Investigation of NARloy-Z Yield Strength in Response to Changes in Ingot Processing and Heat Treatment

A Senior Project

Presented to the Faculty of the Materials Engineering Department

California Polytechnic State University, San Luis Obispo

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science, Materials Engineering.

by

Stanley Goto, Sarah Wattenberg

Advisor: Prof. Blair London

Sponsor: Aerojet Rocketdyne

June, 2018

Abstract

This study investigates the effect of cooling rate on the yield strength of NARloy-Z. NARloy-Z is a copper-based alloy with 3 wt.% silver and 0.5 wt.% zirconium. The types of NARloy-Z were classified by the ingot processing (old or new) and the material lot (old or new). There were three variations of NARloy-Z in this study: old processing and material (Old/Old); old processing and new material (Old/New); and new processing and material (New/New). NARloy-Z undergoes a braze thermal cycle and age (BTCA) heat treatment for its application, and a single cooling rate within the BTCA was manipulated in this study. The three cooling rates used were -5.4ºF/min (fast), -2.2ºF/min (moderate), and -1.1ºF/min (slow). Each material and cooling rate combination was tensile tested according to ASTM E8/E8M. Because of the limited number of Old/Old material, only the fast and slow cooling rates were used for the Old/Old material. The average yield strengths for the fast and slow Old/Old material were 11.2 ksi and 11.3 ksi, respectively. The Old/New material had average yield strengths of 10.7 ksi, 9.0 ksi, and 8.9 ksi for the fast, moderate, and slow cooling rates, respectively. The New/New material showed average yield strengths of 12.1 ksi with the fast cooling rate, 11.3 ksi with the moderate cooling rate, and 12.7 ksi with the slow cooling rate. The tensile data showed that the cooling rate analyzed did not have a significant effect on the NARloy-Z yield strength. The low yield strength values were due to exposure to high temperatures for an extended period of time during the BTCA heat treatment. Metallography was performed on one sample from each material and heat treatment combination. The Old/New material consistently had larger grains than the other materials, regardless of the heat treatment. Conventional understanding of materials engineering would suggest that the larger grains found in the Old/New material is an explanation for its low yield strength. However, this cannot solely be attributed to its grain size because material with finer grain structures had similar yield strengths.

Keywords: NARloy-Z, copper-based alloy, precipitation hardening, copper silver precipitates, zirconium intermetallics, grain boundary pinning, heat treatment, materials engineering, vacuum centrifugal casting, vacuum arc remelt, tensile testing, grain growth, yield strength, solution treat and age, braze thermal cycle and age, overaging, metallography, main combustion chamber, Aerojet Rocketdyne, RS-25, Space Shuttle Main Engine, NARloy-A, vacuum furnace.

Acknowledgements

Thank you, Bryce Simmons and Chris Shipley from Aerojet Rocketdyne. We were very fortunate to land a project with Aerojet Rocketdyne, and without your support this project would have never lifted off the ground. Thank you to our faculty advisor Prof. Blair London from the Cal Poly Materials Engineering Department. It has been a pleasure being your students and we are thankful for your guidance to better ourselves as engineers. Thank you to Leon Jenkins from Ventura Heat Treating Inc. for heat treating our samples. Thank you to Luka Dugandzic for machining our samples. Thank you to Dr. Sklar from the Cal Poly Statistics Department for providing the statistical analysis for this project. Finally, thank you to Lisa Rutherford from the Cal Poly Materials Engineering Department.

Table of Contents

1. Introduction 1
1.1. Company Background 1
1.2. NARloy-Z 2
1.2.1. Composition and Strengthening Mechanisms 2
1.2.2. Heat Treatment 3
1.2.2.1. Response to Heat Treatment: NARloy-A 3
1.2.2.2. Heat Treatment Response to Zirconium Addition in NARloy-Z 4
1.2.2.3. Current Heat Treatments 5
1.2.3. Processing 6
1.2.3.1. Vacuum Centrifugal Casting 7
1.2.3.2. Vacuum Arc Remelt 7
1.3. Problem Statement 8
2. Experimental Procedure 9
2.1. Sample Preparation 9
2.2. Heat Treatment 9
2.3. Tensile Testing 10
2.4. Metallography 10
2.5. Statistics 10
3. Results 11
3.1. Tensile Test Results 11
3.2. Statistical Results 16
3.2.1. Two-Factor ANOVA and Tukey Comparison 16
3.3. Metallography Images 18
4. Discussion 19
4.1. STA and BTCA Heat Treatment 19
4.2. Reduction in Yield Strength 19
4.3. Metallographic Analysis 19
4.4. Grain Size 20
4.5. Statistical Analysis 20
5. Conclusions 20

List of Figures

Figure 1. A field engineer guiding the installation of a RS-25 engine.[2] 1

Figure 2. (a) The RS-25 main combustion chamber liner made of NARloy-Z.[3] (b) A cross-sectional view of the main combustion chamber and its neighboring components.[4] 2

Figure 3: The Cu-Ag phase diagram shows a maximum solubility of Ag in Cu at 779ºC. NARloy-A/NARloy-Z has a Ag content of 3% which allows the material to form a single phase solid solution. Once in solid solution, the material can be quenched and aged to form precipitates.[7] 3

Figure 4. a) Incoherent discontinuous precipitates do not produce lattice strain in the matrix and are typically large and unevenly dispersed. In the case of NARloy-A this is typical of over aging or formation at grain boundaries. b) Coherent continuous precipitates are a result of a proper solution-quench and age. These precipitates are small and evenly dispersed.[8] 4

Figure 5: Heat treatments A, B, C, and D are test thermal profiles for NARloy-Z. Heat treatment A best represents the actual conditions of manufacturing a NARloy-Z MCC liner. 5

Figure 6: Yield strength of NARloy-Z from the same processing and material lot showed little difference between heat treatments. 6

Figure 7: Vacuum centrifugal casting produces high purity material that comes at an equally high cost.[10] 7

Figure 8: The highly controlled solidification during the VAR process is designed to eliminate ingot macrosegregation and significantly reduce microsegregation. Chemical segregation of the elements of an alloy is undesirable and, therefore, must be eliminated if alloys are to achieve peak mechanical properties.[11] 8

Figure 9. Profiles of the three braze thermal cycle and age (BTCA) heat treatments. Cooling rate of interest is between 1700ºF and 1375ºF. 10

Figure 10. Tensile stress plotted against percent elongation of Old/New samples in the as received (rolled, annealed, BTCA) condition. 11

Figure 11. Tensile stress plotted against percent elongation of New/New samples in the as received (STA) condition. These samples showed highest strength of all tested samples. .. 11

Figure 12. Tensile stress plotted against percent elongation of Old/Old samples after the BTCA heat treatment with a fast cool. The negative strain seen in specimen 2 was caused by the slipping of the extensometer, but the yield strength was unaffected; this sample was not taken to fracture. 12

Figure 13. Tensile stress plotted against percent elongation of Old/New samples after the BTCA heat treatment with a fast cool. Only specimen 1 was taken to fracture. 12

Figure 14. Tensile stress plotted against percent elongation of New/New samples after the BTCA heat treatment with a fast cool. The negative strain seen in specimen 1 was caused by the slipping of the extensometer. The yield strength was altered, so this sample was excluded from analysis. 13

Figure 15. Tensile stress plotted against percent elongation of Old/New samples after the BTCA heat treatment with a moderate cool. Incorrect dimensions were entered in the software for

specimen 6, so the yield strength and ultimate tensile strength were calculated using the load and correct cross sectional area. 13

Figure 16. Tensile stress plotted against percent elongation of New/New samples after the BTCA heat treatment with a moderate cool. Specimen 2 had a significantly lower percent elongation than the other three samples, but all yield strengths were similar. 14

Figure 17. Tensile stress plotted against percent elongation of Old/Old samples after the BTCA heat treatment with a slow cool. 14

Figure 18. Tensile stress plotted against percent elongation of Old/New samples after the BTCA heat treatment with a slow cool. The negative strain in the first run of specimen 8 (Old/New 8A) was caused by the slipping of the extensometer, so the test was stopped and re-run (Old/New 8B). The yield strength was taken from 8A, and the tensile strength was taken from 8B. 15

Figure 19. Tensile stress plotted against percent elongation of New/New samples after the BTCA heat treatment with a slow cool. 15

List of Tables

Table I: Yield Strengths of Different Heat Treatments and Material Types 6

Table II: Average Tensile Test Results 16

Table III: Results of the Analysis of Variance (ANOVA) Test 17

Table IV: Grouping Comparison of Average Yield Strengths Based on Condition and Material 17

Table V: Micrographs and Average Yield Strength of NARloy-Z 18

Table A1: Tensile Test Results for As-Received, Fast Cool, and Moderate Cool NARloy-Z 22

Table B1: Tensile Test Results for Slow Cool NARloy-Z 23

1. Introduction

1.1. Company Background

Aerojet Rocketdyne is a leading supplier of propulsion systems for space and defense purposes. Rocket engines such as the RL-10 on the Delta IV and the RS-25 on the Space Shuttle Main Engine (Figure 1) were designed and manufactured by Aerojet-Rocketdyne. The Space Shuttle Main Engine (RS-25) produces 418,000 pounds of thrust from a liquid hydrogen and liquid oxygen reaction in the main combustion chamber (MCC).[1]

