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# Conductivity and Structural Changes in Al-Ni Alloys with Varying Ni Content

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## ABSTRACT

The Al-Si eutectic has been the standard family of aluminum casting alloys system since the early 1900's. However, its conductivity properties are inherently limited to ~50% and 70% of pure Al in the as-cast and heat-treated states, respectively. The Al-Ni system is one of the leading candidates offering a potential for a higher combination of conductivity and mechanical properties. However, relationships between Ni content, conductivity, and structural changes have not been explored thoroughly for cast Al-Ni alloys. This study aims to clarify these microstructure-property relationships to provide guidance to alloy design efforts

**Keywords**: aluminum-nickel alloys, Al-Ni, alternate eutectic systems, conductivity

## INTRODUCTION

Aluminum is one of the most plentiful metallic elements on the earth's crust and is the most utilized nonferrous metal due to its attractive combination of high mechanical properties, low density, and low cost.[1] Pure Al conductivity properties are equally excellent with an electrical and thermal conductivity of 64.94% IACS (International Annealed Copper Standard) and 237 W/m · K, respectively, at room temperature.[2] In fact, 20% of all Al is deployed for high electrical conductivity applications because it is the best conductor on a specific weight basis even relative to Cu.[1,3]

The thermal conductivity of metallic materials has two primary components: 1) phonon propagation through lattice vibrations and 2) free electron movement.[4] Equation 1 provides a simple equation indicating that the total thermal conductivity of a metal is the summation of these two components:[5-7]

$$k_{total} = k_{electron} + k_{phonon} \quad \textbf{Eqn. 1}$$

The high electrical conductivity behavior of Al also dictates its desirable thermal conductivity behavior because the electronic contribution to thermal conductivity is typically ~10-100 times that of the phonon contribution for metals.[6,8,9]

Nevertheless, high conductivity applications are largely limited to wrought, near-pure grades of Al.[1] On the other hand, cast Al-Si alloys account for ~80-90% of global aluminum castings but are severely limited in terms of conductivity properties.[6,10,11] The Al-Si alloys are limited to ~50% of pure Al electrical and thermal conductivity in the as-cast state, and this value only increases to ~70% with over aging heat treatments.[2,6,9,12-14]

Alternatives to the Al-Si eutectic system such as Al-Ni, Al-Fe, Al-Fe-Ni, Al-Ce, and Al-Ca have been explored for its improved conductivity properties attributed to its low solid solubility in Al.[14-23] This fundamental advantage lies in the fact that all alloying elements in the Al solid solution decrease both electrical and thermal conductivity to a greater extent than the precipitated state.[6,14,24] Furthermore, these alloy systems feature intermetallic eutectic phases unlike Si, a non-metal with near zero electrical conductivity.[5] Considering that intermetallic compounds obey Wiedemann–Franz law and electron flow dominates their thermal conductivity properties, there may also be an inherent conductivity advantage with having an intermetallic eutectic phase vs. Si.[25-26]

The Al-Ni alloy system is one of the leading candidates with a eutectic point at 6.1 (wt.%) Ni and 1184F (640 C).[27] Its eutectic $Al_3Ni$ phase is confirmed to have a thermal conductivity of ~30 W/m·K, which is roughly comparable to the upper limit of polycrystalline Si.[4,25,26] There have been previous investigations of cast Al alloys with significant Ni additions to enhance hot tearing resistance, fluidity, and mechanical properties.[19,20.27-31] However, there are significantly less studies on the microstructure-property relationships of cast Al-Ni alloys as it relates to conductivity properties.[14,21,22] Furthermore, no studies have validated the Wiedemann-Franz relationships for Al-Ni alloys with a combination of measured electrical and thermal conductivity data. This study seeks to clarify such relationships to further the pursuit of castable high-strength, high-conductivity Al alloys.

