment is insufficient to achieve the optimum mechanical properties. One advantage of this effect is that it allows the heat energy expended in-service to improve the braze repair, rather than wasting this time and energy optimizing the mechanical properties during the initial braze cycle.
4.7 Sources of Error

As discussed briefly in previous sections, there were a few sources of error that may have greatly affected the integrity of some of the mechanical results, including the interface-adjacent cracking, small sample geometries, and inaccurate equipment.
4.7.1 Pre-existing Cracks

Through discussions with technicians and engineers familiar with the machining of nickel-base superalloy and brazes, it was noticed that they are susceptible to remelt cracking if the Wire EDM is performed by a machinist unfamiliar with the requirements of the alloy. Unfortunately, through metallographic inspection of untested braze joints, small width cracks travelling parallel to the braze-substrate interface were discovered in multiple specimens of the René 108 samples created with 40 wt. pct. BNi-9 and 50 wt. pct. BNi-5 (Figure 4.44). Although there is no definitive proof that these cracks originated because of the Wire EDM process, the location and morphology of the cracks allows for this assumption to be made. The cracks that travelled approximately 0.5 to 1 mm within the braze, were 2 to 3 μm wide, and resided about 20 μm away from the interface, on the internal side of the braze. Examination of these cracks using scanning electron microscopy discovered that the cracks traveled parallel to the interface between the isothermally-solidified zone as affected by the substrate and the intermetallic compounds athermally-solidified within the matrix (Figure 4.45).

Figure 4.44: Polished and etched micrograph of crack (arrow) as discovered in 40 wt. pct. BNi-9 sample, aged at 754°C for twenty hours. Braze microconstituents are identified and labeled.
Figure 4.45: Backscatter electron image of René 108 braze joint containing 40 wt. pct. BNi-9 in the as-brazed condition. Approximate interface is shown as dashed line, as determined by the distribution of darker grey phases. Braze microconstituents are labeled.

When samples with these pre-cracks were mechanically tested, numerous effects were noted, including a severe change in mechanical performance and a distinctive fracture surface. When compared with their stainless steel counterparts, the unaffected René 108 samples exhibited similar trends, with an increase in strength with the decrease in LTP composition. However, in comparison, the values of ultimate bending strength are 25 pct. and 48 pct. of the expected values, for 40 wt. pct. BNi-9 and 50 wt. pct. BNi-5 respectively, as based on the trends from the other alloys in the series.
Additionally, the using the trend developed between the amounts of additive particle interaction zone and the resulting failure strength for alloys, the values for the strength of the joints unaffected by the pre-cracking can be predicted. These calculations indicated that the values for these alloys should be approximately 950 MPa for the 40 wt. pct. BNi-9 alloy (280% greater than recorded values) and 1000 MPa for the 50 wt. pct. BNi-5 alloy (220% greater than recorded values). It was also found that some of the individual tests of the 40 wt. pct. alloy resulted in an ultimate bending strength 25 to 35 pct. (90 to 130 MPa) of the average of the other samples in the series and a tenth of the predicted values. These samples were omitted from all calculations reported throughout this investigation, even prior to the omission of the alloy as a whole.

The failed samples, as examined through fractographic techniques revealed that both the 40 wt. pct. alloys and the 50 wt. pct. alloys failed predominantly with a unique flat, dull, transgranular fracture mode as seen in Figure 4.37 (page 108). While most alloys at least partially failed with intergranular facets visible, these samples failed in an entirely transgranular manner, which often indicates an embrittled or pre-cracked specimen.