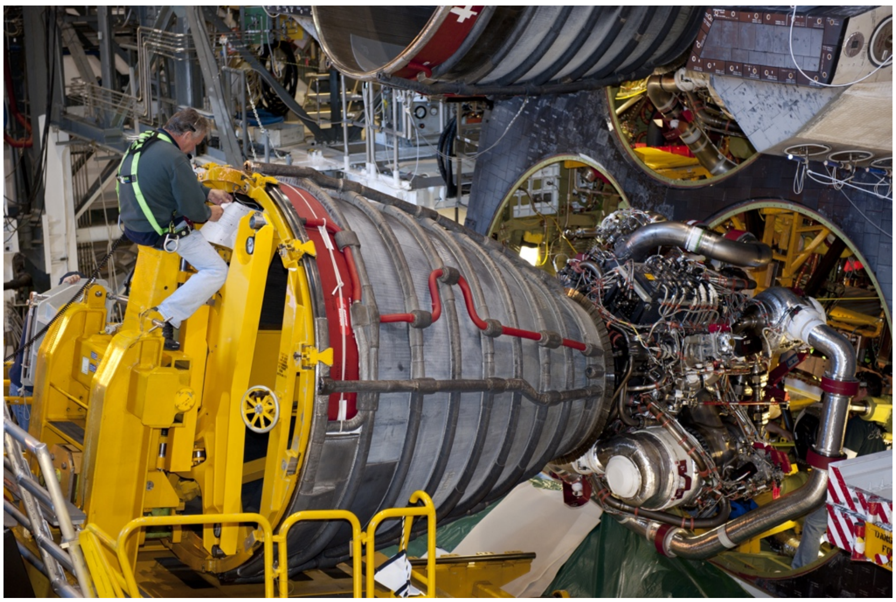
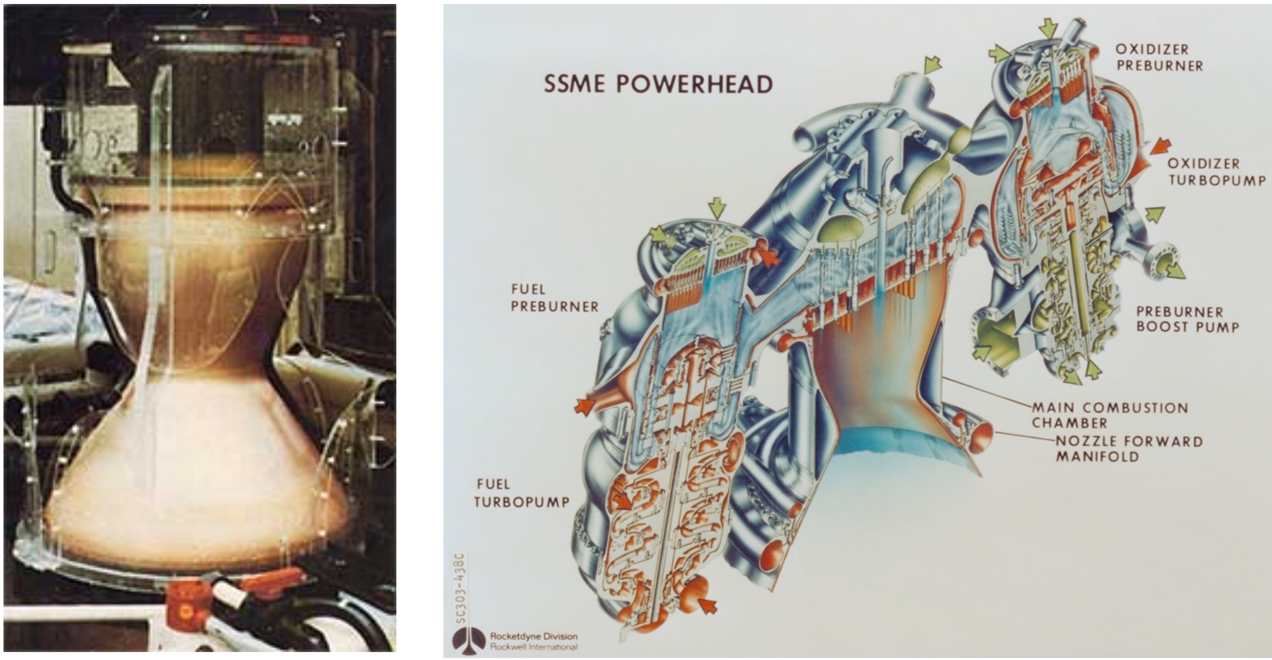


Figure 1. A field engineer guiding the installation of a RS-25 engine.[2]

A product of 418,000 pounds of thrust produced by the rocket engine is a large amount of heat in a concentrated area, this places a high demand on designers to ensure that the unit does not fail due to the heat it produces. Thus, a challenge when manufacturing a rocket booster is to dissipate the heat generated in the MCC to maintain adequate operating temperatures. The demand of the MCC to withstand high temperature gradients and transfer heat effectively while maintaining its strength led to the development of NARloy-Z (North American Rockwell alloy with zirconium). North American Rockwell developed this alloy, and today the company is known as Aerojet Rocketdyne Holdings, Inc. Although the primary load bearing structure of the MCC comes from Inconel© 718, NARloy-Z is used as a liner for the MCC for its high thermal conductivity and relatively high strength at extreme temperatures. Figure 2 depicts the RS-25 main combustion chamber.



(a) (b)

Figure 2. (a) The RS-25 main combustion chamber liner made of NARloy-Z.[3] (b) A cross-sectional view of the main combustion chamber and its neighboring components.[4]

1.2. NARloy-Z

1.2.1. Composition and Strengthening Mechanisms

NARloy-Z is a copper based alloy with 3 wt.% Ag, 0.5 wt.% Zr, balance Cu and trace amounts of oxygen (<50 ppm). Its two strengthening mechanisms are solid solution strengthening and precipitation hardening, the latter being the dominant mechanism. The decomposition of the Cu-Ag supersaturated solid solution is responsible for the age hardening effect. This precipitation occurs both discontinuously and continuously. Discontinuous precipitation occurs selectively at the grain boundaries and forms a lamellar structure, resulting in a weaker alloy. Continuous precipitation strengthens the alloy because it occurs uniformly throughout the grains while being semi-coherent with the copper matrix.[5,6]

Zirconium further strengthens NARloy-Z by forming intermetallic compounds with copper and silver; these precipitates hinder grain growth by pinning grain boundaries. The presence of Zr also reduces the diffusion rate of Ag in Cu, interfering with the discontinuous precipitation and promoting continuous precipitation. Additionally, Zr de-oxidizes the material by acting as an oxygen trap; the zirconium combines with the traces of oxygen and hinders the formation of a brittle compound, cuprous oxide (Cu_2O), at the grain boundaries. Formation of Cu_2O is deleterious to NARloy-Z properties such as yield strength and thermal conductivity.[5,6]

1.2.2. Heat Treatment

NARloy-Z is a precipitation hardened alloy, and proper heat treatment is vital to achieve peak mechanical properties. This hardening mechanism is possible due to silver's increased solubility in copper at elevated temperatures. Increased solubility is observed in many alloyed metals as solute atoms have more free energy when heat treated to substitutionally occupy sites within the solvent's crystal structure. At 1700ºF, the solubility of Ag in Cu is roughly 7 wt.%; at room temperature, the solubility of Ag in to Cu is less than 0.1 wt.% because there is less free energy for Ag to dissolve in Cu.[6] If the material is solutionized and rapidly quenched to trap the Ag atoms in the Cu lattice, a metastable phase of α_{ss} is formed. An aging heat treatment at 900ºF (480ºC) for 4 hours allows the metastable phase of α_{ss} to decompose into fine continuous precipitates of an Ag rich phase within Cu-rich grains[6] (Figure 3). The continuous precipitation mode of Ag precipitates forms semi-coherently within the Cu lattice and therefore restricts the movement of dislocations and strengthens the material (Figure 4). It is important to understand NARloy-Z's response to heat treatment as the strengthening mechanism of continuous semi-coherent precipitation is sensitive to temperature and time of heat treatment. Before discussing NARloy-Z's response heat treatment it is important to discuss the heat treatment response of NARloy-A, the predecessor to NARloy-Z, as it provides context for NARloy-Z's existence.

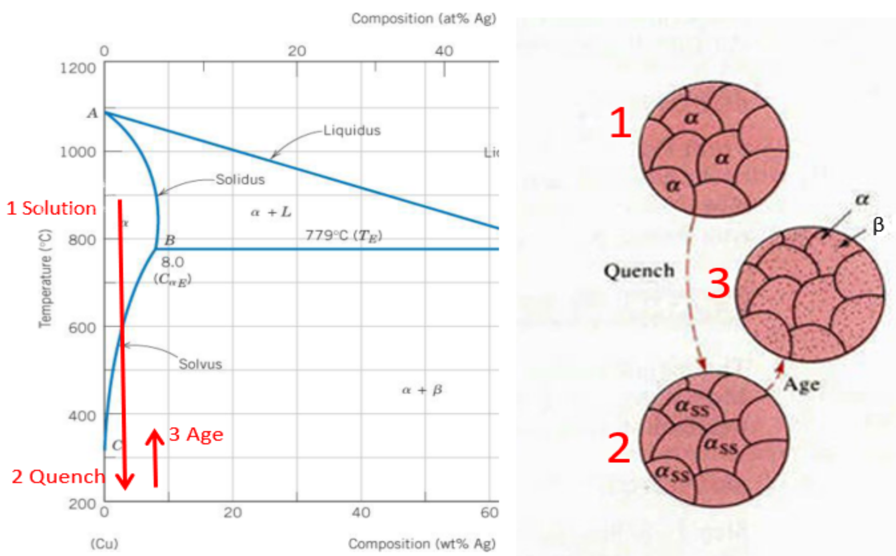


Figure 3: The Cu-Ag phase diagram shows a maximum solubility of Ag in Cu at 779ºC. NARloy-A/NARloy-Z has a Ag content of 3% which allows the material to form a single phase solid solution. Once in solid solution, the material can be quenched and aged to form precipitates.[7]

1.2.2.1. Response to Heat Treatment: NARloy-A

NARloy-A has a composition of Cu- 3 wt.% Ag and is the predecessor to NARloy-Z. The ideal heat treatment of the material is as follows: solutionize to dissolve the Ag in Cu, quench to produce a supersaturated solution, and age to form continuous Ag rich precipitates. This heat treatment is referred to as a solution treat and age or STA. These conditions are documented as solution at 1700ºF, quench to room temperature and age at 900ºF for 4 hours. A challenge when processing this material is NARloy-A's susceptibility to discontinuous precipitation and grain growth which reduces the yield strength of the material.[7] This issue is exacerbated for NARloy-A when processed in a manufacturing setting where the large unit size of the component will expose the alloy to a slower quench and extended times at or above the aging temperature. NARloy-Z is considered an improvement on this alloy because the chemistry is slightly changed to improve the material kinetics to better suit the MCC manufacturing process which exposes the material to high temperature longer than the ideal STA heat treatment.