## EXPERIMENTAL PROCEDURE

Seven hypoeutectic Al-Ni alloys were cast by mixing pure Al (99.9% purity) with Al-36Ni (wt.%) master alloys through using two Thermolyne box furnaces.
The nominal target compositions were Al-1Ni, Al-1.5Ni, Al-1.75Ni, Al-2Ni, Al-3Ni, Al-4Ni, and Al-5Ni (wt.%). Initially, a crucible with the pure Al alloy of interest was placed and raised to 1562F (850C) and held for 1 hour. The Al-36Ni (wt.%) master alloys were pre-heated to the same temperature within the other furnace, then introduced into the molten metal, and mixed for 5 minutes. According to a binary Al-Ni phase diagram, the liquidus and solidus of Al-36Ni (wt.%) master alloy is approximately 2066F (1130C) and 1562F (850C), respectively. Therefore, the intent of preheating the Al-36Ni (wt.%) was to facilitate full incorporation into the pure Al master alloy, which was also inferred through previous experimental trials. Subsequently, the crucible was returned to the furnace, the temperature was lowered to 1382F (750C), held at temperature for 30 minutes, and then removed from the furnace for immediate pouring. The molten metal was poured into an Arc Spark Optical Emission Spectroscopy (OES) mold preheated to 662 ± 18F (350 ± 10C) and a copper mold preheated to 257 ± 18F (125 ± 10C) to ensure consistent cooling rates during the casting process across samples. An infrared thermometer was used to validate the temperature of the molds and molten metal prior to the casting process.

The OES was conducted via an Ametek Spectrolab S unit to verify the alloying element content of the cast samples. 10 measurements were taken from each sample, and the average readings of these measurements were reported. The Al-5Ni (wt.%) exceeded the Ni content of available commercial databases and was determined via using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) area maps. This was conducted via three area measurements at low magnification yielding an average Ni content of 5.06 ± 0.1.

Electrical and thermal conductivity predictions were conducted with Thermo-Calc software using the binary Al-Ni composition. Both the equilibrium and Scheil model were used to assess the impact of solidification rate and consequent Ni partitioning.

A circular sample with 3 ± 0.1 mm thickness was sectioned at a consistent location for each Al-Ni sample cast in Cu molds. The electrical conductivity measurements of these samples were conducted with an Olympus Nortec 600 eddy current detection device. Sample thickness was standardized because Eddy current techniques are sensitive to sample geometry. Five measurements were taken for each sample with a calibration process performed prior to measuring a sample to minimize sensor drifting.

Electric discharge machining (EDM) was employed to extract a Ø6±0.1 mm cylinder with 2.5 ± 0.1 mm thickness for thermal diffusivity measurements. The test cylinder was obtained from the 3 ± 0.1 mm thick sample used for electrical conductivity measurements of the Al-3Ni (wt.%) alloy. Thermal diffusivity measurements were performed at Oak Ridge National Laboratory using a Netzsch LFA 467HT xenon flash diffusivity instrument.[32] The data reported in this study pertains to the average of five thermal diffusivity measurements taken at 77 ± 1.8F (25 ± 1C). This thermal diffusivity data was converted to thermal conductivity using specific heat and density values predicted by the software using OES composition data. Another sample was sectioned from an adjacent region of the casting, mounted for metallographic preparation, and then polished to a surface finish of 0.06 µm. Optical micrographs were taken using an Olympus GX53.

## RESULTS

The electrical conductivity of the various Al-Ni alloys with respect to varying Ni content is shown in Figure 1. Generally, a linearly decreasing trend of electrical conductivity vs. Ni content (wt.%) was observed across predictions and measurements. Since Ni's maximum solubility in Al is 0.05 wt.%, the gradual decrease in electrical conductivity can be attributed to increased volume fraction of Al3Ni.[12,22,34,35]

The equilibrium and Scheil model overpredicted and underpredicted electrical conductivity, respectively, compared to that of the cast specimen. This may potentially be attributed to minor differences in Ni content in the Al solid solution and/or segregation of Ni content that may lead to increased electron scattering.

