Thermal and Microstructural Characterization of the Multicomponent Alloy Al33wt%Cu1wt%Ni-1.2wt%Ta Solidified with Transient Heat Flow

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Abstract

The demand for materials with specific properties continues to grow in modern industry, necessitating a deeper understanding of metal solidification processes. This study investigates the thermal and microstructural characteristics of a novel multicomponent alloy, Al33wt%Cu1wt%Ni-1.2wt%Ta, which has not been previously reported in the literature. This alloy, comprising aluminum, copper, nickel and tantalum, exhibits superior mechanical strength, thermal stability and corrosion resistance compared to conventional alloys, making it suitable for various applications. Utilizing transient heat flow techniques, thermal characterization and microstructural analysis were performed on the alloy after solidification. Thermal mapping revealed variable growth and cooling rates along the ingot, influencing macrostructural transitions from columnar to equiaxed grains. Microstructural examination uncovered a complex evolution, with refined dendritic spacings initially, followed by the formation of intermetallic phases such as Al₃Ta, α-Al and Al₄Cu. The study also proposed a hypothesis on the formation of diamond-shaped intermetallics like Ni₃Ta and Ta(Cu,Al)₂, which were consumed to form Al₇Cu₄Ni at the edges. Secondary dendritic spacing analysis supported this hypothesis, showing correlation with growth laws. The findings provide valuable insights into solidification behavior and microstructural evolution, aiding in parameter optimization and enhancing the alloy’s properties for specific applications. However, limitations include the need for further research to explore mechanical and thermal properties and validate industrial potential.

Keywords: Solidification, Thermal characterization, Intermetallic phase, Kinetics, Columnar grains, Secondary dendrite arm spacing

Introduction

Multicomponent alloys have garnered considerable attention in recent years for their diverse range of properties, rendering them attractive for industrial applications [1,2]. In this investigation, the focus centers on a novel cast high-entropy or multicomponent alloy, Al33wt%Cu1wt%Ni-1.2wt%Ta, a composition hitherto unexplored in the existing literature. Unlike many previous studies that have primarily examined binary or ternary alloy systems [1,3-7], this research delves into the complexities of a quaternary alloy with composition not found in the literature, thereby paving the way for a deeper understanding of its behavior and potential applications. By incorporating aluminum (Al), copper (Cu), nickel (Ni) and tantalum (Ta), each imparting distinct properties, our study ventures into uncharted territory, aiming to elucidate the synergistic effects and performance of this unique alloy composition, which underscores its significance in advancing the field of multicomponent alloys and provides valuable insights for future research and industrial applications.

The inclusion of aluminum (Al), copper (Cu), nickel (Ni) and tantalum (Ta) in this multicomponent alloy composition holds great importance both in industrial and environmental contexts. Each element contributes distinct properties, thereby enabling the alloy to exhibit enhanced mechanical strength, improved thermal stability and exceptional corrosion resistance [1,3]. These attributes make the alloy a promising candidate for various engineering applications, including aerospace, automotive and electronics industries [1].

Moreover, the industrial and environmental significance of this multicomponent alloy lies in its potential to supplant traditional materials with adverse environmental impacts. Aluminum offers a
lightweight alternative to steel, thereby curbing energy consumption and emissions during transportation while enhancing fuel efficiency. Additionally, copper, nickel and tantalum possess unique electrical and thermal conductivity properties, rendering them invaluable for electrical components and heat exchangers, respectively [1]. By comprehensively understanding the thermal and microstructural characteristics of this alloy, its potential can be harnessed as a sustainable and environmentally friendly material across various sectors.

The Al-Cu-Ni-Ta alloy system has the potential to form various intermetallic compounds, which can significantly influence the alloy’s properties. For example, the addition of nickel (Ni) to aluminum-copper (Al-Cu) alloys has been shown to improve tensile properties [1,4]. Interdiffusion and the formation of intermetallic compounds at Al/Cu interfaces have also been studied [3]. Tantalum (Ta) additions to Cu-Al-Ni shape memory alloys have been found to affect the microstructure and properties of the alloys [5]. Additionally, first-principles studies have investigated Ni-Ta intermetallic compounds [6]. These studies provide insights into the possible intermetallic compounds that may form in the Al-Cu-Ni-Ta alloy system. Many alloys in the Al-Cu-Ni system, with or without the addition of other elements, are produced by mechanical alloying (MA) due to the capability of this process to create unique microstructures and enhanced properties [5,8,9]. However, the production of these alloys by conventional casting presents significant advantages, especially when considering the directional solidification process [4,6].