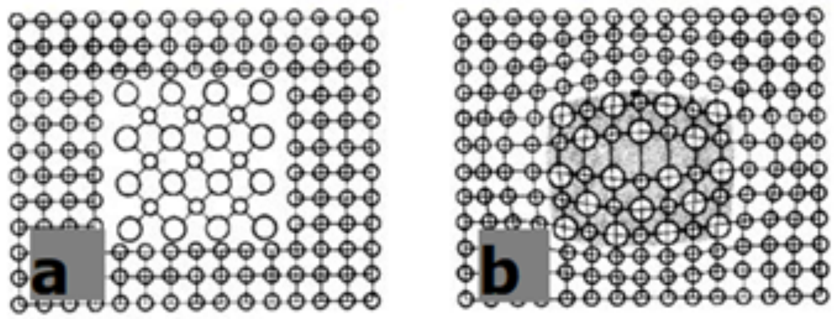


Figure 4. a) Incoherent discontinuous precipitates do not produce lattice strain in the matrix and are typically large and unevenly dispersed. In the case of NARloy-A this is typical of over aging or formation at grain boundaries. b) Coherent continuous precipitates are a result of a proper solution-quench and age. These precipitates are small and evenly dispersed.[8]

1.2.2.2. Heat Treatment Response to Zirconium Addition in NARloy-Z

NARloy-Z achieved the following changes to the material with the zirconium addition:[9]

1. Zirconium pins grain boundaries therefore becomes less susceptible to grain growth. Zr has a solubility of about 0.1% in Cu at 1700ºF. The composition of NARloy-Z has 0.5% Zr which means that at solutionizing temperatures, the Zr or Zr intermetallics do not dissolve into the microstructure. These intermetallics form at grain boundaries and prevent grain growth; therefore, the material is less susceptible to a reduction in yield strength due to thermocycling.
2. Formation of continuous coherent Ag rich precipitates is promoted therefore increasing strength. While the interaction between the Zr intermetallics and Ag precipitates is complex and yet to be fully understood, literature has shown that the 0.5% Zr addition reduces the formation of discontinuous Ag precipitates at grain boundaries. This is most likely a result of the Zr intermetallics preferentially forming at those locations and Zr slowing the diffusion of Ag atoms in the Cu matrix. By preventing discontinuous Ag precipitate formation, the material is less susceptible to overaging.
3. Zr works as a sink for oxygen which makes the material less susceptible to embrittlement. Oxygen is readily absorbed by copper to form Cu_2O. Copper oxide is detrimental as it forms at grain boundaries which embrittles the material. Zr has a higher affinity to oxygen, effectively working as a getter for oxygen. ZrO_2 has less of an embrittling effect than Cu_2O on the material and therefore improves material properties.

As it relates to the heat treatment of the alloy, points 1-3 state that Zr additions to NARloy-Z allow engineers the process the material with fewer complications because of heat treatment.

Specifically, 1 and 2 stabilize the hardening mechanism of the material when heat treated and 3 prevents embrittlement at higher temperatures.

1.2.2.3. Current Heat Treatments

When testing NARloy-Z samples, Aerojet Rocketdyne designs test heat treatments to represent what the alloy experiences when manufacturing an MCC liner such as the braze cycle to bond the MCC liner with the MCC body. The braze procedure is reported to reach the solutionizing temperature of the NARloy-Z. After brazing, the entire unit is aged at 1375ºF for 4 hours to age the braze material, and then the unit is lowered to the NARloy-Z aging temperature at 900ºF. The historical average yield strength from this heat treatment is about 20 ksi. Currently Aerojet Rocketdyne has four different heat treatments (Figure 5) that imitate the processing heat treatments that a NARloy-Z MCC liner would experience during manufacturing. Heat Treatment A is reported to best represent real processing conditions. It is important to note that Heat Treatment A does not have a quench from the solution temperature at 1700ºF. The theory behind this omission from an ideal heat treatment (STA) is that Zr intermetallics slow the diffusion of Ag atoms enough to prevent formation of discontinuous Ag precipitates even when not quenched from solution temperature 1700ºF. The result of this resistance to Ag diffusion is a more favorable distribution of Ag precipitates and a stronger material. Preliminary data suggests this is not true as Aerojet Rocketdyne has reported yield strength data below 20 ksi from samples heat treated with A, B, C, or D (Table I, Figure 6). The different processes refer to the old process which involves a vacuum centrifugal casting method to produce ingots, and the new process which uses a vacuum arc remelt process. In addition to the braze age at 1375ºF which deviates from heat treatments outlined in the literature, heat treatments A, B, C, and D have a longer aging time. Where the literature suggests a 4 to 8-hour age at 900ºF, the aging times of A, B, C, and D are 24 hours long. Aerojet Rocketdyne claims that the aging time for this material is standard at 24 hours and a shorter aging time is not recommended.

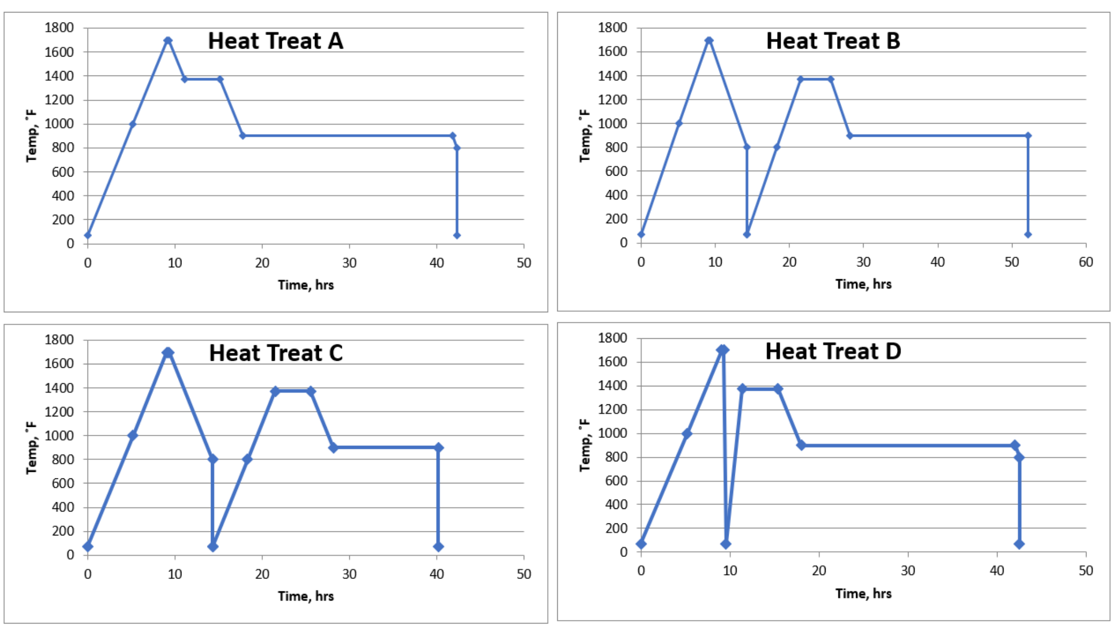


Figure 5: Heat treatments A, B, C, and D are test thermal profiles for NARloy-Z. Heat treatment A best represents the actual conditions of manufacturing a NARloy-Z MCC liner.

Table I: Yield Strengths of Different Heat Treatments and Material Types

Heat Treatment	Material Type (Process/Material Lot)	Yield Strength (ksi)
A	Old/Old	20.1
		20.3
	New/New	14.4
		13.9
		15.1
		14.8
	Old/New	10.8
		11.1
B	Old/New	10.7
		10.9
C	Old/New	11.9
		14.8
D	Old/New	10.0
		10.1

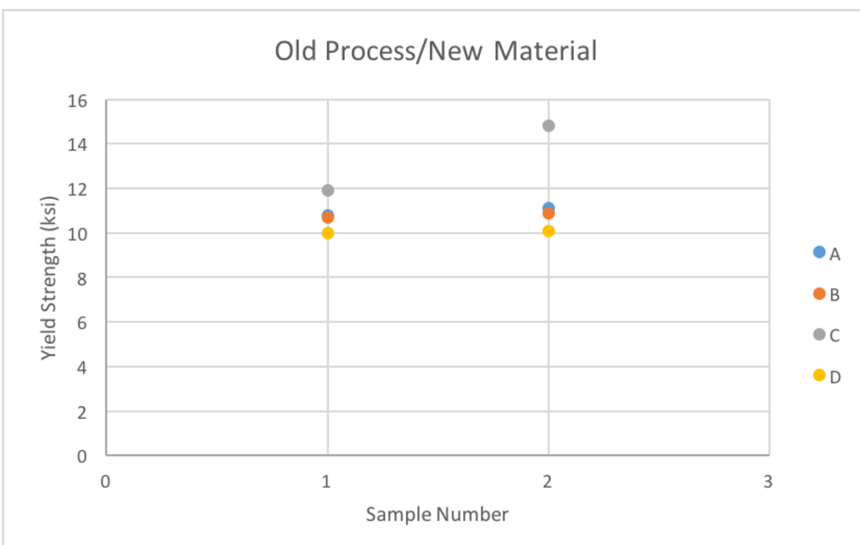


Figure 6: Yield strength of NARloy-Z from the same processing and material lot showed little difference between heat treatments.

