Volume 17, Number 1, 2024. pp. 35-43

Jordan Journal of Physics

ARTICLE

Thermodynamic Analysis of Al-Ni, Al-Cu Alloys System Using Calphad Method

Dil Faraz Khan[a], **Sadaf Iqbal**[a], **Waseem Ullah Shah**[a], **Mudassir Mahmood**[a] and **Haiqing Yin**[b]

[a] *Department of Physics, University of Science and Technology Bannu 28100, Pakistan.*
[b] *School of Material Science and Engineering, University of Science and Technology, Beijing 100083, China.*

Doi: **https://doi.org/10.47011/17.1.4**

Received on: 05/04/2022; *Accepted on: 30/06/2022*

Abstract: The CALPHAD technique, in conjunction with the PBIN database, is employed to conduct a thorough thermodynamic analysis and assessment of the binary alloy systems Al-Cu and Al-Ni. This study explores the thermodynamic properties, including phase diagrams, Gibbs free energies, and thermodynamic molar activities across the entire compositional range. The temperature maintained for assessment is 2000-2050 K. The doping characteristic of the AL-Ni binary system is more epitaxial and useful for doping industries. The correspondence of Raoult's law is more precise in the Al-Ni binary alloy system due to its better doping characteristics. The entropy and the enthalpy of both systems increase. The greater decrease in the Gibbs curve and activity predicted the more stability of the alloying system Al-Ni. Within the Al-Ni system, a composition range of 0.4-0.6 mole percent at a temperature of 2050 K is identified as the most stable, contrasting with the Al-Cu system, which exhibits the least stability. The lattice vibrations mode and Brillion zone growth during alloying contribute to highly epitaxial characteristics, with pure and sharp attractive interactions among alloying elements. Negative deviation from ideality in activity is observed in the Al-Ni system, further supporting its increased stability. This is attributed to the lower Gibbs energy and higher enthalpy accordance. Both Al-Cu and Al-Ni binary systems show the highest level of equilibrium and stability. The enthalpy values of both alloying systems gradually increase with temperature. In the solid era of both binary alloy systems, Al-Cu and Al-Ni, the ferrite phase is identified as the stable phase. The most stable ferrite phase, capable of withstanding the highest temperatures, holds promise for applications in industrial sectors and materials metallurgy.

Keywords: Thermodynamic properties, CALPHAD method, Thermo-calc simulation package, Alloys.

Introduction

Aluminum-based alloys have been a subject of study and commercial use for several decades. Researchers continue to show significant interest in aluminum and its alloys due to their importance in industries such as aircraft and the automotive industry, where properties like tensile strength, corrosion resistance, and heat resistance are highly valued [1, 2].

One area of particular focus in research is the precipitation behavior of aluminum-based alloys, especially in metastable phase Al-Cu alloys, which are utilized for their combination of high strength and light weight. Both theoretical and experimental investigations have been conducted over an extended period to understand precipitation phenomena [3]. The liquid phase

Corresponding Author: Waseem Ullah Shah **Email**: waseemullahshah303@gmail.com

and FCC phase occur at Al and Ni-rich ends, resulting in the formation of melting compounds. The non-congruent solubility, characterized by a variable range on the two sub-lattices, can be replaced by vacancies by the cluster variation method for Al-Ni systems [4].

In the Al-Ni system, the FCC phase (LI$_1$) exhibits both ordered and disordered (LI$_2$) configurations, as calculated by the regular sub-lattice model [5].