The directional solidification process in conventional casting allows for precise control and careful control of the parameters influencing the microstructures and properties of the alloys. By solidifying the alloy in a controlled manner, it is possible to achieve preferential crystal orientations, homogeneous phase distribution and elimination of structural defects. This results in alloys with superior mechanical properties, enhanced corrosion resistance and optimized thermal stability [4,6].

Furthermore, conventional casting is more suitable for large-scale production and complex shapes, meeting industry demands. The ability to control the directional solidification process makes it possible to adjust cooling and solidification conditions to obtain the desired microstructures, ensuring consistency and quality of the produced alloys [4,6].

To fully harness the benefits of the cast Al33wt%Cu1wt%Ni-1.2wt%Ta alloy, it is crucial to study the solidification process and its associated thermal variables. Solidification plays a vital role in determining the final microstructure and mechanical properties of alloys. The cooling rate, heat flow and alloy composition significantly influence the formation of different phases, grain size and defect formation [1,4,7]. Therefore, a comprehensive understanding of the solidification process and its thermal variables is essential to optimize the alloy’s properties for specific applications.

In addition to thermal analysis, characterization of the macro and microstructure is of paramount importance. Macrostructural examination provides insights into the overall morphology and distribution of phases, while microstructural analysis enables us to observe the finer details such as grain boundaries, defects and precipitates. These structural features directly affect the alloy’s mechanical strength, hardness and corrosion resistance [1]. By conducting a thorough characterization, researchers can gain a deeper understanding of the alloy’s structure-property relationships, enabling further advancements in alloy design and optimization.

According to this, the aim of this study is to investigate the thermal behavior and microstructural evolution of the Al33wt%Cu1wt%Ni-1.2wt%Ta alloy during solidification using transient heat flow techniques. Through a combination of thermal analysis and microstructural characterization, the seek is to enhance the knowledge of this unexplored multicomponent alloy composition, contributing to the advancement of alloy design and optimization, ultimately facilitating its utilization in diverse industrial sectors [1-5].

Following the introduction of the alloy composition and its significance, this paper proceeds with a methodological exposition. Firstly, the experimental methods employed in the investigation are detailed, encompassing thermal analysis techniques and microstructural characterization methods. Subsequently, the focus shifts to the results and discussion section, where the thermal behavior and microstructural evolution of the Al33wt%Cu1wt%Ni-1.2wt%Ta alloy during solidification are examined in depth. Through a comprehensive analysis of transient heat flow techniques and microstructural observations, this study aims to enrich the understanding of this unexplored multicomponent alloy composition, thereby unlocking its potential for various industrial applications. Finally, the main objective of the paper can be clarified and reiterated at the end of the introduction.
Materials and methods

Firstly, this research presents the solidification path of the alloy and 2 pseudo-binary phase diagrams, varying the copper (Cu) and nickel (Ni) content, generated by ThermoCalc® [10] to identify the possible phases present. The solidification path represents the sequence of phase transformations during cooling and solidification, providing insights into phase formation. The pseudo-binary phase diagrams help identify potential phases by varying the copper and nickel content. These diagrams offer a graphical representation of the relationship between composition and phases. By analyzing the diagrams, we can predict the presence of specific phases and their distribution within the alloy.

Understanding the possible phases is crucial for elucidating the alloy’s microstructure and properties. Through comprehensive analysis, researchers can gain insights into the alloy’s structure-property relationships. In subsequent sections, it is discussed experimental methods, sample preparation, thermal analysis and microstructural characterization.

Figure 1 Generated solidification path and pseudo-binary phase diagrams for the multicomponent alloy.

The multicomponent alloy developed in this study was prepared using commercially obtained high-purity aluminum and nickel raw materials. The copper used was sourced from tubes used in air conditioning installations, which contained a percentage of tantalum. The nominal composition of the alloy was confirmed using a thermal characterization technique. A small volume of the alloy was introduced into a silicon carbide crucible, melted in a muffle furnace and slowly cooled until complete solidification. This resulted in an experimental cooling curve representative of the investigated alloy’s solidification path, as shown in Figure 2(a).
Figure 2 (a) experimental cooling curve and (b) experimental cooling curves obtained via solidification process.