Furthermore, cast specimen have defects such as porosity that cannot be accounted for in the conductivity modeling. However, it is significant that conductivity of cast Al-Ni samples is bounded by the Scheil and equilibrium model. Van Horn reported an increase in resistivity due to increase in Ni content in Al solid solution and out of solid solution is 0.81 and 0.061 µΩ·cm/wt.%, respectively.[36-38] Using the resistivity of pure Al, these values can be approximated as a decrease of 19.89 and 1.5 IACS%/wt.%, respectively. This study determined a trendline indicating that conductivity decrease is 1.4 IACS%/Ni (wt.%) while Kotiadis' previous study noted approximately 1.2 IACS%/Ni (wt.%).[22]

In general. conductivity properties were comparable but slightly lower than that of Yavari's study.[14] It appears that Ni is slightly less detrimental than what is traditionally reported by Van Horn for cast Al-Ni alloys.[37] The minor discrepancy between this study and that of Yavari and

Kotiadis may potentially be accounted for by impurity content as well. Table 1 provides a tabulated form of the measured and predicted electrical conductivity (IACS%) vs. Ni content.

***Table 1. Ni Content (wt.%) vs. Measured and Predicted Electrical Conductivity (IACS%)***

| **Ni** (wt.%) | **Measurement** (IACS%) | **Equilibrium** Prediction (IACS%) | **Scheil** Prediction (IACS%) |
|---|---|---|---|
| 1.11 | 59.91±0.1 | 62.36 | 56.55 |
| 1.66 | 60.97±0.12 | 62.03 | 54.97 |
| 1.89 | 60.41±0.22 | 61.89 | 54.43 |
| 2.04 | 60.11±0.13 | 61.79 | 54.11 |
| 3 | 59.51±0.21 | 61.20 | 52.52 |
| 3.66 | 56.37±0.16 | 60.78 | 51.80 |
| 5.06 | 55.57±0.05 | 59.89 | 50.92 |

Figure 2 shows the measured thermal conductivity vs. predicted thermal conductivity of the Al-3Ni (wt.%) sample.