The phase diagram of the Al-Ni system, with transitions between ordered and disordered phases, has been investigated by Ansara *et al*. In this system, both the FCC phases LI1 and LI2, as well as the BCC phases LI2 and B2 undergo order-disorder transitions [6, 7]. The Gibbs energy and other thermodynamic parameters for the Al_2Ni_3 phase need improvement in the homogeneity range using Scheill calculations [8]. The Calphad method is an important procedure for the advancement and designing of different materials, offering a cost-effective alternative to experimental approaches, especially for studying phase transformations in metastable phases in the Al-Cu system [9]. The Al-Cu system exhibits a complex phase diagram, with twelve stoichiometric phases, seven of which are marked as stable at high temperatures [10]. In the Al-Ni systems, defects, particularly antisite defects, are commonly observed, due to a high fraction of vacancies in the normal disordered phases. The two types of vacancies are formed on a thermal and structural basis. Thermal vacancies arise from sub-lattice in thermodynamic equilibrium and are prevalent in the disordered phases [11]. In Al-Ni systems, the BCC phase exists in an intermediate phase, with similar motilities observed for Al and Ni. Entropies in the Al-Ni system have been calculated by zeroth approximations. Models were developed for both ordered and disordered states, revealing a miscibility gap that stabilizes the system at low temperatures but leads to instability at high temperatures, particularly in FCC metastable sites [12]. Only thermodynamic enthalpies of both alloys have been studied in detail, as seen from the literature. There remains a need for further refinement in thermodynamic modeling to accurately characterize Gibbs free energy, thermodynamic molar activity, and entropy in the Al-Ni system.

Procedure

All thermodynamic simulations and calculations in the presented research were performed using the widely employed thermo-calc (Thermodynamic Calculation) package, which utilizes the Calphad (calculation of phase diagram) method as its foundation. The calculations were performed manually with the PBIN (Phase Binary) database, which is specifically designed for Calphad calculations. The called calculation of phase diagram method is globally recognized as one of the most accurate and reliable techniques for thermodynamic simulations particularly in the field of alloy materials. This method, known for its precision, is extensively utilized for predicting phase diagrams, phase equilibria, and various thermodynamic parameters in alloy systems and phase transition [13]. All the thermodynamic parameters like, phase diagram, phase equilibria and figures curves section are calculated through modeling and simulations of Calphad method. The PBIN database is particularly valuable for exploring material properties such as phase diagrams, thermodynamic parameters, and other modeling projections within alloy systems, providing comprehensive information modules. Through the Calculation of Phase Diagram method, phases and free energy of alloying system through analytical expression to formulate alloying elements as:

$$G = G_1X_{Al} + G_2x_{Cu} + K_BT\ (X_{Al}LnX_{Al} + X_{Cu}Ln_{Cu}) + G_{ex}$$

$$G = G_1X_{Al} + G_2x_{Ni} + KBT\ (X_{Al}LnX_{Al} + X_{Ni}Ln_{Ni}) + G_{ex} \qquad (1)$$

While the G_{ex} shows the excess free energy of the alloying elements, x_{Al}, x_{Cu} x_{Al}, x_{Ni} are the molar concentrations of alloying elements. Ln shows the angular momentum of the orbits of the alloying elements. KBT shows the Boltzmann constant with temperature dependence. The calculation of phase diagram method is used in material industries for many years with best results [14-16].

Phase Diagram

Phase diagrams play a crucial role in various industries, including engineering, materials science, and heat treatment. They provide valuable insights into the microstructure and mechanical properties of materials, particularly in the context of crystallization and casting techniques used in materials design. By depicting the energy states of materials and the phase equilibria of their constituent elements, phase diagrams facilitate a deeper understanding of the relationships among different phases within a material system. This information is essential for optimizing material systems and conducting phase diagram calculations using the Calphad method, especially in binary alloy systems. Key aspects such as phase identification, liquidus and solidus temperatures, and solubility systems are fundamental for accurately determining phase diagrams [17-18].