Once the alloy composition was confirmed, a larger volume of liquid metal was poured into the water-cooled upward solidification device’s cylindrical ingot, as depicted in Figure 3. The device consisted of electric resistance mounted on a cylindrical refractory piece with controlled power for the unidirectional solidification process. When the thermocouple closest to the base of the mold recorded a temperature 10% above the liquidus temperature (T\text{L}), approximately 627 °C, the forced cooling system was activated, initiating the upward unidirectional solidification process in the device, and thermal data were recorded for further analysis.

Figure 3 Schematic drawing of the upward vertical unidirectional solidification device [11].

To determine the thermal parameters of solidification, growth and cooling rates (V\text{L} and T\text{R}), a thermal mapping was conducted using the 6 type K thermocouples inserted into the cylindrical ingot from the heat transfer surface, from the lower base to the top, and cooling curves were obtained as shown in Figure 2(b). Similar experimental methodology used to determine V\text{L} and T\text{R} is well-documented in the literature [4,7,12-14].

After cooling the alloy, the ingot was demolded and sectioned according to Figure 4, for the acquisition and analysis of macrostructure and microstructure using optical microscopy and scanning electron microscopy (SEM) with EDS. To conduct the analysis, the acquired sectioned face surfaces were
sanded using abrasive papers with grit sizes from #80 to #1,200 mesh and etched using Keller’s reagent to reveal the ingot’s macro and microstructure.

After this step, the samples were analyzed using optical microscopy. Scanning electron microscopy (SEM) with EDS was performed to obtain microstructures, verify the elements and identify intermetallic compounds.

Based on the micrographs obtained from optical microscopy, measurements of secondary dendrite spacings ($\lambda_2$) were conducted using the intercept method. This method involved calculating the value of $\lambda_2$ by averaging the distances between adjacent arms (secondary branches) on the longitudinal section (parallel to the heat flow or growth direction) of a primary dendrite, where $n$ is the number of secondary branches. This procedure is widely accepted in the literature [7,13-15].

**Figure 4** Sectioning of the ingot, direction and positions of measurements of $\lambda_2$ and measurement technique.

**Results and discussion**

**Figures 5(a) - 5(b)** presents the experimental results of growth and cooling rates from the cooling curves presented in **Figure 2(b)**, obtained for each thermocouple, resulting from the solidification process under the conditions assumed in this work. As can be seen, and expected, the refrigeration system of the upward directional solidification device imposed a decreasing profile of $V_L$ and $T_R$ values along the length of the as-cast ingot, that is, high $V_L$ and $T_R$ values were obtained in positions closer to the cooled mold plate (heat transfer surface), which decrease with the course of solidification.

The macrostructure of the ingot exhibits a very fine columnar structure up to approximately 10 mm from the cooled base, transitioning to a columnar/equiaxed structure until approximately 45 mm, and then becoming entirely equiaxed until the end of the ingot. This variation in macrostructure is a result of the solidification conditions experienced during the cooling process combined with alloy composition. Siqueira *et al.* [16] proposed a columnar-to-equiaxed transition (CET) criterion based on critical cooling rates of about 0.2 K/s, for Al-Cu alloys, with the columnar growth prevailing throughout the casting for cooling rates higher than these critical values. Besides, Gomes *et al.* [17] noted that the effect of higher density of Cu alloying element as well as the Cu segregation at the solidification front can favor anticipation of CET in Al-Cu alloys. The results of the present work are in line with the literature, showing a similar columnarto-equiaxed transition behavior as observed by the referred literature, with probably, the presence of nickel (Ni) and tantalum (Ta) likely contributed to an even further advancement.
Figure 5 (a) and (b) experimental rates of growth and cooling and (c) solidification macrostructure.

The microstructure of the alloy initially exhibits refined dendritic spacings and limited intermetallic identification in the interdendritic region. Subsequently, the dendritic spacings start to increase, and the presence of the Al$_2$Cu eutectic structure, other lamellar structures and diamond-shaped precipitates becomes evident. Towards the end of the ingot, the dendritic spacings become coarser, and all mentioned structures appear well-defined. Figure 6 presents the quantification of secondary dendritic arm spacings as a function of position, along with corresponding microstructures from some of these positions. It can be observed that $\lambda_2$ increases with increasing distance from the metal/mold interface, and a power-law-type representative function was formulated.

