TECHNICAL UNIVERSITY OF CLUJ-NAPOCA

ACTA TECHNICA NAPOCENSIS

Series: Applied Mathematics, Mechanics, and Engineering
Vol. 66, Issue Special II, October, 2023

COMPUTATIONAL THERMODYNAMICS APPROACH FOR PHASE PREDICTION OF Ni-BASED ALLOY

Maria BALANOU, Angelos P. MARKOPOULOS

Abstract: *CALPHAD (Calculation of Phase Diagrams) is a computational method used to predict the thermodynamic properties and phase behavior of materials based on their chemical composition. It has found extensive application in the development of advanced lightweight metallic materials. In the present study, a computational thermodynamic method was employed to investigate aspects of microstructure during the rapid solidification of a Ni-based alloy, specifically, a Ni-Al-Cr alloy with a Cr/Al ratio of 2:1. CALPHAD modeling was utilized to predict solidification behavior using the Classic Scheil-Gulliver solidification model. Additionally, the volume fractions of the main solidified phases and structures were predicted. According to the thermodynamic calculations, the main predicted structures were γ, FCC_L12 (γ'), and BCC_B2 microstructures.*

Key words: *Alloy design, Ni-based alloys, CALPHAD, Scheil-Gulliver, Solidified phases*

1. INTRODUCTION

Ni-based alloys are multi-component alloys with Ni as the matrix element. Nickel alloys are widely known as the most important materials for gas and aero-engine turbines due to their high-temperature oxidation resistance and excellent mechanical properties in high-temperature ranges [1]. As commonly known**,** the material's microstructure strongly affects the mechanical properties of Ni-based alloys.

Their excellent high-temperature mechanical resistance is attributed to precipitation hardening and solid-solution hardening. Specifically, the formation of γ' phase, an intermetallic phase with an $L1_2$ crystal structure, in Ni-based alloys enhances the material's mechanical properties as a precipitation strengthening phase within the *FCC* structure [2].

The exceptional mechanical characteristics of Ni-based alloys rely on the substantial proportion of the γ' phase and so on, determined by the γ'/γ ratio at a specific temperature [3].

The Ni-Cr-Al alloy has significant importance as a primary system within Ni-based superalloys. Chromium (Cr) and Aluminum (Al) are two of the most important elements in Ni-based alloys, where the Ni_3Al (γ') structure is used to strengthen the *FCC* structure of Ni (γ). Although the addition of Cr contributes to increasing the oxidation resistance in Ni-based alloys, it also alters the γ' to γ ratio in the microstructure [1].

Therefore, it becomes crucial to study the effect of the Al and Cr content in Ni-Al-Cr alloy at a specific temperature.

The CALPHAD (Calculation of Phase Diagrams) method has been widely used for computational design to investigate the microstructure of Ni-based alloys. CALPHAD is a computational method used in materials science and engineering to predict the thermodynamic and phase behavior of multi-component systems. It is based on the integration of thermodynamic data, including phase equilibria, thermodynamic properties like enthalpy, entropy, heat capacity, and chemical compositions, to develop a database that describes the thermodynamic properties of a system. The method is based on the concept of

Gibbs free energy, which is used to calculate the equilibrium conditions of a system [4-6].

An effective way to predict phase transformations during solidification is the use of the CALPHAD method. The solidification process is directly linked to various aspects, such as thermodynamics, kinetics, heat transfer, fluid flow, stress analysis, defect formation, microstructure evolution, as well as thermophysical and mechanical properties.

Consequently, it is vital to obtain an accurate solidification path to monitor and assess the alloy's solidification process. By utilizing the phase diagrams of alloys, one can attain control and comprehension of the solidification path for a given alloy [7, 8].

Within the framework of the CALPHAD method, the solidification path of an alloy can be approximated through the application of both equilibrium and non-equilibrium (Scheil-Gulliver) models.

The Scheil-Gulliver model, contributed by Gulliver, is a widely used solidification model in materials science and engineering.

This model describes the solidification process of an alloy under non-equilibrium conditions. It makes assumptions about the phases and their composition, based on the thermodynamic approach of how the phases solidify.

As previously noted, the Scheil-Gulliver solidification process occurs under non-equilibrium conditions, resulting in rapid solidification and the subsequent segregation of solute. Consequently, the Scheil-Gulliver solidification model calculates the solid phases that form from a molten substance, which changes in composition because of the separation of dissolved components from the liquid through local equilibrium at the interface between the solid and liquid phases [9].