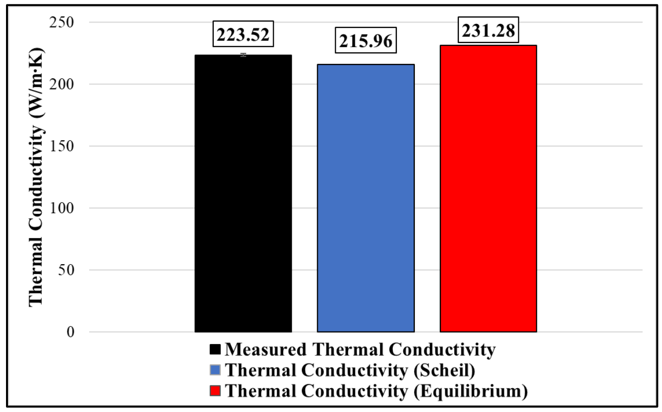


***Figure 2. Al-3Ni (wt.%) measured thermal conductivity vs. predictions (W/m·K).***

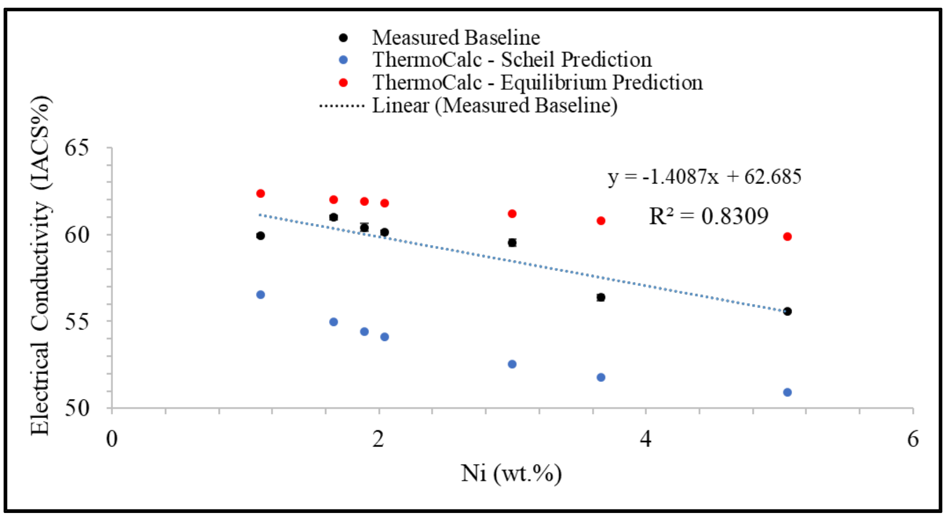


***Figure 1. Nickel content (wt.%) vs. measured and predicted electrical conductivity (IACS%).***

The measured thermal conductivity ranges between that of the Scheil and equilibrium model, correlating with trend for electrical conductivity. The raw measured value for thermal diffusivity is 89.89±0.53 $mm^2/s$ and was converted into 223.52±1.33 W/m·K. The Wiedemann-Franz law relates the electronic thermal conductivity (k) to electrical conductivity (σ) as noted in Equation 1.[5-7]

$$\frac{k_e}{\sigma} = L_0 T \qquad \textbf{Eqn. 2}$$

Where T is the absolute temperature while $L_0$ is the Lorenz coefficient, a near constant value for aluminum alloys that is approximately $2.1*10^{-8} W\Omega K^{-2}$.[12] The sectioned piece from the Al-3Ni (wt.%) sample for thermal diffusivity measurements was slightly lower in electrical conductivity with 58.35 vs. 59.51 IACS%. This 58.35% IACS% was converted to $3.384 * 10^7$ S/m. Considering the measured thermal conductivity and using a Lorenz number of $2.1*10^{-8} W\Omega K^{-2}$ leads to a calculated electronic thermal conductivity component of approximately 213.21 W/m·K. This, in turn, suggests that the phononic thermal conductivity component is approximately ~10.31 W/m·K. Consequently, the electronic and phononic component of electrical conductivity are approximately 95.4% and 4.6% of the total thermal conductivity, respectively. The phononic thermal conductivity component of pure Al is approximately ~6 W/m·K or ~2.4% of the total thermal conductivity.[6,39] Olaffson's review of commercial aluminum alloys with significant alloying element content in Al solid solution suggests that the phononic component of such alloys are generally between 10.5~12.6 W/m·K.[3,40] These values suggest that high conductivity Al-Ni alloys are relying on its electronic thermal conductivity to a comparatively closer degree to pure Al relative to Al alloys with high alloying element solubility content.

The OES measurements were taken to evaluate the presence of major and minor alloying elements in the cast sample as shown in Table 2. All alloying elements in solid solution decrease both electrical and thermal conductivity to a greater extent than the precipitated state.[5,6,9,24,36,41] Transition metal elements such as Cr, V, Ti, and Mn are particularly detrimental to conductivity properties when present in the Al solid solution due to having a large difference in atomic radii vs. Al and causing severe lattice distortion.[5,42,43] These elements in solid solution of pure Al cause a decrease in conductivity of approximately 98.20, 87.89, 70.71, and 72.18 IACS%/wt.%, respectively.[44]

***Table 2. Major and Minor Alloying Element Content Detected by OES***

| Alloy | Al (wt.%) | Ni (wt.%) | Si (wt.%) | Fe (wt.%) | Cu (wt.%) | Mn (wt.%) | Ti (ppm) | Cr (ppm) | V (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| Al-1.11Ni | bal | 1.11 | 0.0304 | 0.0515 | 0.274 | 0.0086 | 0.0015 | 0.00011 | 0.00053 |
| Al-1.66Ni | bal | 1.66 | 0.0248 | 0.0354 | 0.0512 | 0.0022 | 0.00082 | 0.00019 | 0.00064 |
| Al-1.89Ni | bal | 1.89 | 0.0172 | 0.0368 | 0.047 | 0.0019 | 0.00031 | 0.00016 | 0.00082 |
| Al-2.04Ni | bal | 2.04 | 0.017 | 0.0385 | 0.125 | 0.005 | <0.00030 | 0.00032 | <0.00030 |
| Al-3Ni | bal | 3 | 0.0135 | 0.0287 | 0.00044 | 0.00075 | 0.00031 | 0.00014 | 0.00042 |
| Al-3.66Ni | bal | 3.66 | 0.0193 | 0.0389 | 0.0921 | 0.023 | 0.00047 | 0.00019 | 0.00044 |
| Al-5.06Ni | bal | 5.06 | 0.0198 | 0.034 | 0.0413 | 0.0024 | 0.00092 | 0.00015 | 0.001 |