Figure 6 Variation of secondary dendritic spacings with ingot position and some microstructures observed along the ingot.
Figures 7 and 8 display the microstructures and corresponding map scans obtained with a scanning electron microscope for an initial and final position of the ingot, respectively. In the initial position, the presence of aluminum is observed in the dendritic region, while copper, nickel and tantalum are dispersed in the interdendritic region. However, these elements are not uniformly distributed. In the final position, the microstructure exhibits more pronounced features. Alongside aluminum-rich dendrites, a clear lamellar phase rich in aluminum and copper is visible in the interdendritic region. Another lamellar phase, containing aluminum, copper and nickel, is observed surrounding the diamond-shaped phase composed of aluminum, copper, nickel and tantalum. The presence of these various phases demonstrates the complex composition and microstructural evolution within the alloy during solidification.

By examining the solidification path shown in Figure 1, it can be observed that under equilibrium conditions, the intermetallic compounds Al$_3$Ta, Al$_7$CuNi, θ-Al$_2$Cu and Ni$_3$Al would be formed throughout the solidification process. However, due to the non-equilibrium solidification and variable cooling rates, the microstructures and EDS mapping lead to a likely hypothesis regarding the formation process of these structures during solidification.

Figure 7 Optical and SEM microscopies and map scans from an initial position of the ingot.

Figure 8 Optical and SEM microscopies and map scans from an initial position of the ingot, showing probable intermetallic compounds.
The peritectic reaction is a solidification process in which a solid and a liquid phase transform into another solid phase. This reaction occurs when the primary solid phase reacts directly with the liquid phase to form a secondary solid phase, known as the peritectic product [18]. The peritectic reaction is preferred to occur at low cooling rates because it allows for more time for diffusion to take place. At low cooling rates, there is sufficient time for the atoms or molecules to rearrange and diffuse, leading to the formation of new intermetallic compounds. In contrast, at high cooling rates, the solidification process occurs rapidly, leaving less time for diffusion to take place [18,19].

In the case of the upward directional solidification of the Al-33wt.%Cu-1wt.%Ni-1.2wt.%Ta alloy, as the cooling rate decreases, various peritectic reactions with the formation of new intermetallic compounds can occur. The hypothesis suggests that the initial stages of solidification involve the formation of the intermetallic compound Al$_3$Ta, followed by the primary α-Al phase and the intermetallic Al$_2$Cu. It should be noted that the Al$_3$Ta intermetallic does not exhibit a diamond-shaped morphology. As a result, in the early positions, it appears as distinct highlighted points in both the microstructure and map scans of the initial positions. These positions experience relatively higher cooling rates compared to the subsequent stages.

As the cooling rate decreases, allowing for sufficient time for diffusion, the formation and growth of complex intermetallics, namely Ni$_3$Ta and Ta(Cu,Al)$_2$, begin. These intermetallics exhibit the diamond-shaped morphology as seen in the microstructures of more advanced positions in the alloy. It is worth mentioning that similar intermetallic phases have been reported in previous studies [20,21], demonstrating the consistency of the findings reported on this paper with existing knowledge. The difference between the present work and the literature lies in the methodology and experimental approach. While the literature primarily focuses on materials cast in equilibrium in a crucible and presents results using X-ray diffraction (XRD), the present study employs a transient directional solidification process and presents results using Energy-Dispersive X-ray Spectroscopy (EDS).

A correlation between the results of the present study, which evaluated the samples using EDS, and those from the literature, which analyzed the samples via XRD can be made. While EDS analysis offers information on the elemental composition of specific points within the sample, XRD analysis provides data on the crystalline structure and phase identification. Therefore, the results obtained from EDS can complement those from XRD by confirming the elemental composition of the phases identified in the XRD patterns. By comparing the elemental composition obtained from EDS spectra with the phase identification from XRD patterns, it is possible to validate the presence of specific phases in the alloy, as can be shown in Figure 9.

![Figure 9](image_url)

**Figure 9** Comparison between the structure of the CuNiTa intermetallic found (a) in the present work and (b) in the literature [20].

With further reduction in the cooling rate, these formed complex intermetallics are gradually consumed, giving rise to the “edges” of the diamond-shaped region. This region is constituted by the intermetallic compound Al$_7$Cu$_4$Ni, which is clearly observable in the microstructures of the final positions of the ingot.

In the final positions, characterized by very low cooling rates, a dendritic microstructure is observed, featuring coarse and widely spaced dendritic arms. The interdendritic region contains a combination of α-Al+Al$_2$Cu, Ni$_3$Ta+Ta(Cu,Al)$_2$ and Al$_7$Cu$_4$Ni compounds, as clearly visualized in the microstructures of
these positions. The distinct morphology and composition of these intermetallic phases provide insights into the intricate solidification process and the influence of cooling rates on their formation.