1.2.3. Processing

Currently there are two ways to process NARloy-Z MCC liners. Both processes start with an NARloy-Z ingot which is then forged, ring rolled and machined. The key difference between the processes is the way the NARloy-Z ingots are produced. The original method is by vacuum centrifugal casting (VCC) and a newer method, which was adopted as a cost reducing measure, is vacuum arc remelt (VAR).

1.2.3.1. Vacuum Centrifugal Casting

The original method of producing NARloy-Z ingots was by vacuum centrifugal casting. This method involves pouring liquid metal into a die (Figure 7). The die is preheated and spun on its vertical or horizontal axis as the liquid metal is poured. In addition to the advantages of processing in a non-contaminating atmosphere, this process produces material with high purity, directional solidification, absence of voids, and uniform grain structure.[10] This manufacturing process is only used for specialized applications because it is often cost prohibitive.

1.2.3.2. Vacuum Arc Remelt

Vacuum arc remelt (VAR), much like vacuum centrifugal casting (VCC), is considered a premium melting process that is reserved for specialty purposes where material purity is paramount. The VAR process starts with a tall cylindrical ingot (Figure 8). A DC electric current is passed through the electrode in a vacuum atmosphere. The electrical arc between the electrode and some initial material in the crucible melts the electrode thus becoming a consumable electrode. The liquid metal from the electrode falls into the crucible and its cooling rate is carefully controlled producing a remelted material with superior properties. Many chemical reactions are favored at the low pressures and high temperatures obtained during VAR, including dissociation of less stable oxides and undesirable elements, solutionizing of carbides, deoxidation, and degasification. In addition, the VAR process results in a homogenous microstructure. The VAR process, while considered expensive is generally not as expensive as VCC.[11]

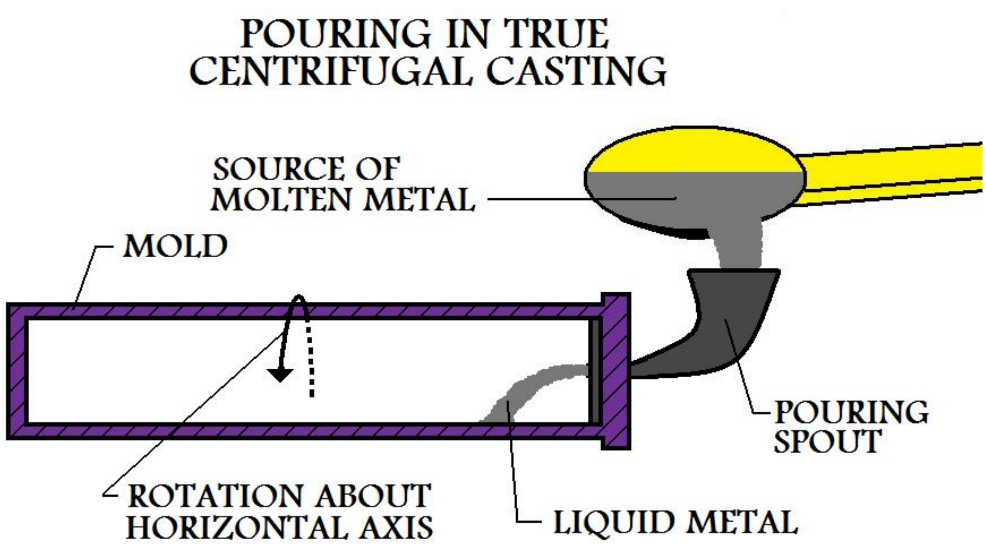


Figure 7: Vacuum centrifugal casting produces high purity material that comes at an equally high cost.[10]

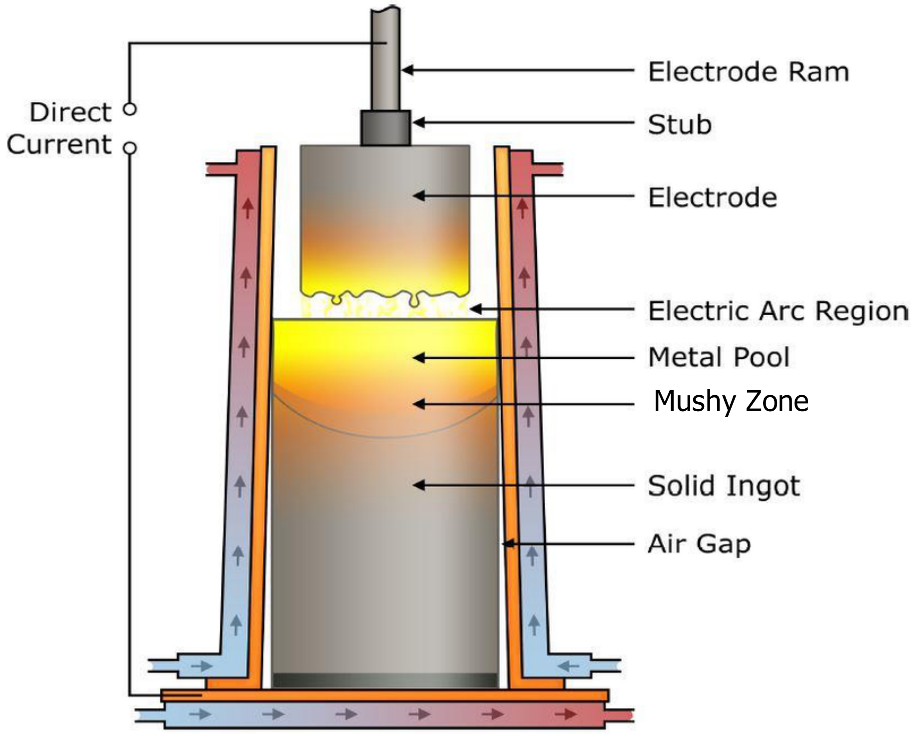


Figure 8: The highly controlled solidification during the VAR process is designed to eliminate ingot macrosegregation and significantly reduce microsegregation. Chemical segregation of the elements of an alloy is undesirable and, therefore, must be eliminated if alloys are to achieve peak mechanical properties.[11]

1.3. Problem Statement

Copper and its alloys are used in a wide variety of aerospace applications for its high thermal conductivity. Aerojet Rocketdyne developed NARloy-Z to line the inside of the rocket combustion chambers. NARloy-Z is composed of 97 wt.% Cu, 3 wt.% Ag and 0.5 wt.% Zr, and the primary strengthening mechanism is precipitation hardening. Specifically, the formation of semi-coherent CuAg precipitates strengthens the material. Since the inception of the material in the 1970s, NARloy-Z has seen changes in ingot processing and heat treatment. These changes were a result of different material suppliers, needed cost reduction, and changes in MCC manufacturing. In conjunction with these changes, data has shown approximately a 40% reduction in yield strength compared to older lots of NARloy-Z. The specific goal of this project is to determine the main factors contributing to the reduction in yield strength and propose process improvements particularly relating to the heat treatment of the alloy. In order to solve this problem, the team heat treated NARloy-Z samples of different processing backgrounds and material lots while manipulating the cooling rate from the solution temperature 1700ºF to the braze aging temperature 1375ºF. Tensile tests and a metallographic analysis were performed on all samples to identify which factor has the greatest impact on tensile strength.

2. Experimental Procedure

Standard lab safety protocol was followed during the experimental procedures of this project. All chemicals were properly stored in a fume hood. A standard operating procedure (SOP) was written for making the metallography etchant. Proper personal protective equipment (PPE) was worn during the preparation and conduction of etching.

2.1. Sample Preparation

The types of NARloy-Z were classified by the ingot processing (old or new) and the material lot (old or new). The old ingot processing method was vacuum centrifugal casting (VCC) which is an expensive process that is no longer available for NARloy-Z. A less expensive and more common process called vacuum arc remelt (VAR) was used as the new ingot processing method. The old material lot was material manufactured over four years ago, and the new material was any material produced within the last four years. The three variations of NARloy-Z used in this study were Old/Old, Old/New, and New/New. The Old/Old material was received as two 4-inch diameter ring sections in the solution treat and age (STA) condition. The New/New material was also received in the STA condition as two blocks with approximate dimensions of 0.25 by 3 by 3 inches. The Old/New material was received in a 12 × 12-inch sheet after being rolled, annealed, and brazed thermal cycled and aged (BTCA) by Aerojet Rocketdyne. ASTM Standard E8/E8M-16A was followed to machine the Old/New material into sheet-type specimens and the Old/Old and New/New material into subsize specimens.[12] Because the Old/Old material was received as two ring sections, the edges of the tensile samples were slightly curved. The average thickness of the Old/Old and New/New samples was 0.30 inches and 0.24 inches, respectively.

2.2. Heat Treatment

The typical BTCA heat treatment for NARloy-Z in the combustion chamber assembly is as follows: heat to 1700ºF to solutionize and braze the copper liner to the combustion chamber material (Inconel© 718); cool to 1375ºF over a 2.5-hour period (a cooling rate of -2.17ºF/min) and hold to age the braze material; cool to 900ºF and hold to age the NARloy-Z. This heat treatment is over a span of 24 hours and is depicted in Figure 9. The cooling rate manipulated in this study is between the solution or braze temperature and the braze alloy aging temperature. In addition to the cooling rate in the typical BTCA heat treatment, two additional cooling rates were investigated: a faster cooling rate of -5.42ºF/min (a 1-hour cool) and a slower cooling rate of -1.08ºF/min (a 5-hour cool). These two cooling rates were chosen because they would most likely be feasible in the BTCA heat treatment of the combustion chamber assembly. The heat treatments were done by Ventura Heat Treating Inc. in Oxnard, CA because NARloy-Z requires an inert atmosphere when exposed to high temperatures to prevent the formation of copper oxides which are detrimental to material properties. All samples were heat treated in a controlled environment of argon gas.