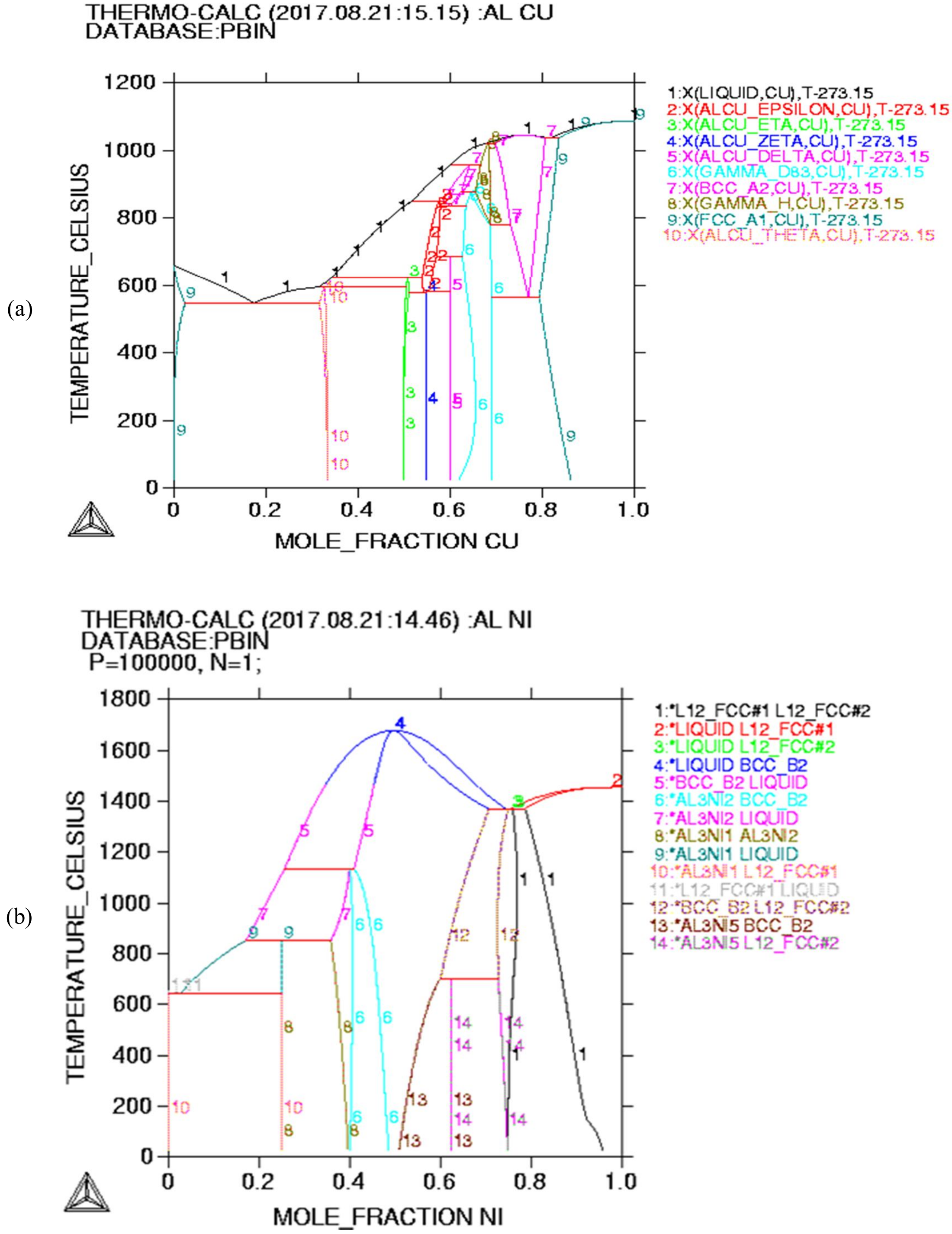


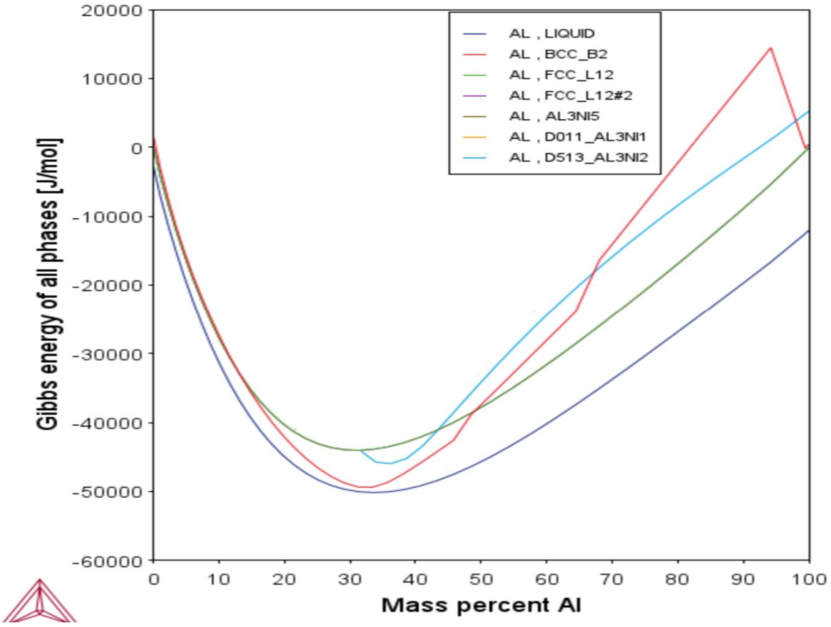
FIG. 1. (a) Phase diagram Al-Cu. (b) Phase diagram Al-Ni.