With the amount of evidence mounted against the mechanical values obtained for these two alloys, they were omitted from all of the trend calculations in Sections 4.4, 4.5, and 4.6. However, the results recorded remain in the tables, but are crossed through to signify omission. To rectify this issue for future experiments, alternative methods, such as WaterJet cutting, should be pursued to mitigate this error.
4.7.2 Sample Geometry

For the mechanical test performed during this experimental program, two individual configurations were used based on the AWS specifications for braze qualification; [35] the stainless steel samples were designed to have a cross-sectional area of 12 mm$^2$ (.0021 in.$^2$) while the René 108 samples had a cross-section of 3 mm$^2$ (0.005 in.$^2$). This sizeable difference in sample geometries was done in an effort to maximize the sample yield from the slab of material provided by GE Energy. Other than the sample geometry, substrate material, and crosshead displacement speed (see page 46), the testing procedures were identical. However, when comparing the standard deviations of the ultimate bending strength, the stainless steel joints had an average standard deviation of 75.7 MPa and the René 108 joints had an average standard deviation of 213.2 MPa. While this effect could be attributed to the differences in the substrates, it is possible that the smaller cross-sectional area for the René 108 samples magnified the imperfections inherent in the brazes. It is also possible that the small amount of braze alloy was insufficient to result in a proper value for the bulk mechanical properties. For future test specimens, larger cross-sectional areas should be used to help to alleviate these potential sources of error.

4.7.3 Inaccurate Equipment

During the mechanical tests, the strain and deflection were calculated based on the crosshead displacement, as reported by the MTS test frame, which is not a very accurate sensor. The inaccuracy of this equipment could result in an increased amount of error in the strain, deflection, and elastic modulus calculations. Unfortunately, a deflectometer was not available for use, which would have resulted in more accurate data.
CHAPTER 5 CONCLUSIONS

Throughout all of the experiments performed during this thesis, definitive trends can be determined in regards to the mechanical and metallurgical effects of silicon and boron as melting point suppressants in wide gap braze alloys. These trends allow for recommendations to be made in regards to which experimental braze alloy is best for use in a repair process, and for future research within this same investigation.

In general, the mechanical performance and the resulting microconstituents of the boron-based brazes, BNi-9 and BNi-2, are dependent on the low-temperature powder (or LTP) composition of the alloy. As the LTP composition increases, the amount of isothermal solidification that occurs decreases, which in turn leads to a decrease in the strength and maximum strain of the alloys. For the silicon-based braze (BNi-5), the microstructure and mechanical properties were found to be independent of LTP composition. The existence of silicon in the BNi-2 braze alloys was seen to temper the effect of boron on the microstructure and mechanical performance of the alloys, therefore decreasing the LTP dependence for all of the trends observed.

5.1 Melting Point Suppressant Considerations

It has been seen that boron and silicon have very distinctive benefits and disadvantages as melting point suppressants in wide gap braze alloys. These considerations, including spreadability, brazing temperature, joint metallurgy, mechanical performance, and thermal stability, must be weighed in order to reach a conclusion as to the best alloy composition for use in the wide gap braze repair of René 108.
In regard to braze temperature and spreadability, a cursory examination of the Ni-B and Ni-S binary phase diagrams reveals the temperatures required to fully melt boron-bearing alloys will be less than that of the silicon-bearing alloys. This assumption is confirmed by the isothermal spreadability experiments and the determination of the braze temperature for each of the alloys as described earlier. Therefore, using alloys containing boron will require less energy than alloys containing silicon, lowering the costs required to braze these large parts. Additionally, the lower brazing temperature allows for more spreading of the braze alloys which will allow for the complicated crack geometries to be completely infiltrated with a lower chance for entrapped porosity.

Concerning the metallurgy of the joints, it is seen that silicon promotes the growth of the mechanically beneficial additive particle interaction zone (APIZ) microconstituent. The promotion of APIZ growth is the direct result of the larger solid solubility limit of silicon into nickel, in comparison to the solubility of boron into nickel. This difference means that silicon-bearing braze alloys can isothermally solidify more of the molten matrix before the braze cycle is completed, therefore reducing the amount of liquid that athermally solidifies and decreasing the quantity of ternary eutectic matrix within the braze joint. In terms of mechanical performance, the brazes containing silicon outperformed the alloys containing boron and proved to be less dependent on the composition of the low temperature braze powder. The silicon alloys also proved to be more stable at in-service temperatures as a result of the high diffusivity of boron in comparison to silicon. These results are the direct effects of the increased amounts of the APIZ microconstituents.
5.2 Alloy Recommendations