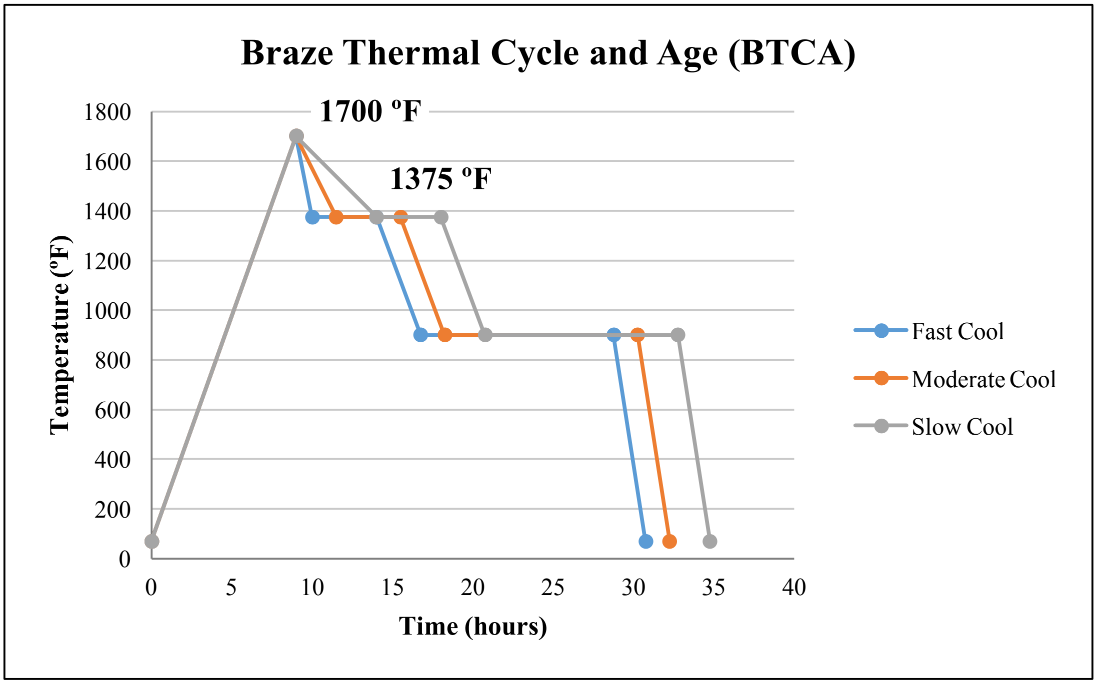


Figure 9. Profiles of the three braze thermal cycle and age (BTCA) heat treatments. Cooling rate of interest is between 1700ºF and 1375ºF.

2.3. Tensile Testing

Each specimen was measured and tensile tested in an Instron 5584 using Bluehill software. The crosshead displacement rate used was 1 mm/min. Yield strength (ksi), tensile strength (ksi), and percent elongation (in/in) were recorded. An extensometer with a gauge length of 0.98 in (25 mm) was used on all samples to measure the first 1.5% of strain. All specimens were taken to fracture except one fast cool Old/Old sample and seven fast cool Old/New samples.

2.4. Metallography

Metallography was performed on the cross section of one sample from each material and cooling rate pair. The samples chosen for metallography had a yield strength closest to the average for their respective combination of material and cooling rate. Metallography was also done on each material in the as-received condition. All samples were mounted in Bakelite and ground starting with 240 grit followed by 320, 400, 600, 800, and 1200 grits. The samples were then polished using 6µm, 3µm, and 1µm monocrystalline diamond suspension abrasive. A final polish was performed with a 0.05µm colloidal silica abrasive. All specimens were etched with a solution of 10g of ammonium persulfate in 100mL of water.[5]

2.5. Statistics

Averages and standard deviations were calculated for the yield strengths and tensile strengths of all tensile tested samples when possible. A two-factor ANOVA and a comparison of means using the Tukey method were also performed only on the yield strengths of the Old/New material and New/New material because tensile data was only collected from two different cooling rates with the Old/Old material.

3. Results

3.1. Tensile Test Results

Tensile stresses were plotted as a function of percent elongation for all tensile samples of NARloy-Z. The tensile tested as received samples (Figures 10 and 11) showed a higher strength than those tested after a BTCA heat treatment. The fast cool samples (Figures 12 through 14) had similar yield strengths, but the Old/Old samples had the most deviation. The New/New samples showed the most variation in percent elongation of the fast cool samples. The moderate cool tensile samples (Figures 15 and 16) were the most consistent among all tested samples, but the New/New samples had a slightly higher yield strength than the Old/Old samples. The slow cool samples (Figures 17 through 19) also showed similar yield strengths, and the Old/Old samples had the greatest variance. All yield and tensile strength values from each condition were similar and within a few ksi of each other. The Old/Old samples showed the most deviation, and the Old/New samples were the most consistent. Percent elongation varied from about 40% to 80%. The recorded yield strength, tensile strength, and percent elongation of each specimen are listed in Appendix A and B.

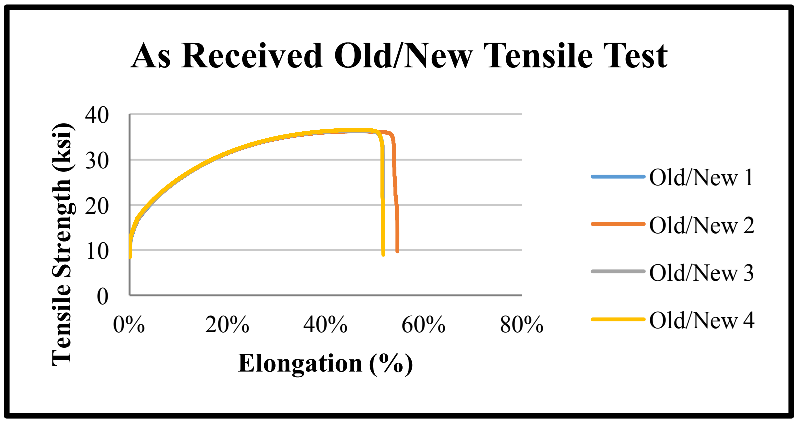


Figure 10. Tensile stress plotted against percent elongation of Old/New samples in the as received (rolled, annealed, BTCA) condition.

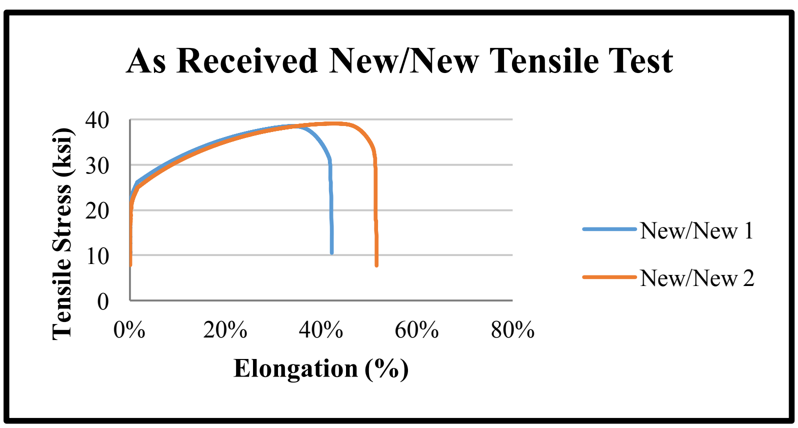


Figure 11. Tensile stress plotted against percent elongation of New/New samples in the as received (STA) condition. These samples showed highest strength of all tested samples.

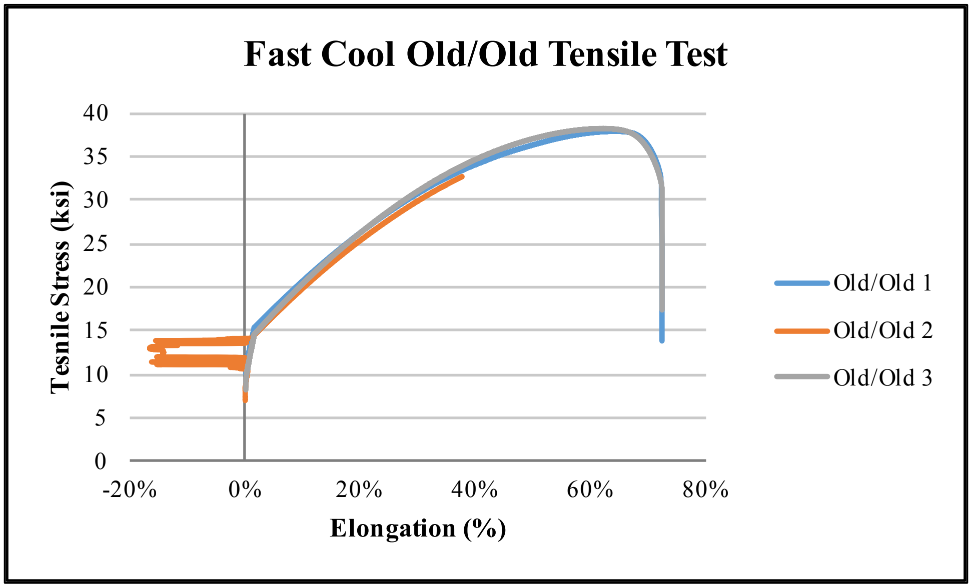


Figure 12. Tensile stress plotted against percent elongation of Old/Old samples after the BTCA heat treatment with a fast cool. The negative strain seen in specimen 2 was caused by the slipping of the extensometer, but the yield strength was unaffected; this sample was not taken to fracture.