The literature indicates that only a few research have been conducted on Ni-based alloys using CALPHAD. Wen et al. [10] introduced a ternary phase field model for the Ni-Al-Cr alloy, which was integrated with CALPHAD software to provide precise quantitative thermodynamic driving forces. Wang et al. [11] performed a thermodynamic reassessment of the Al-Cr-Ni system using the CALPHAD method. The optimization of thermodynamic interaction parameters has been made by using the available experimental data. Keller et al. [12] utilized FEA, phase-field, and CALPHAD methods to study the microstructure and micro-segregation during L-PBF for Inconel 625. De Luca et al. [13] aimed to enhance the comprehension of defects and cracks in Ni-based alloys fabricated through additive manufacturing techniques. They examined the impact of parameters using a simplified model of a Ni-Cr-Al-Ti alloy with a reduced solidification interval, reinforced by the γ/γ' phase. Moreover, Mohammadpour et al. [14] also employed the CALPHAD method to assess the solidified microstructure and the development of precipitates in the as-built L-PBF (Laser Powder Bed Fusion) microstructure of Inconel 625 (IN625). The micro-segregation occurring during solidification was computed utilizing both the Scheil-Gulliver and DICTRA methodologies. Finally, Xu et al. [15] used the CALPHAD method to develop high-strength, long-term, high-temperature Ni-Al-V-Nb-Cr alloys reinforced by γ' and γ''.

In this study, thermodynamic calculations using the CALPHAD method were performed on the Ni-Cr-Al system to promote the formation of the γ' phase. The solidification microstructure and the volume fractions for the major solidified phases were investigated for two Ni-Al-Cr alloys with a Cr/Al ratio of 2:1, at non-equilibrium conditions. Furthermore, the micro-segregation of the alloys during rapid solidification was simulated via Thermo-Calc using the classic Scheil–Gulliver model.

2. METHODOLOGY

To determine the thermodynamic equilibrium of the system, the calculation involves finding the minimum Gibbs free energy. The total Gibbs energy is obtained by summing the individual Gibbs energies of each phase. The energy of each phase φ (G_m^{φ}) is computed by combining Gibbs energies from various contributions, as expressed in Equation 1 [16]:

$$G_m^{\varphi} = G_{ref}^{\varphi} + G_{id}^{\varphi} + G_E^{\varphi} + G_{mag}^{\varphi} + G_P^{\varphi} + G_{surf}^{\varphi} + \cdots \quad (1)$$

where G_{ref}^{φ}: the summation of the Gibbs energies of all the elements or compounds that exist within the crystallographic structure of a specific phase. It considers the contributions of each element in their respective states within the phase. For solid and liquidus G_{φ}^{ref} are given by Equation 2:

$$G_{\varphi}^{ref} = \sum_{i=1}^{n} x_i \cdot {}^{0}G_i^{\varphi} \quad (2)$$

and its temperature dependence is given by Equation 3:

$${}^{0}G_i^{\varphi}(T) = a + bT + cTln(T) + \sum_i d_i T^n \quad (3)$$

where α and d_i are coefficients that can be adjusted. Equation 4 provides the description of G_{id}^{φ} which represents the contribution to the Gibbs energy resulting from the perfect mixing of chemical elements in the crystal lattice for an n-constituents system:

$$G_{id}^{\varphi} = RT \sum_{i=1}^{n} x_i \ln(x_i), \quad i = 1, \dots n \quad (4)$$

G_E^{φ} is the excess Gibbs energy that describes the actual behavior of the phases in general, covering other contributions of Gibbs energy that are not described in other terms in Equation 1.

$$G_E^{\varphi} = \sum_{\substack{i,j=1 \\ i \neq j}}^{n} x_i\, x_j \sum_{z=0}^{m} {}^{z}L(x_i - x_j)^z + \sum_{\substack{i,j,k=1 \\ i \neq j \neq k}}^{n} x_i x_j x_k L_{ijk} \quad z = 0, \dots, m \quad (5)$$

where ${}^{z}L$ refers to the interaction parameters that vary with temperature. These parameters describe the impact of the interaction between elements i and j on the overall Gibbs energy of the phase φ.

For a stoichiometric compound A_aB_b, Gibbs energy G_m^{φ} is calculated by the hypothetical Gibbs energy (G_{form}^{φ}) that is required to form the phase from the pure elements in the selected state:

$$G_m^{\varphi} = \frac{a}{a+b} G_A^{\varphi} + \frac{b}{a+b} G_B^{\varphi} + G_{form}^{\varphi} \quad (6)$$