Figs. 1(a) and 1(b) show the phase diagrams of Al-Cu, Al-Ni binary alloy systems as calculated using the Calphad method within the temperature range of 2000-2050 K. In both systems, the phase with the highest temperature stability is the liquid phase, while the solid phase is characterized by an FCC phase with ferrite coordination. In Al-Cu system, the ferrite phase shows highest stability, particularly at temperatures around 1100 K, with a composition range of 0.8-1.0 mole percent across the entire composition spectrum of the alloy system. Conversely, in the Al-Ni binary system, the fertile phase is predicted to be most stable at temperatures ranging from 1400 to 1440 K, with a composition range of 0.65-1.0 mole percent. The stability region of the ferrite phase in the Al-Ni system is notably broader compared to that of the Al-Cu system, indicating its superior temperature resilience. The phases exhibit sharp transitions, and a high degree of heterogeneity is observed. The liquid phase demonstrates the highest degree of tolerance, contributing to the overall equilibrium of the alloy system. Precipitation behavior in the Al-Ni system results in the compositional heterogeneity, enhancing the stability of the ferrite FCC phase compared to the Al-Cu system. The difference in electronegativity between alloying elements influences electron density mixing within lattice cells, contributing to positive enthalpy and entropy changes in the alloy systems, as reported in the literature.

Figs. 2(a) and 2(b) show Gibbs energy calculations for the Al-Cu and Al-Ni binary systems within the temperature range of 2000-2050 K. In the Al-Cu system, the calculated Gibbs energy curves indicate that the liquid phase is most stable, withstanding the highest temperatures, while the FCC ferrite phase is the alternate stable phase in the solid regime at temperatures of 2000, 2025, and 2050K, respectively. Thermodynamic analysis show a decrease in the Gibbs curve with increasing temperature, particularly in the elevated temperature range. The FCC phase, characterized by ferrite coordination, demonstrates stability in the solid region but exhibits fluctuations at high temperatures, transitioning to the liquid phase for stability. Similarly, in the Al-Ni binary system, the liquid phase exhibits a decrease in Gibbs energy with increasing temperature, while the solid phase consists of FCC ferrite coordination. The system shows equilibrium fluctuations at the highest temperature range, with the ferrite phase demonstrating enhanced stability compared to the Al-Cu system, withstanding temperatures ranging from 1400 to 144 K across the composition range of 0.65-1.0 mole percent.

Figs. 3(a) and 3(b) show the molar thermodynamic activity of the Al-Cu and Al-Ni binary alloy systems within elevated temperature range of 2000-2050 K.

(a)