Each transition metal of interest is present in amounts less than 0.001 ppm and is only in the order of magnitude of impact of ~0.001 ppm in total. This content does not appear to be making a significant impact on conductivity across Al-Ni alloys. On the other hand, the major impurity content is significant with up to ~0.3645 wt.% for the Al-1.11Ni (wt.%). The Al-1.11Ni (wt.%) and Al-3.66Ni (wt.%) appear to be lower on the trendline of Ni content vs. conductivity while Al-2.04Ni (wt.%) does not exhibit this behavior despite comparable major impurity content. This suggests that impurity content may play a role, however the overall conductivity behavior seems to be dominated by Ni content.

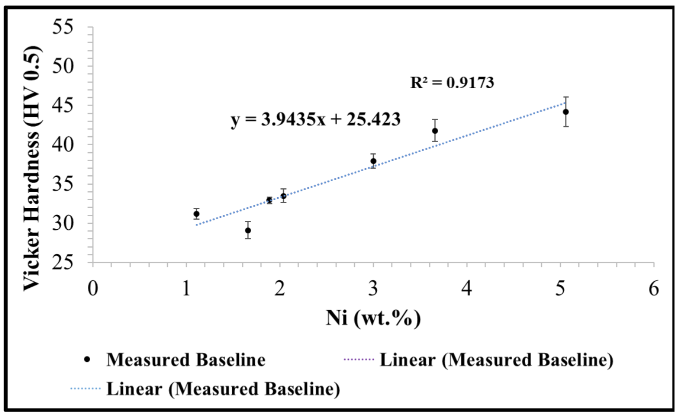


***Figure 3. Nickel content vs. Vickers hardness.***

Figure 3 shows a generally increasing linear trend of Vickers microhardness vs. Ni content (wt.%). This can be attributed to the increased volume fraction of the $Al_3Ni$ phase as a function of Ni content.[22] These microhardness values are comparable to that of Kotiadis' study, which for instance noted a 30.9±2.5 HV for a nominally Al-1Ni (wt.%) alloy.[22] Table 3 shows the raw data associated with Figure 3.

An example of backscattered micrographs taken of each alloy at identical magnification are shown in Figure 4.

***Table 3. Nickel content (wt.%) vs. Vickers Hardness (HV 0.5)***

| **Ni** (wt.%) | **Vickers Hardness** (HV 0.5) |
|---|---|
| 1.11 | 31.2±0.7 |
| 1.66 | 29.1±1.1 |
| 1.89 | 32.9±0.4 |
| 2.04 | 33.5±0.9 |
| 3 | 37.9±0.9 |
| 3.66 | 41.8±1.38 |
| 5.06 | 44.2±1.9 |