Once all of the advantages and disadvantages of each of the melting point suppressants were weighed, it is clear that both boron and silicon affect molten filler metal flow that play a vital role in the creation of a high-integrity wide gap braze joint. Boron affects the ease of processing with its enhanced melting point suppressant capabilities and silicon greatly benefits the resulting microstructure, mechanical performance, and thermal stability of the braze joints. Since the boron creates a greater LTP composition dependence than the silicon, the amount of LTP present in the alloy should be minimized. Therefore, the 40 wt. pct. BNi-2 alloy is the best, with the optimum brazing temperature, as a result of the boron content, and mechanical performance, as a result of the silicon content.

5.3 Future Research Recommendations

Due to the large experimental scope of this project, and the complex metallurgical nature of the wide gap brazing alloys and process, a lot of questions went unanswered and speculations went unconfirmed. The following lines of inquiry should be followed to enhance the results of this research program and the strength of the results and recommendations made:

- **Examine the effects of brazing time and temperature on the microstructure and mechanical properties**: This examination will allow for brazing temperature to be set based on metallurgical principles, rather than the qualitative and loosely quantitative methods used to determine the temperatures for the purposes of this experimental program.
• **Perform Creep and Stress-Rupture to verify mechanical performance at service temperatures:** Creep and Stress-Rupture testing is an extremely common testing method for wide gap braze joints and nickel-base superalloys. The collection of this data will help to supplement the mechanical properties collected at room temperature during this experiment and allow for the comparison to existing results.

• **Verify mechanical data with tensile testing to correlate with flexural strength and strain:** In addition to creep testing, tensile tests are a more common method for braze joint testing and the analysis procedures are well defined and tested, unlike the standards and methodology for the four-point bend testing of metallic specimens.

• **Conduct Low-Cycle Fatigue tests to correlate data found in bend tests with LCF life:** The LCF life of the braze joints is a required metric when ranking the mechanical integrity and performance of a turbine braze repair, especially when considering the stress the joint will undergo within a turbine.

• **Perform thermodynamic calculations to verify and correlate experimentally identified phases:** Due to the complex metallurgical and thermodynamic driving forces affecting the microstructure and thermal stability of the wide gap braze joints, thermodynamic modeling can be used to confirm and enhance assumptions made in regards to the solidification process, the constituent phases, and the effects of aging.

• **Conduct detailed Microstructural Characterization including more SEM, TEM, and XRD analysis of resulting joints:** A detailed microstructural characterization is required to fully understand the performance of the wide gap braze joint. The specific identification of all of the specific phases in the microconstituent zones, concentration
gradients, crystal lattices, and $\gamma/\gamma'$ interactions can be analyzed through Transmission Electron Microscopy and X-Ray Diffraction.

- **Examine metallurgical (TLP) mechanisms driving Wide Gap Brazing process:** The diffusion mechanism is at the heart of the wide gap brazing process. The conclusions made in this research could be supplemented and supported by an in-depth metallurgical analysis of items such as: the diffusivity of the constituent elements, the elimination of centerline eutectics, and the effect of the internal concentration gradients.

- **Develop a braze alloy to allow for the solutionizing of the braze substrate during the brazing process:** While turbine components are in-service, the microstructure of the substrate is subjected to the precipitation of detrimental intermetallic phases at the grain boundaries. An braze alloy designed to remove these detrimental precipitates, while a part undergoes braze repair, would remove the need to perform two separate procedures to repair the component, thus reducing costs.