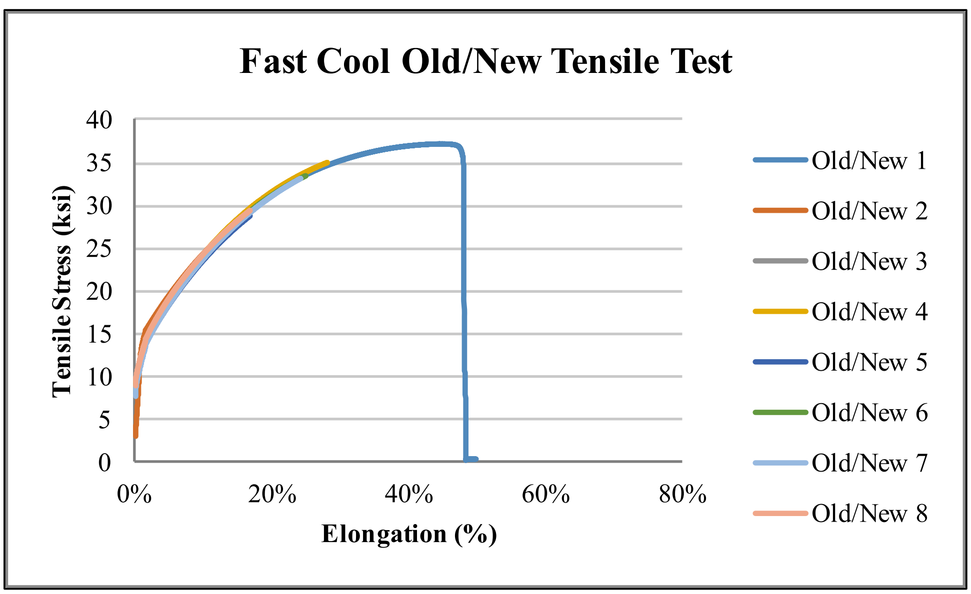


Figure 13. Tensile stress plotted against percent elongation of Old/New samples after the BTCA heat treatment with a fast cool. Only specimen 1 was taken to fracture.

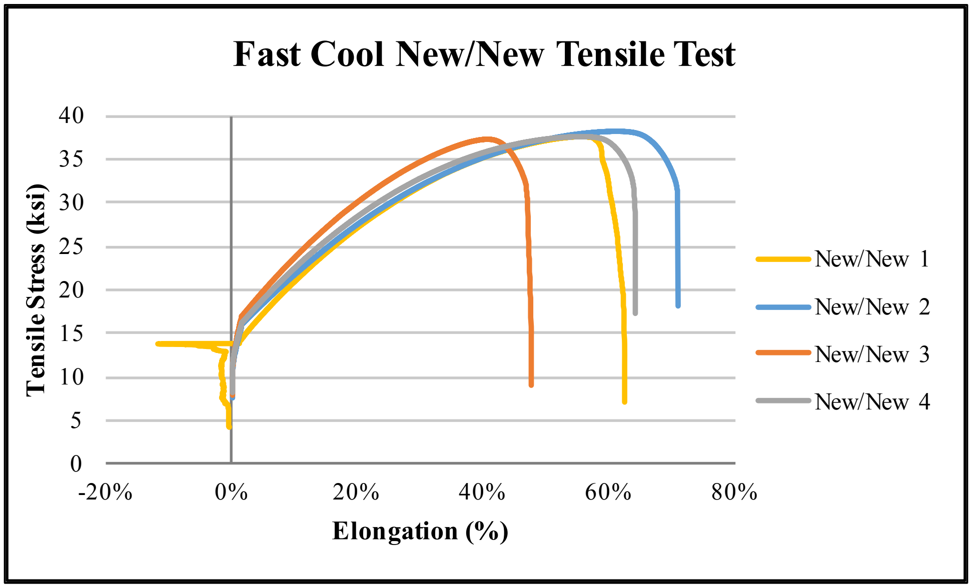


Figure 14. Tensile stress plotted against percent elongation of New/New samples after the BTCA heat treatment with a fast cool. The negative strain seen in specimen 1 was caused by the slipping of the extensometer. The yield strength was altered, so this sample was excluded from analysis.

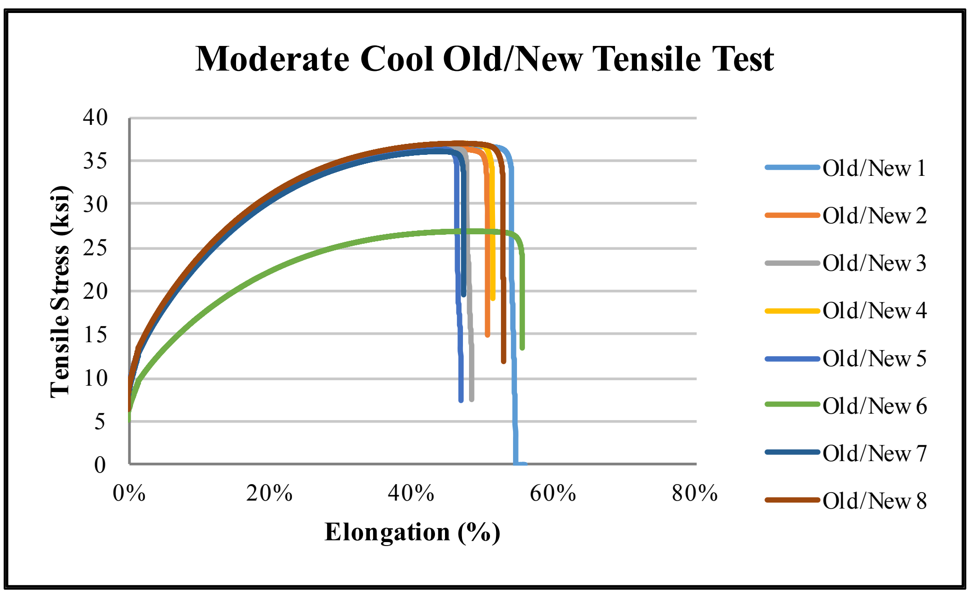


Figure 15. Tensile stress plotted against percent elongation of Old/New samples after the BTCA heat treatment with a moderate cool. Incorrect dimensions were entered in the software for specimen 6, so the yield strength and ultimate tensile strength were calculated using the load and correct cross sectional area.

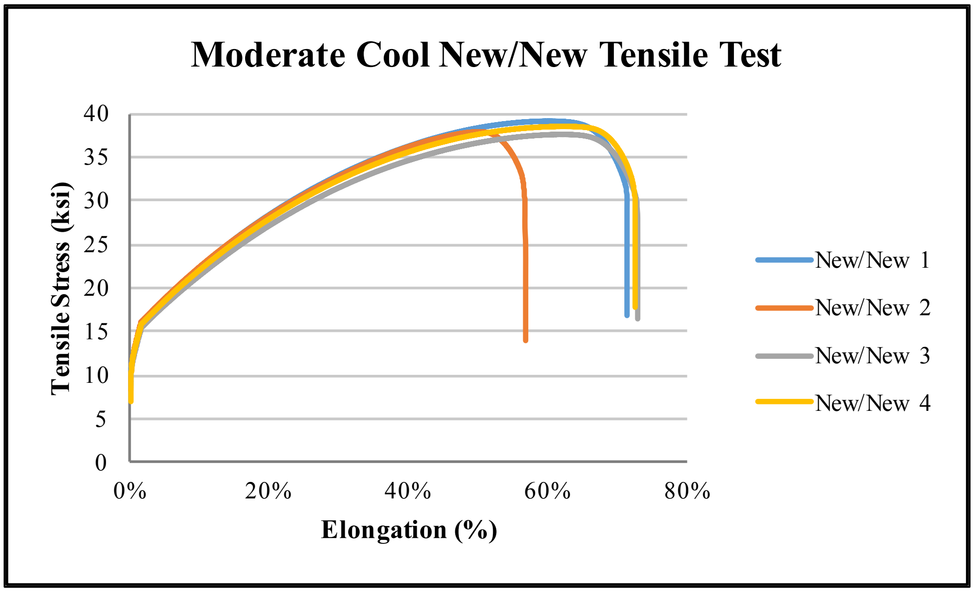


Figure 16. Tensile stress plotted against percent elongation of New/New samples after the BTCA heat treatment with a moderate cool. Specimen 2 had a significantly lower percent elongation than the other three samples, but all yield strengths were similar.

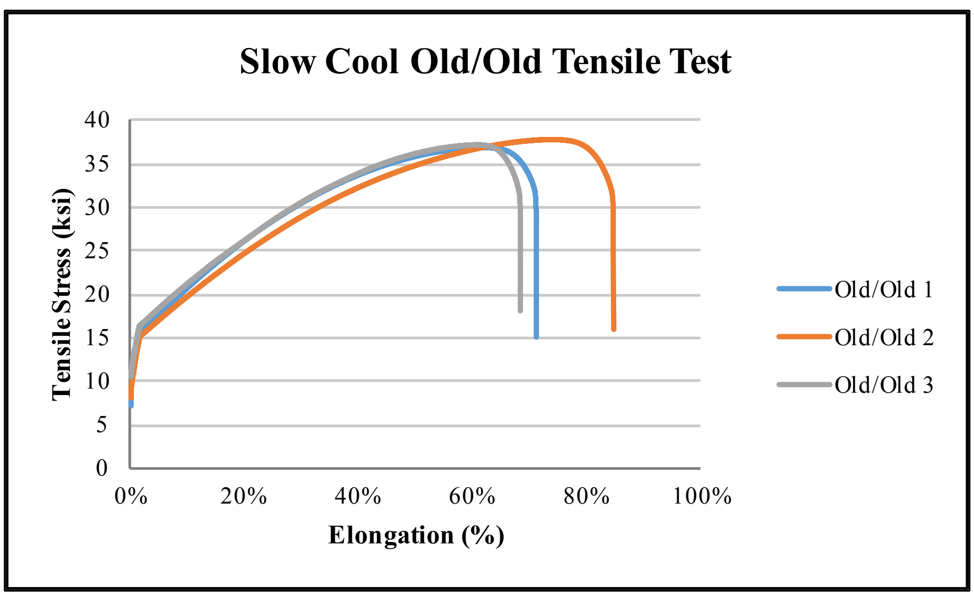


Figure 17. Tensile stress plotted against percent elongation of Old/Old samples after the BTCA heat treatment with a slow cool.