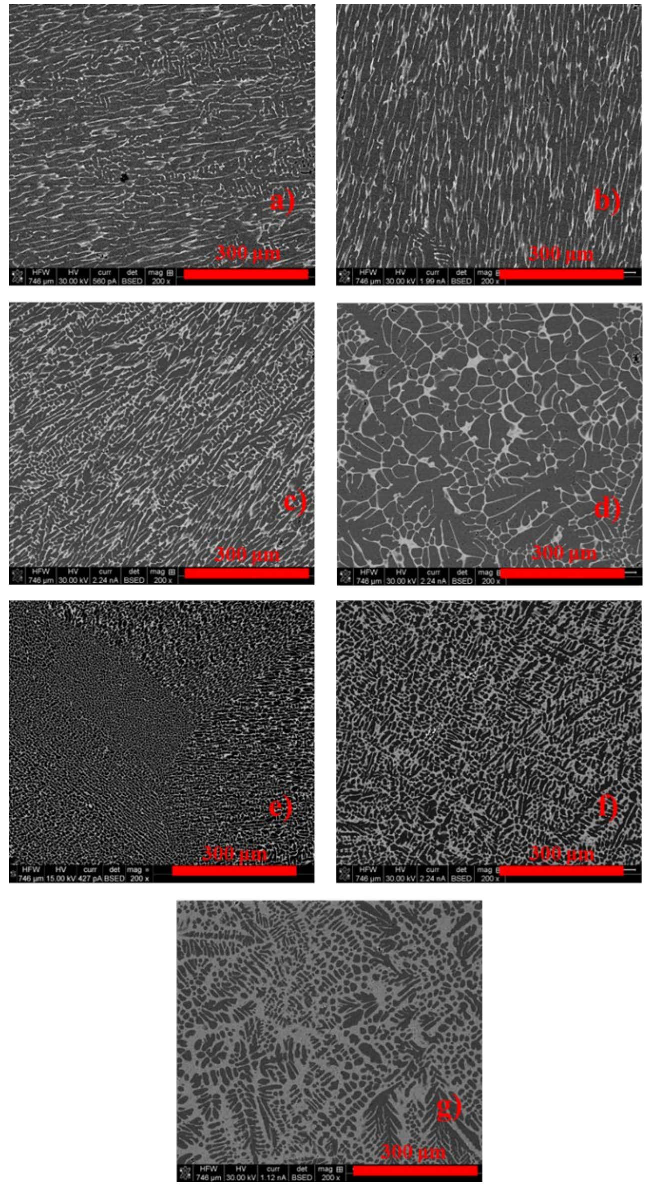


***Figure 4. SEM Micrographs of Hypoeutectic (a) Al-1.11Ni (b) Al-1.66Ni (c) Al-1.89Ni (d) Al-2.04Ni (e) Al-3.00Ni (f) Al-3.66Ni, and (g) Al-5.06Ni (wt.%) alloys at 200x magnification.***

Four to six of these micrographs of each alloy were estimate the $Al_3Ni$ area fraction plotted in Figure 5.

A generally increasing trend of $Al_3Ni$ area fraction can be observed. However, there is a scatter in the trend especially within the Al-3Ni (wt.%) sample indicating potential sensitivity to parameters during solidification despite attempts to control this across all samples. These values are comparable to those reported by Yavari, but there is a higher degree of deviation from a linear trend reported in this study.[14] Table 4 provides raw data associated with Figure 5**.**

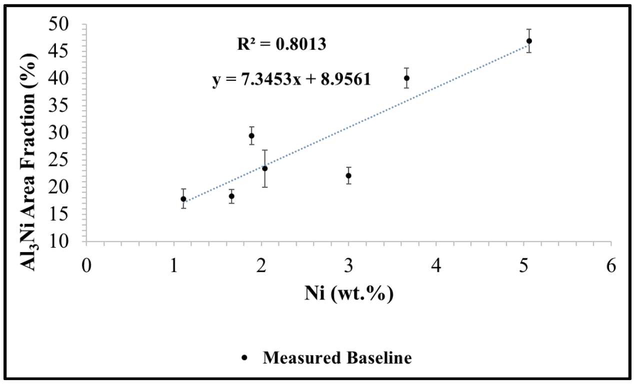


*Figure 5. Nickel content (wt.%) vs. $Al_3Ni$ area fraction.*

**Table 4. Nickel Content (wt.%) vs. Area Fraction of $Al_3Ni$ Eutectic Phase**

| **Ni** (wt.%) | **$Al_3Ni$ Area Fraction** (%) |
|---|---|
| 1.11 | 17.86±1.79 |
| 1.66 | 18.28±1.29 |
| 1.89 | 29.45±1.62 |
| 2.04 | 23.38±3.39 |
| 3 | 22.08±1.55 |
| 3.66 | 40.04±1.84 |
| 5.06 | 46.9±2.11 |

Figure 6 provides a relationship between Ni (wt.%) and secondary dendrite arm spacing (SDAS) in µm obtained through measurements of several optical micrographs per alloy.