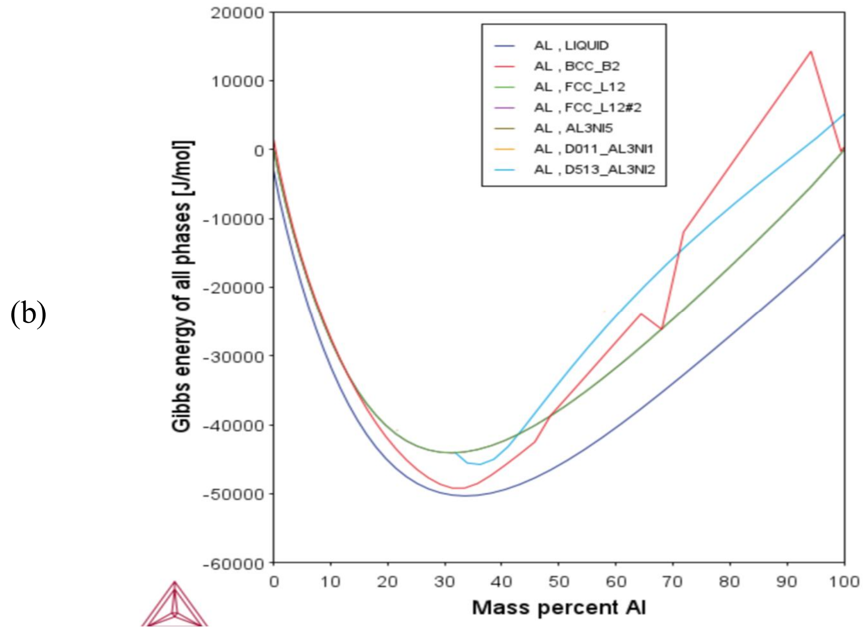


FIG. 2. (a) The Gibbs free energy of Al-Cu at 2025 K under a pressure of 10^5 MPa. (b) The Gibbs free energy of Al-Ni at 2050 K with pressure of MPa, considering composite heterogeneity.

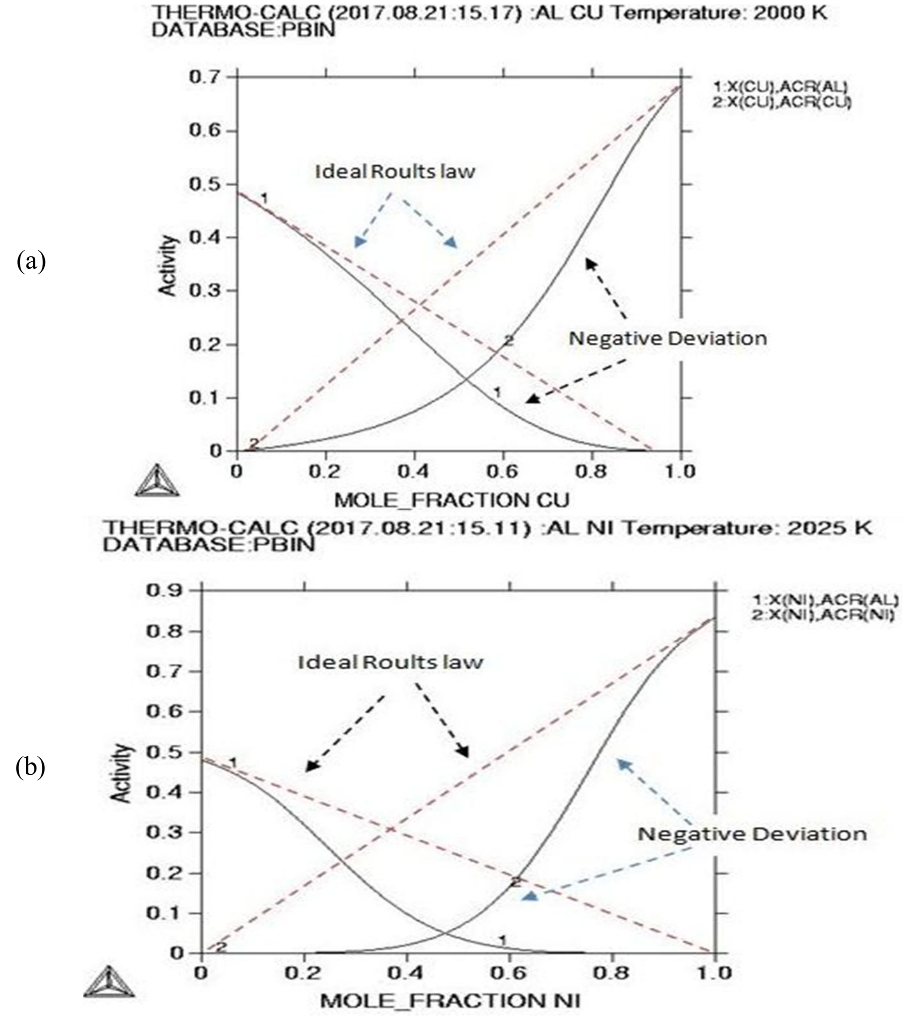


FIG. 3. (a) Activity of Al-Cu at 2050 K under a pressure of 10^6 MPa. Sharp deviation from ideality (Raoult's law) is observed. (b) Activity of Al-Ni at 2050 K under a pressure of 10^6 MPa. Expended deviation from Raoult's law. Positive deviation observed for rare doping era.