The evolution of the microstructure and the presence of specific intermetallic phases are attributed to the non-equilibrium solidification conditions and varying cooling rates experienced during the solidification process. The interplay between diffusion and cooling rates dictates the formation and growth of intermetallic compounds, leading to the observed microstructural variations. This study provides valuable insights into the solidification behavior and microstructural development of the investigated alloy, contributing to the understanding and control of its properties for potential applications.

In their studies, Wu et al. [22] indicated that the refined and functionalized surface of nanometric diamond particles could enhance the ability to fill and repair surface irregularities on friction pairs, while their potential to enter friction interfaces might facilitate a rolling effect, thereby contributing to improved anti-wear and friction-reducing properties. Just as nanoparticles can be added to a metal matrix or fluid to enhance its properties [23-27], intermetallics can be formed as intermediate phases during the solidification process to confer specific characteristics to the alloy. Intermetallics can form distinct phases within the matrix, affecting its properties, while nanoparticles can act as nucleation sites or dispersed reinforcements, altering the matrix characteristics.

Aligning these findings with this work, it can be supposed that the morphology of the diamond-like particles in the present study may have similar tribological effects as described. Modern mechanical engineering seeks these correlations to facilitate the production process and reduce costs [28], therefore further studies regarding the tribology of this alloy can be conducted.

Figures 10(a) - 10(b) present the results of secondary dendritic spacing as a function of growth rate (\(V_L\)) and cooling rate (\(T_R\)). In both cases, a decrease in \(l_2\) is observed with increasing \(V_L\) and \(T_R\), and both results can be expressed by power-law-type functions. A comparison with the experimental growth laws proposed by Rocha et al. [29] was also conducted, but a good correlation was only found for higher cooling rates when there was insufficient time for peritectic reactions to occur, resulting in the observed intermetallic quantity. These observations provide support for the hypothesis proposed in this study regarding the formation of the phases.

![Figure 10](image_url)

**Figure 10** Dependence of dendritic scale length on growth and cooling rates.

**Conclusions**

Based on the discussions and results presented, the following conclusions can be suggested for the developed work: (1) The study provided a comprehensive understanding of the microstructural evolution of the new multicomponent aluminum alloy during the solidification process. The transition from columnar to equiaxed structure was clearly observed and attributed to solidification conditions and alloy composition. (2) The microstructural analysis revealed a complex evolution, with refined dendritic spacings initially, that increase with the position from metal/mold interface. A hypothesis was proposed, suggesting the formation of Al₃Ta, \(\alpha\)-Al and Al₃Cu in the initial stages, followed by the growth of complex diamond-shape intermetallics such as Ni₃Ta and Ta₄Cu₃Al₂. The consumption of these intermetallics led to the formation of Al₃Cu₃Ni at the edges of the diamond-shaped region. (3) The use of transient directional solidification...
allowed for the observation of a previously unreported microstructural and phase modification for this specific type of alloy. This innovative approach provided a deeper understanding of the effects of solidification kinetics on morphology and phase distribution in the alloy. (4) The results obtained in this study are consistent with observations reported in the literature regarding the formation of microstructures and intermetallic phases in aluminum-copper alloys. This validates the consistency and relevance of the findings of this work in the context of established knowledge. All of the numerical results were condensed in Table 1, as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Length unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature - (T_{L})</td>
<td>570 °C</td>
</tr>
<tr>
<td>Growth rate as a function of position - (V_{L}(P))</td>
<td>1.04(P)^{-0.41}</td>
</tr>
<tr>
<td>Cooling rate as a function of position - (T_{R}(P))</td>
<td>11.63(P)^{-0.6}</td>
</tr>
<tr>
<td>Secondary dendrite arm spacings as a function of position - (\lambda_{d}(P))</td>
<td>8.3(P)^{0.5}</td>
</tr>
<tr>
<td>Secondary dendrite arm spacings as a function of growth rate - (\lambda_{d}(V_{L}))</td>
<td>8.7(V_{L})^{1.2}</td>
</tr>
<tr>
<td>Secondary dendrite arm spacings as a function of cooling rate - (\lambda_{d}(T_{R}))</td>
<td>59(T_{R})^{-0.84}</td>
</tr>
</tbody>
</table>

Enhanced understanding of microstructural evolution and intermetallic phases in the new alloy paves the way for future studies, especially in the field of tribology. Investigating the tribological performance of the alloy, along with optimization of processing conditions, may provide additional insights and facilitate industrial application of this alloy.

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References