It is worth noting that these measurement were unable to be taken for the Al-1.11Ni and Al-1.66Ni (wt.%) alloys as they did not exhibit dendritic microstructures. Otherwise, the SDAS remained relatively constant regardless of Ni content (wt.%) although scatter in the data is present. The slope is nearly zero with the value of ~0.28, and the coefficient of variation for alloys is relatively comparable, bounded between 10~30. A one-way ANOVA analysis was conducted to evaluate whether SDAS differs significantly with respect to Ni content. With a p value of 0.92563 and a null hypothesis of $p > 0.05$, this ANOVA analysis supports the conclusion that SDAS remains constant relative to variations in Ni content. This validates that increase in hardness can be accounted by the fraction of the intermetallic $Al_3Ni$ phase vs. Hall-Petch effects.[30] This result may also suggest that solidification rate is a more critical determinant of SDAS regardless of the exact Ni content. Studies have demonstrated that finer SDAS measurements correlate to higher conductivity properties.[4] However, the drastic differences in Ni content seem to outweigh such potential benefits.

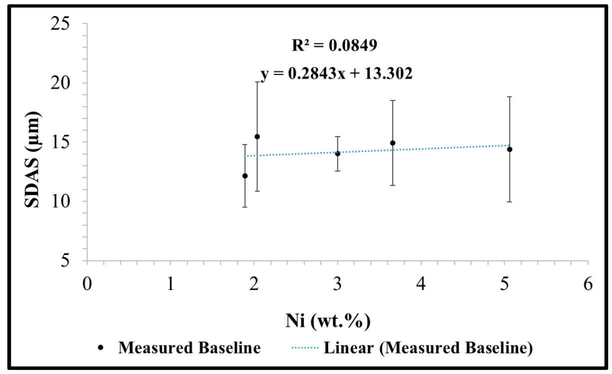


*Figure 6. Nickel content (wt.%) vs. Secondary Dendrite Arm Spacing (µm).*

The raw data associated with Figure 6 is noted in Table 5.

**Table 5. Nickel Content (wt.%) vs. SDAS (µm)**

| **Ni** (wt.%) | **SDAS** (µm) | **CV** |
|---|---|---|
| 1.89 | 12.15±2.64 | 21.73 |
| 2.04 | 15.48±4.61 | 29.78 |
| 3 | 14.02±1.45 | 10.34 |
| 3.66 | 14.92±3.59 | 24.06 |
| 5.06 | 14.39±4.42 | 30.71 |

## CONCLUSIONS

Key findings of this study examining the microstructure-property relationships of Al-Ni alloys with varying Ni content include the following:

- A relatively linear decrease in electrical conductivity was observed with increasing Ni content, comparable in magnitude relative to existing publications;
- The Thermo-Calc Scheil and Equilibrium models underpredict and overpredict conductivity properties, respectively;
- This discrepancy between predicted and measured conductivity properties may reflect the impact of solidification rate on the Al solid solution content and/or partitioning of Ni;
- Wiedemann–Franz relationship calculations for electronic thermal conductivity using measured electrical and thermal conductivity data suggest that the electronic and phononic component conductivity account for 95.4% and 4.6% of total thermal conductivity, respectively;
- The phononic component of thermal conductivity is significantly lower than other commercial alloys featuring alloying elements with significant solubility in Al and is closer to that of pure Al;

- Area fraction and microhardness generally increased linearly with respect to Ni content, suggesting the direct impact of the $Al_3Ni$ fraction;
- The area fraction may be more sensitive to solidification conditions as the trend exhibited more outliers;
- The SDAS remained relatively constant regardless of Ni content, suggesting that cooling rate is a more critical determinant of this feature;
- For binary Al-Ni alloys, Ni content dominates over any potential increases in conductivity correlated with finer SDAS.

These insights may help guide future alloy design endeavors for castable high strength, high conductivity Al alloys.

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