The thermodynamic molar activity of the Al-Ni binary system exhibits a more negative deviation compared to that of the Al-Cu binary system. This indicates that the Al-Ni alloy system is more stable at higher temperature levels. There is a stronger attractive interaction present among the constituents of the Al-Ni alloy system compared to the Al-Cu system. The doping characteristics of the Al-Ni binary system are more epitaxial and advantageous for doping industries. Raoult's law is more accurately represented in the Al-Ni binary alloy system compared to Al-Cu. Vegard's law and Henry's law have negligible effects in both alloy systems. Despite increases in entropy and enthalpy, the significant decrease in Gibbs curve and activity of the Al-Ni system suggest enhanced stability. These stability characteristics are crucial for industrial applications and research. In the Al-Ni system, the most stable composition range is found to be 0.4-0.6 mole percent at 2050 K, while the Al-Cu system shows stability mostly in the composition range of 0.1-0.85 mole percent at 2050 K. The lattice vibrations mode and Brillion zone growth during alloying are highly epitaxial, and the interaction among alloying elements is sharp and attractive, resulting in negative deviation from ideality in activity.

Tables 1 and 2 show the thermodynamic molar activity of the alloying elements in the Al-Cu and Al-Ni binary systems at various elevated temperature ranges. In the Al-Cu binary system calculation, the Gibbs energy values decrease gradually from (-1.32709×10^{5}, -1.35130×10^{5}, -1.37561×10^{5}) J/mol, at temperatures of 2000, 2025, and 2050K, respectively. This decrease in Gibbs energy indicates increased stability of the system at the highest temperature of 2050 K, with value of -1.37561×10^{5} J/mol. The enthalpy of the system also increases gradually as (6.05630×10^{4}, 6.13532×10^{4}, 6.21433×10^{4}) J/K, which shows that the alloying ability and heat contents of the system increase temperature. The highest enthalpy value of 6.21433×10^{4} J/K is observed at 2050 K in the Al-Cu system. The molar activity of aluminum at 2000K is observed to be 2.3236×10^{-2}, 1.000×10^{-2}, 2.0205×10^{-7}, -2.5633×10^{5}, and 9.9000×10^{-1}, while the activity of Cu in the alloying process is 9.7676×10^{-1}, 9.900×10^{-1}, 4.0821×10^{-4}, -1.2977×10^{5} at a temperature of 2000 K. The increase in temperature from 2000K to 2050K results in fluctuations and decreases in Gibbs energy to -1.35130×10^{5} J/mol, -1.37561×10^{5} J/mol with corresponding increases in enthalpy to 6.13532×10^{4} J/K, 6.21433×10^{4} J/K. The mass in mole of the alloying elements changes with temperature to $6.26964\ \times10^{1}$ moles, with a constant pressure value of 1.000000×100^{5} MPa. The activity fluctuation of Al and Cu with temperature changes from 2000 K to 2050 K shows the values of 2.3236×10^{-2}, 1.000×10^{-2}, 2.0595×10^{-7}, -2.5921×10^{5}, 2.3236×10^{-2}, 1.00×10^{-2}, 2.0967×10^{7}, -2.6211×10^{5}, and 1.000×10^{-2} for Al, while for Cu the values are 9.7676×10^{-1}, 9.900×10^{-1}, 3.8955×10^{-4}, -1.3218×10^{5}, 9.7676×10^{-1}, 9.900×10^{-1}, 3.7196×10^{-4}, and -1.3460×10^{5}. In the Al-Ni system the enthalpy increases from 2000 K to 2050 K as (7.66502×10^{4}, 7.43639×10^{4}, 7.54353×10^{4}) J/K indicating an increase in the heat content of the system. The corresponding decrease in Gibbs energy is calculated as (-1.27552×10^{5}, -1.34097×10^{5}, -1.36677×10^{5}) J/mol. The activity of Ni is 1, 4.6642×10^{-4}, -1.2755×10^{5}, 9.7850×10^{1}, 9.900×10^{-1}, 4.3084×10^{-4}, -1.3048×10^{5}, 9.7850×10^{-1}, 9.90×10^{-1}, 4.0709×10^{-4}, -1.3306×10^{5} , and 9.900×10^{-1}. The activity of Al is 2.1499×10^{-2}, 1.000×10^{-2}, 1.9848×10^{-8}, -2.9860×10^{5}, $2.1499\times10^{-}2$, 1.00×10^{-2}, 2.1008×10^{-8}, -3.0132×10^{5}, and 1.00×10^{-2}. The increase in the nickel content indicates rapid solubility of the elements in the Al-Ni alloy system. The mass changes to 5.86900×10^{1}, 5.8008×10^{1} moles. The highest temperature withstanding phase in both alloy systems is the liquid phase, while the solids stable phase is ferrite with FCC coordination.