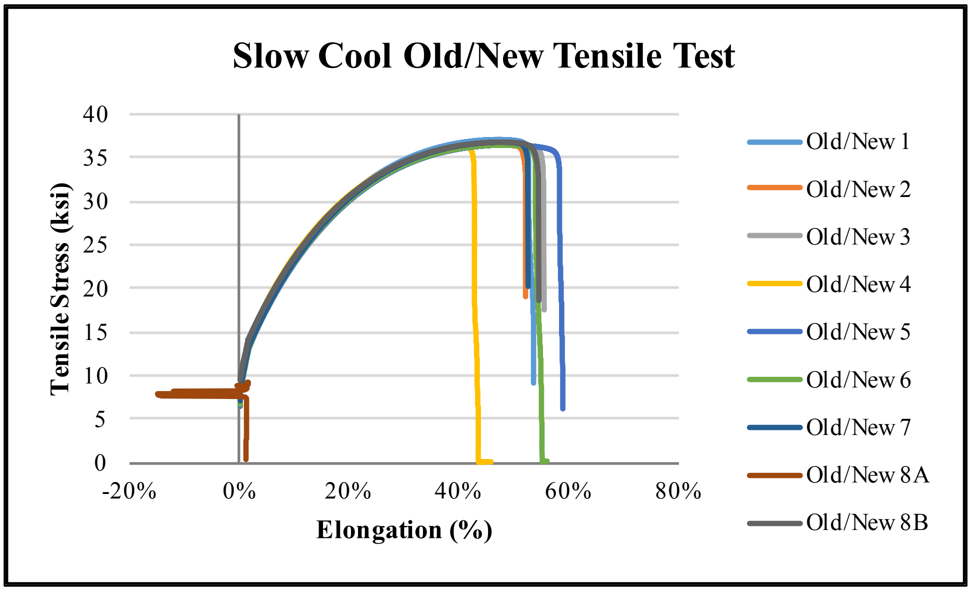


Figure 18. Tensile stress plotted against percent elongation of Old/New samples after the BTCA heat treatment with a slow cool. The negative strain in the first run of specimen 8 (Old/New 8A) was caused by the slipping of the extensometer, so the test was stopped and re-run (Old/New 8B). The yield strength was taken from 8A, and the tensile strength was taken from 8B.

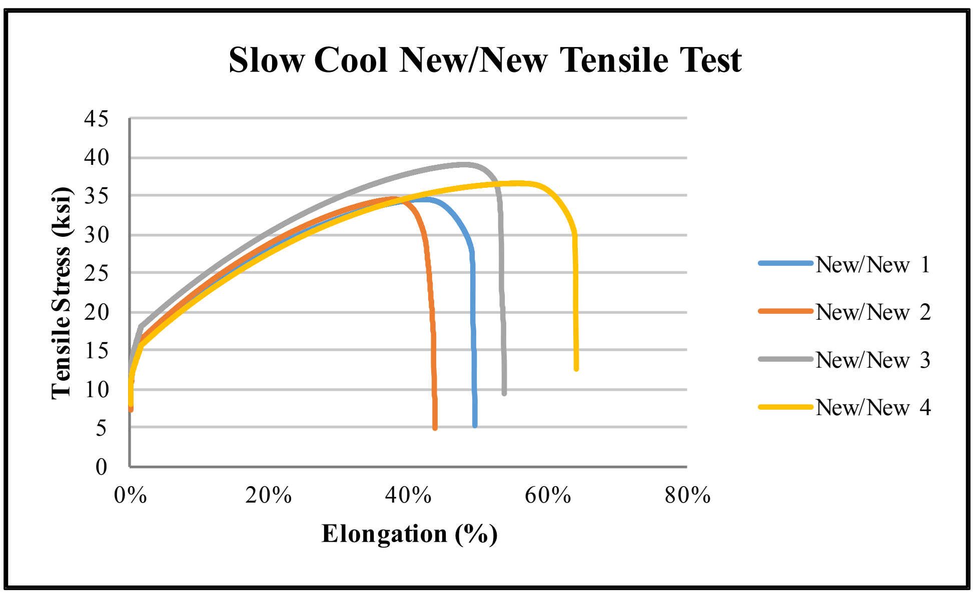


Figure 19. Tensile stress plotted against percent elongation of New/New samples after the BTCA heat treatment with a slow cool.

3.2. Statistical Results

Average yield and tensile strengths and standard deviation for each condition/material combination are listed in Table II. In general, the tensile strength had a smaller standard deviation than the yield strength with the exception of the slow-cooled New/New material. The yield strength of the Old/Old tensile samples had a higher standard deviation than the Old/New and New/New materials. Table II also shows the average yield strength of each of the BTCA heat treatments. These values show that the cooling rate had little effect on NARloy-Z yield strength.

Table II: Average Tensile Test Results

Condition	Material	Average Yield Strength (ksi)	Average Tensile Strength (ksi)	Average Yield Strength of Condition (ksi)
As Received	Old/New	12.4 ± 0.23	36.4 ± 0.16	-
As Received	New/New	21.9 ± 0.51	38.5 ± 0.33	-
BTCA with Fast Cool	Old/Old	11.2 ± 2.00	38.1 ± 0.10	11.3
	Old/New	10.7 ± 0.27	37.2 ± 0.00	
	New/New	12.1 ± 0.21	37.6 ± 0.33	
BTCA with Moderate Cool	Old/New	9.0 ± 0.17	36.6 ± 0.29	10.2
	New/New	11.3 ± 0.15	38.4 ± 0.59	
BTCA with Slow Cool	Old/Old	11.3 ± 1.60	37.3 ± 0.40	11.0
	Old/New	8.9 ± 0.18	36.6 ± 0.27	
	New/New	12.6 ± 0.95	36.2 ± 1.75	

3.2.1. Two-Factor ANOVA and Tukey Comparison

The results of the two-factor ANOVA test and Tukey comparison are shown in Tables III and IV, respectively. The ANOVA test showed that the yield strength of the New/New material was higher than the Old/New material in every condition, but the difference depended on the process. The Tukey comparison showed that even though there were significant differences between some of the means, there was not a visible trend as to which material or cooling rate proved to have a higher yield strength.

Table III: Results of the Analysis of Variance (ANOVA) Test

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Process	3	192.401	64.134	368.79	0.000
Material	1	143.882	143.882	827.37	0.000
Process*Material	3	59.572	19.857	114.19	0.000
Error	32	5.565	0.174		
Total	39	330.421			

Table IV: Grouping Comparison of Average Yield Strengths Based on Condition and Material

Grouping Information Using the Tukey Method and 95% Confidence

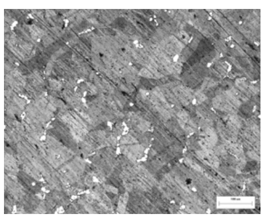
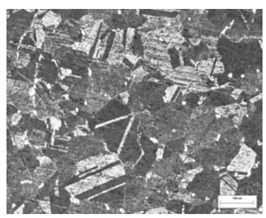
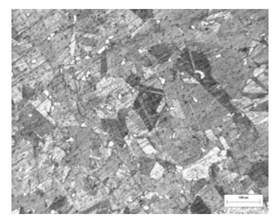
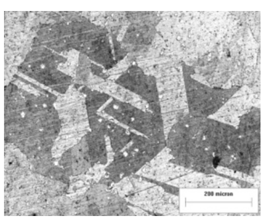
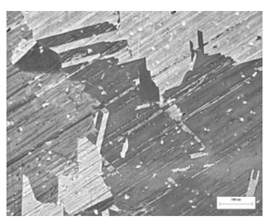
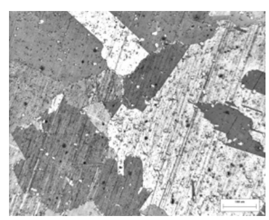
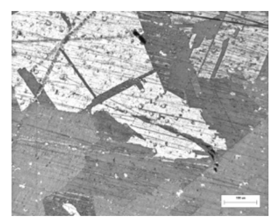
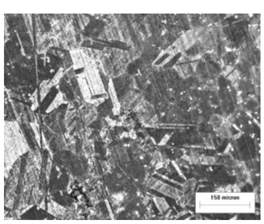
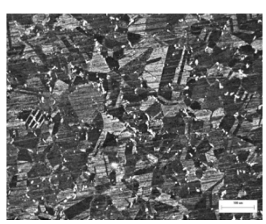
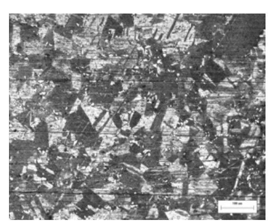
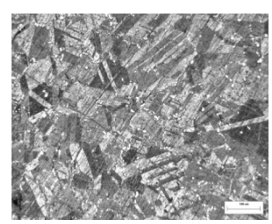
Process*Material	N	Mean	Grouping				
As Received New/New	2	21.8450	A				
Slow cool (A3) New/New	4	12.6400		B			
As Received Old/New	4	12.4425		B			
Fast cool (A1) New/New	3	12.0633		B	C		
Moderate cool (A2) New/New	4	11.3493			C	D	
Fast cool (A1) Old/New	7	10.6571				D	
Moderate cool (A2) Old/New	8	9.0498					E
Slow cool (A3) Old/New	8	8.8859					E

Means that do not share a letter are significantly different.

3.3. Metallography Images

Metallography was performed on the cross section of one tensile sample from each combination of material and condition. Although there was not enough material to machine a tensile sample for the as received Old/Old material, enough was available to perform metallography. Table V shows the micrographs taken at 100X and the average yield strength of each sample. Brightness of each microstructure and contrast between the matrix phase and precipitate phase were not indications of material differences as there was inherent variation in the etching process; an example of this is between Old/Old As Received and Old/Old Fast Cool. Qualitatively, there was little variation for each material regardless of heat treatment condition. This suggested that within a material type, there was not an observable difference in grain size, grain morphology, or precipitation phase morphology. It was clear that the Old/New samples had significantly larger grains than Old/Old and New/New.