- **Examine bulk material properties of wide gap braze alloys:** Determining the affect the substrate has on the material properties of the resulting braze joint can be achieved by analyzing the braze alloys without the substrate. The conclusions and data determined through this research effort would give greater insights into the behavior of the braze joints and the extent of substrate interaction.
REFERENCES CITED


www.praxair.com


APPENDIX A FIGURES AND TABLES

This Section contains figures and tables that were developed and used in the analysis, but not included in the main body of the text. The following figures can be found in this section:

Figure A.1: Isothermal spreadability droplets for each brazing temperature for René 108 series alloys. The abnormal spreading of the 40 wt% BNi-2 alloy was caused by defect on the reverse side, causing the molten braze alloy to erode through the substrate and flow into the defect................................................................. 133

Figure A.2: Optical micrographs of the BNi-9-series braze microstructures as applied to 304 stainless steel substrates. Microconstituents indicated are APIZ (1), Ternary Eutectic Matrix (2), and Intermetallic compounds (3).......................................................... 134

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Figure A.6: Isothermal spreadability results for 50 wt% BNi-9 on type 304 stainless steel.
Figure A.7: Isothermal spreadability results for 70 wt% BNi-9 on type 304 stainless steel.

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Figure A.11: Isothermal spreadability results for 30 wt% BNi-5 on type 304 stainless steel.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Spreadability Results</th>
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<tbody>
<tr>
<td>1100°C</td>
<td>0 mm² (0%) Unmelted</td>
</tr>
<tr>
<td>1150°C</td>
<td>1.1 mm² (4.2%) Unmelted</td>
</tr>
<tr>
<td>1200°C</td>
<td>0.7 mm² (2.7%) Unmelted</td>
</tr>
<tr>
<td>1250°C</td>
<td>0 mm² (0%) Unmelted</td>
</tr>
<tr>
<td>1300°C</td>
<td>98 mm² (98%) Uniform</td>
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</table>

Figure A.12: Isothermal spreadability results for 50 wt% BNi-5 on type 304 stainless steel.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Spreadability Results</th>
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<tbody>
<tr>
<td>1100°C</td>
<td>0.7 mm² (0%) Unmelted</td>
</tr>
<tr>
<td>1150°C</td>
<td>1.8 mm² (4.5%) Unmelted</td>
</tr>
<tr>
<td>1200°C</td>
<td>18 mm² (2.7%) Non-Uniform</td>
</tr>
<tr>
<td>1250°C</td>
<td>94 mm² (185%) Uniform</td>
</tr>
<tr>
<td>1300°C</td>
<td>118 mm² (322%) Uniform</td>
</tr>
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</table>
Figure A.13: Isothermal spreadability results for 70 wt% BNi-5 on type 304 stainless steel

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<tr>
<th>Temperature</th>
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<tr>
<td>1100°C</td>
<td>5.3 mm² (12%)</td>
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<tr>
<td>1150°C</td>
<td>94 mm² (185%)</td>
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<td>1200°C</td>
<td>247 mm² (241%)</td>
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<td>587 mm² (542%)</td>
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<tr>
<td>1300°C</td>
<td>216 mm² (482%)</td>
</tr>
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</table>

Unmelted Non-Uniform Uniform Over-Spread Over-Spread

Figure A.14: Pure BNi-9 braze joint with type 304 stainless steel substrate. Solid nickel solution, binary (2; Ni+Ni₃B), and ternary (3; Ni+Ni₃B+Cr-B) microconstituents are visible. (Continued on next page)
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40 wt. pct. BNi-9

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Margin of error is ±3%.

<table>
<thead>
<tr>
<th>Time</th>
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<td></td>
<td>60 wt%</td>
<td>-8.9%</td>
<td>-10.6%</td>
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<tr>
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<td>40 wt%</td>
<td>2.3%</td>
<td>-17.3%</td>
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<td>50 wt%</td>
<td>-17.9%</td>
<td>1.5%</td>
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Table A.2: Microconstituent zone changes for BNi-9-series alloys on René 108.

Margin of error is ±3%.

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<td></td>
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<td>Matrix</td>
<td>APIZ</td>
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<td>4.2%</td>
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Table A.3: Microconstituent zone changes for BNi-5-series alloys on René 108.

Margin of error is ±3%.

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