Table 1. Thermodynamic Database Calculations of Al-Cu Binary Alloy System at 2000 K, 2025 K and 2050 K.

Temperature: Degree Kelvin	Pressure: pascal	Number of moles	ACRX: activity of a component relative ratio (Al)	Mass: mole	Total Gibbs energy: J/Mol	Vol: Cm^3	Enthalpy: J/Mol	Activity Al. SER:stable element reference state	Activity Cu. SER: Stable element reference state
2000K	1×10^5	1	1×10^{-2}	6.26964×10^1	-1.32709×10^5	0.0	6.05630×10^4	2.3236×10^{-2} 1.0000×10^{-2} 2.0205×10^{-7} -2.5633×10^5	9.7676×10^{-1} 9.9000×10^{-1} 4.0821×10^{-4} -1.2977×10^5
--	1×10^5	--	1×10^{-2}	--	--	--	--	-2.5633×10^5	-1.2977×10^5
LIQUID#1	1×10^5	1	1×10^{-2}	6.2696×10^1	--	--	--	--	--
--	--	--	--	--	--	--	--	9.9000×10^{-1}	1.0000×10^{-2}
2025K	1×10^5	1	1×10^{-2}	6.26964×10^1	-1.35130×10^5	--	6.13532×10^4	2.3236×10^{-2} 1.0000×10^{-2} 2.0595×10^{-7} -2.5921×10^5	9.7676×10^{-1} 9.9000×10^{-1} 3.8955×10^{-4} -1.3218×10^5
LIQUID#1	--	1	--	6.2696×10^1	--	--	--	1.0000×10^{-2}	9.9000×10^{-1}
2050K	1×10^5	1	--	6.26964×10^1	-1.37561×10^5	--	6.21433×10^4	2.3236×10^{-2} 1.000×10^{-2} 2.0967×10^{-7} -2.6211×10^5	9.7676×10^{-1} 9.900×10^{-1} 3.7196×10^{-4} -1.3460×10^5
LIQUID#1	--	1	--	6.2696×10^1	--	--	--	1.0000×10^{-2}	9.900×10^{-1}

Table 2. Thermodynamic Database Calculations of Binary Alloy System Al-Ni at 2000-20150 K.

Temperature: Degree Kelvin	Pressure: pascal	Number of moles	ACRX: (activity of a component relative ratio (Al)	Mass: moles	Total Gibbs energy: J/Mol	Vol: Cm^3	Enthalpy: J/Mol	Activity Al. SER:stable element reference state	Activity Ni. SER: stable element reference state
2000K	1×10^{5}	1	1×10^{-2}	5.869×10^{1}	-1.27552×10^{5}	0.0	7.66502×10^{4}	--	4.6642×10^{-4} -1.2755×10^{5}
LIQUID#1	1×10^{5}	1	1×10^{-2}	5.869×10^{1}	--	--	--	--	--
2025K	1×10^{5}	1	1×10^{-2}	5.80083×10^{1}	-1.34097×10^{5}	--	7.43639×10^{4}	2.1499×10^{-2} 1.0000×10^{-2} 1.9848×10^{-8} -2.9860×10^{5}	9.785×10^{-1} 9.900×10^{-1} 4.3084×10^{-4} -1.3048×10^{5}
LIQUID#1	1×10^{5}	1	--	5.8008×10^{1}	--	--	--	1.0000×10^{-2}	9.900×10^{-1}
2050K	1×10^{5}	1	--	5.80083×10^{1}	-1.36677×10^{5}	--	7.54353×10^{4}	2.1499×10^{-2} 1.0000×10^{-2} 2.1008×10^{-8} -3.0132×10^{5}	9.785×10^{-1} 9.900×10^{-1} 4.0709×10^{-4} -1.3306×10^{5}
LIQUID#1	1×10^{5}	1	1×10^{-2}	5.8008×10^{1}	--	--	--	1.0000×10^{-2}	9.900×10^{-1}