Table V: Micrographs and Average Yield Strength of NARloy-Z

Heat Treatment / Material	As Received	Fast Cool	Moderate Cool	Slow Cool
Old/Old	 -	 11.2 ksi	-	 11.3 ksi
Old/New	 12.4 ksi	 10.7 ksi	 9.0 ksi	 8.9 ksi
New/New	 21.9 ksi	 12.1 ksi	 11.3 ksi	 12.6 ksi

4. Discussion

4.1. STA and BTCA Heat Treatment

For the material tested in this project, the yield strength of NARloy-Z in response to the BTCA heat treatment produced strengths significantly under the 20 ksi historical average. This result was seen in all samples regardless of cooling rate in the BTCA heat treatment or sample type (old processing method and old material lot or Old/Old, old processing method and new material lot or Old/New, and new processing method and new material lot or New/New).

What is most interesting about this result is that the Old/Old material responded poorly to the BTCA heat treatment even though historical data has suggested that the Old/Old material responded favorably to this BTCA heat treatment. This would suggest that there was a significant difference between the material that produced the historical average of 20 ksi and the Old/Old material tested in this project. However, the NARloy-Z material that did meet the 20 ksi historical average was the New/New material tested in the as-received STA condition. There is a clear division in mechanical properties of NARloy-Z in the STA condition versus material in the BTCA condition regardless of material type. This is most likely because the CuAg precipitates do not strengthen the material when the material is not quenched rapidly from the solution temperature (1700ºF) or if the material is held at high temperatures for extended periods of time.

4.2. Reduction in Yield Strength

A few factors contributed to the decrease in yield strength from the historical average. One of these factors is the extended time at high temperature during the BTCA heat treatment. The BTCA heat treatment does not cool fast enough to a low enough temperature from solution to produce a supersaturated solution of CuAg. Supersaturation of Ag in Cu is required for an effective aging process. The STA heat treatment is ideal for forming a supersaturated solution because the material is quenched from the solution temperature to room temperature. Instead of a rapid quench, the BTCA heat treatment cools the material from 1700ºF to 1375ºF. Once at 1375ºF, the material is held at that temperature for 4 hours. This extended time at a high temperature allows the CuAg precipitates to grow in size. With larger and fewer precipitates, there is less impedance of dislocation movement which results in a weaker material.

4.3. Metallographic Analysis

All NARloy-Z samples analyzed in this project had a two phase microstructure. The microstructure contained alpha copper and a Cu-Ag phase. In all samples, the precipitate phase was globular with a formation that was randomly scattered. The Cu-Ag phase primarily formed at grain boundaries, but some formed within alpha grains. There was not a qualitative difference between samples of high yield strength (STA condition) and samples of low yield strength (BTCA condition). When comparing the New/New as received STA sample with a yield strength of 21.3 ksi to the BTCA samples (fast, moderate, and slow cool) with an average yield strength of 11 ksi, there was not a significant visible difference in microstructure. There was no observable grain growth as a result of heat treatment performed in this study which ruled out grain size enlargement as the source of a reduction in yield strength after a BTCA. Qualitatively, a slight difference was found in the amount of the Cu-Ag phase with less of this phase in the STA condition. Further trends between yield strength and micrographs could not be made with optical microscopy because the precipitates responsible for strengthening NARloy-Z were on the nano-scale.

4.4. Grain Size

Through metallographic observation, the Old/New material consistently had larger grains than the other two materials. With this distinct difference in grain size, a difference in yield strength was expected because a coarser microstructure typically has a lower strength. The yield strength data did not support this assumption; large grains in the Old/New material had little effect on the yield strength of the material. Even with identical heat treatment, the average yield strength of the Old/New material was only slightly below the Old/Old and New/New material. This suggested that the grain size did not greatly affect the yield strength after a BTCA heat treatment. It is important to note that the New/New as received (STA condition) material, which tested above the 20 ksi historical average, had a fine grain structure. This could mean that a fine grain structure was a prerequisite for a yield strength above 20 ksi, but after BTCA heat treatment, grain size was no longer a significant factor in strengthening. The increased grain size of the Old/New material was believed to be a result of two additional processing steps that the Old/New material experienced between ingot processing and final heat treatment. The Old/New material was rolled and annealed between ingot processing and final heat treatment. The result of the rolling and annealing process increased the driving force for recrystallization and grain growth, producing a coarser grain structure.

4.5. Statistical Analysis

Using a two-way ANOVA model showed that the yield strength was typically higher for the New/New material than for the Old/New material, but that difference between the means depends on the Process. The results of the two-factor ANOVA (Figure 20) indicated that there was a significant interaction effect between Process and Material (F-stat = 114.19, $p < .001$). This implied that the association between Process and Yield Strength depends on whether Material is New/New or Old/New. It is important to note that statistical analysis was not performed on Old/Old material because there was no yield strength data for the as received or moderate cool conditions.

5. Conclusions

1. The cooling rates of the braze thermal cycle and age (BTCA) heat treatment had little effect on yield strength which were always low at 11 ksi.
2. Solution, quench and age (STA) heat treatment produced the highest yield strength as seen in the as received new processing and new material lot (New/New) samples with an average yield strength of 21.9 ksi.
3. Old/New samples consistently had a lower yield strength; however, this cannot solely be attributed to its grain size because material with finer grain structures had similar yield strengths.

References

1. "Space Shuttle Main Engine." Aerojet Rocketdyne. Web. Feb. 6, 2018.

2. Siceloff, Steven "There's the Orbiter, Go Put a Rotor in It." NASA John F. Kennedy Space Center. Dec. 22, 2010. Web. Feb. 6, 2018.

3. "NASA relies on Copper for Shuttle Engine." *Copper Development Association, Inc.* Issue #73, 1992.

4. "RS-25 SSME." High Power Rocketry. Jan. 22, 2012. Web. Feb. 6, 2018.

5. Singh, J., Jerman, G., Poorman, R., Bhat, B.N, Kuruvilla, A.K. "Mechanical Properties and Microstructural Stability of Wrought, Laser, and Electron Beam Glazed NARloy-Z Alloy at Elevated Temperatures." *Journal of Materials Science,* vol. 32, 1997, pp. 3891-3903.

6. Singh, J., Jerman, G., Poorman, R., Bhat, B.N. "Microstructural Evolution of NARloy-Z at Elevated Temperatures." NASA, George C. Marshall Space Flight Center, 1993.

7. Skrócie, W. "Precipitation Hardening of Aluminum Alloys." *Precipitation Hardening of Aluminum Alloys: Total Materia Article*, Jan. 2010, www.totalmateria.com.

8. SEQUEIRA, C. A. C. e AMARAL, L.. Strengthening mechanisms of materials for high temperature application. *Corros. Prot. Mater.* [online]. 2013, vol.32, n.3 [citado 2018-02-09], pp.75-81. Disponível em: www.scielo.mec.pt. ISSN 2182-6587.

9. J.H Sanders, P.S. Chen, S.J. Gentz, R.A. Parr, "Microstructural Investigation of the effects of oxygen exposure on NARloy-Z." *Material Science and Engineering:* A Volume 203 Issue 1-2, 15 November 1995.

10. Olsen, Dave. "Ask The Metals Experts." *What Is Centrifugal Casting and How Does It Work?*, MetalTek International, 18 Apr. 2017, marketing.metaltek.com/smart-blog/what_is_centrifugal_casting_and_how_does_it_work.

11. "An Introduction to Premium Melting." *Carpenter*, www.cartech.com/globalassets/literaturefiles/carpenterintrotopremiummelting_whitepaper.pdf.

12. "Standard Test Methods for Tension Testing of Metallic Materials." ASTM E8/E8M-16A. ASTM International Standards Worldwide, 2015.

Appendix A

Table A1: Tensile Test Results for As-Received, Fast Cool, and Moderate Cool NARloy-Z

Condition	Material	Sample Number	Yield Strength (ksi)	Tensile Strength (ksi)	Elongation (%)
As Received (Rolled, Annealed, BTCA)	Old/New	1	12.1	36.2	46
		2	12.4	36.3	55
		3	12.5	36.4	52
		4	12.8	36.6	52
As Received (STA)	New/New	1	22.4	38.5	42
		2	21.3	39.2	52
BTCA with Fast Cool	Old/Old	1	14.0	38.0	72
		2	9.7	-	-
		3	10.0	38.2	72
	Old/New	1	10.8	37.2	50
		2	13.8*	-	-
		3	10.5	-	-
		4	10.9	-	-
		5	10.1	-	-
		6	10.6	-	-
		7	10.8	-	-
		8	10.9	-	-
	New/New	1	20.4*	37.6	62
		2	11.8	38.1	71
		3	12.2	37.2	48
		4	12.3	37.5	64
BTCA with Moderate Cool	Old/New	1	8.7	36.8	56
		2	9.0	36.5	51
		3	9.2	36.5	48
		4	9.1	36.9	52
		5	9.4	36.3	47
		6	9.1	36.8	56
		7	8.9	36.1	47
		8	9.1	36.9	53
	New/New	1	11.4	39.3	71
		2	11.4	38.1	57
		3	11.1	37.7	73
		4	11.5	38.6	72

*value not used in analysis

Appendix B

Table B1: Tensile Test Results for Slow Cool NARloy-Z

Condition	Material	Sample Number	Yield Strength (ksi)	Tensile Strength (ksi)	Elongation (%)
BTCA with Slow Cool	Old/Old	1	10.6	36.8	71
		2	9.9	37.9	85
		3	13.6	37.1	68
	Old/New	1	8.9	37.0	54
		2	9.0	36.6	52
		3	8.6	36.4	56
		4	9.2	36.1	46
		5	8.8	36.6	59
		6	8.7	36.4	56
		7	8.9	36.7	52
		8	9.0	36.8	55
	New/New	1	12.2	34.6	49
		2	12.2	34.7	44
		3	14.3	38.9	54
		4	11.9	36.6	64