Conclusion

The thermodynamic analysis and assessment of the binary alloy systems Al-Cu and Al-Ni were conducted using the Calphad method and PBIN database. Both alloy systems were assessed for their suitability in industrial applications. The doping characteristics of the Al-Ni binary system are more epitaxial and useful for doping industries. The correspondence of Raoult’s law is more precise in the Al-Ni binary alloy system. Vegard’s law and Henry’s law were found to be negligible in both the Al-Cu and Al-Ni alloy systems. The entropy and the enthalpy of the systems increased, but a greater decrease in the Gibbs curve and activity predicted greater stability in the Al-Ni alloying system. Within the Al-Ni system, the composition range of 0.4-0.6 mole percent at a temperature of 2050 K was found the most stable, while the Al-Cu system showed the era of stability mostly in the composition range of 0.1-0.85 mole percent at the same highest temperature of 2050 K. The lattice vibrations mode and Brillion zone growth during alloying were found highly epitaxial, and the interaction among alloying elements exhibited a negative deviation from ideality in activity. The Al-Ni system demonstrated more stability due to lower Gibbs energy and higher enthalpy accordance compared to the Al-Cu system. Both alloy systems showed a high level of equilibrium and stability. The enthalpy values of both alloying systems increased gradually with temperature, but the corresponding decrease in Gibbs energy was most pronounced in the Al-Ni system. The most stable phase identified was the Al-Ni ferrite phase, which exhibited high-temperature resistance and is well-suited for industrial sectors and materials of metallurgy applications.

References

[1] Belov, N.A., Skin, D.G. and Asimov, A.A., "Multicomponent Phase Diagrams: Applications for Commercial Aluminum Alloys", (Elsevier, 2005), ISBN 10:1280637749

[2] Klancˇnik, G. and Medved, J., Min. Metall. Sect. B-Metall., 47 (2011) 179.

[3] Gainer, A., Ann. Phys., 12 (1939) 161.

[4] Huang, W., Calphad, 13 (3) (1989) 231.

[5] Jansson, B., Thesis, Royal Institute of Technology, Stockholm, Sweden, (1984).

[6] Kaufman, L., Calphad, 2 (2) (1978) 325.

[7] Ansara, I., Sundman, B. and Wollemi, P., Acta Metall., 36 (1988) 977.

[8] Dupin, N., Ansara, I. and Sundman, B., Calphad, 25 (2001) 279.

[9] Chen, L.-Q., JOM, 1996 (48) 12.

[10] Liu, X.J., Ohnuma, I., Kainuma, R. and Ishida, K., Alloys Comp., 264 (1998) 201.

[11] Taylor, A. and Doyle, N.J., J. Appl. Crystallogr., 5 (1972) 210.

[12] Yang, C.N. and Li, Y., Chinese J. Phys., 7 (1947) 59.

[13] Bock, F.E., Aydin, R.C., Cyron, C.J., Huber, N., Kalidindi, S.R. and Klusemann, B., Front. Mater., 6 (2019) 110.

[14] Li, X., Miodownik, A.P. and Saunders, N., J. Phase Equilib., 22 (2001) 247.

[15] Zhu, Z. and Pelton, A.D., J. Alloy. Compd., 641 (2015) 261.

[16] Delsante, S., Borzone, G., Novakovic, R., Piazza, D., Pigozzi, G., Janczak-Rusch, J., Pillion, M. and Ennas, G., J. Phys. Chem. Chem. Phys., 17 (2015) 28387.

[17] Levy, M.C. et al., Phys. Plasmas, 18 (10) (2011) 103110.

[18] Shah, W.U., Khan, D.F., Haiqing, Y. and Mamalis, A.G., Kuwait J. Sci., 49 (2) (2022).