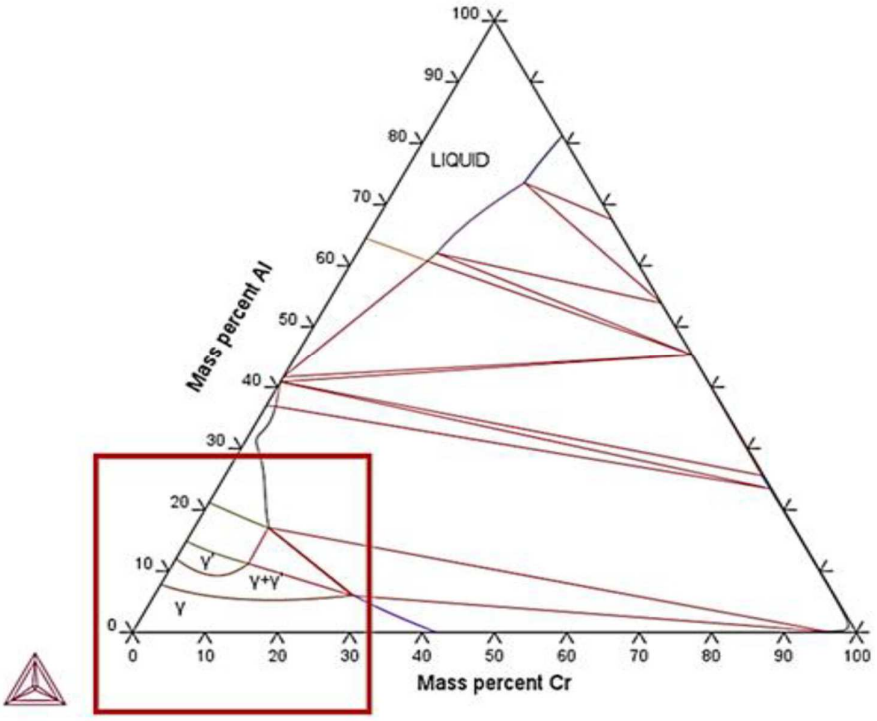

Fig.1. Phase Diagram of Ni-Cr-Al at 1000 °C

Thermodynamic calculations were conducted for the Ni-Cr-Al system using the CALPHAD method. These calculations were performed using Thermo-Calc software, which was coupled with thermodynamic databases [17]. Figure 1 represents the phase diagram of the Ni-Cr-Al system, specifically highlighting the region of interest, at a temperature of 1000 °C. The solidification microstructure and the volume fractions of the major solidified phases were studied for two Ni-Al-Cr alloys with a Cr/Al ratio of 2:1: Ni-10Cr-5Al and Ni-16Cr-8Al (wt.%), under non-equilibrium conditions. Furthermore, micro-segregation of the alloys during rapid solidification was simulated via Thermo-Calc using classic Scheil–Gulliver model.

Scheil Solidification Simulations refer to transformations that occur under non-equilibrium or partial-equilibrium conditions and are used to predict the microstructure of an alloy during solidification. The classic Scheil solidification model assumes zero diffusion within the solid phase and very rapid diffusion within the liquid phase.

3. RESULTS AND DISCUSSION

3.1 Solidification behavior

Equilibrium phase diagrams and solidification simulations provide a worthy elementary understanding of general solidification behavior, but they are not fully applicable to real processes as equilibrium is not achieved in real processes. The solid diffusion in equilibrium condition is slow enough to balance the concentration gradients, and this affects the solidification behavior and the formation of phases, ultimately resulting in negative effects on the performance of the final product.

The formation of the solidification microstructure is influenced by the temperature gradient, solidification rate, and undercooling during the solidification process. These parameters also impact the physical and mechanical properties of the alloy. Therefore, it is crucial to have the capability to forecast the evolution of microstructure under non-equilibrium conditions.

Fig. 2 (a), (b), and (c) represent the evolution of phases with temperature according to the Scheil-Gulliver model in the Ni-16Cr-8Al (wt.%) alloy during the solidification process, the fractions of solid phases with respect to time during solidification, and the segregation of Cr and Al within the γ phase along the solidification path, respectively. In Fig. 2 (a) the dotted line represents equilibrium solidification. In this case, fast diffusion of all elements takes place in both the liquid and the solid phases. On the other hand, in the Scheil solidification model (represented by the solid line), there is absence of diffusion within the solid phase, while fast diffusion occurs in the liquid phase. The solidification begins at around 1363 °C. The simulation predicts the development of γ' *(FCC_L1$_2$)* and *BCC_B2*. The predicted equilibrium solidification temperature range is ΔT= 27 °C. In the absence of diffusion within the solid phase, the theoretical temperature range for solidification under Scheil conditions is ΔT= 66 °C. At the begging of solidification there is no micro-segregation; however, bellow 1359 °C, the equilibrium and non-equilibrium lines separate, which means segregation is occurring in the alloy. Based on Fig. 2 (b), the Ni-16Cr-8Al (wt.%) alloy exhibits a significant fraction of γ' phase and a relatively high solvus temperature for the γ' phase. Classic Scheil solidification is illustrated in Fig. 2 (c), showing the redistribution behaviors of Cr and Al during solidification of the calculated solute concentrations for a mass fraction of ~0.69.

Similar conclusions can be drawn for Ni-10Cr-5Al (wt.%). Fig. 3 (a), (b), and (c) illustrate the relationship between solid fraction and temperature for a classic Scheil simulation, the fractions of solid phases with respect to time during solidification, and the segregation of Cr and Al within the γ phase along the solidification path, respectively.

The solidification begins at around 1415 °C. Micro-segregation occurrs below 1359 °C.

The classic Scheil simulation predicts only the creation of *γ' (FCC_L1₂)* (Fig 3 (a)).

The predicted equilibrium solidification temperature range is ΔT= 9 °C. In the case of Scheil conditions, where there is zero diffusion within the solid phase, the theoretical temperature range for solidification is less than 100 °C. According to Fig. 3 (b), the *γ'* fraction in Ni-10Cr-5Al (wt.%) is lower than the first alloy but still significant. Classic Scheil solidification is illustrated in Fig. 3 (c), showing the redistribution behaviors of Cr and Al during solidification of the calculated solute concentrations for a mass fraction of ~0.67.

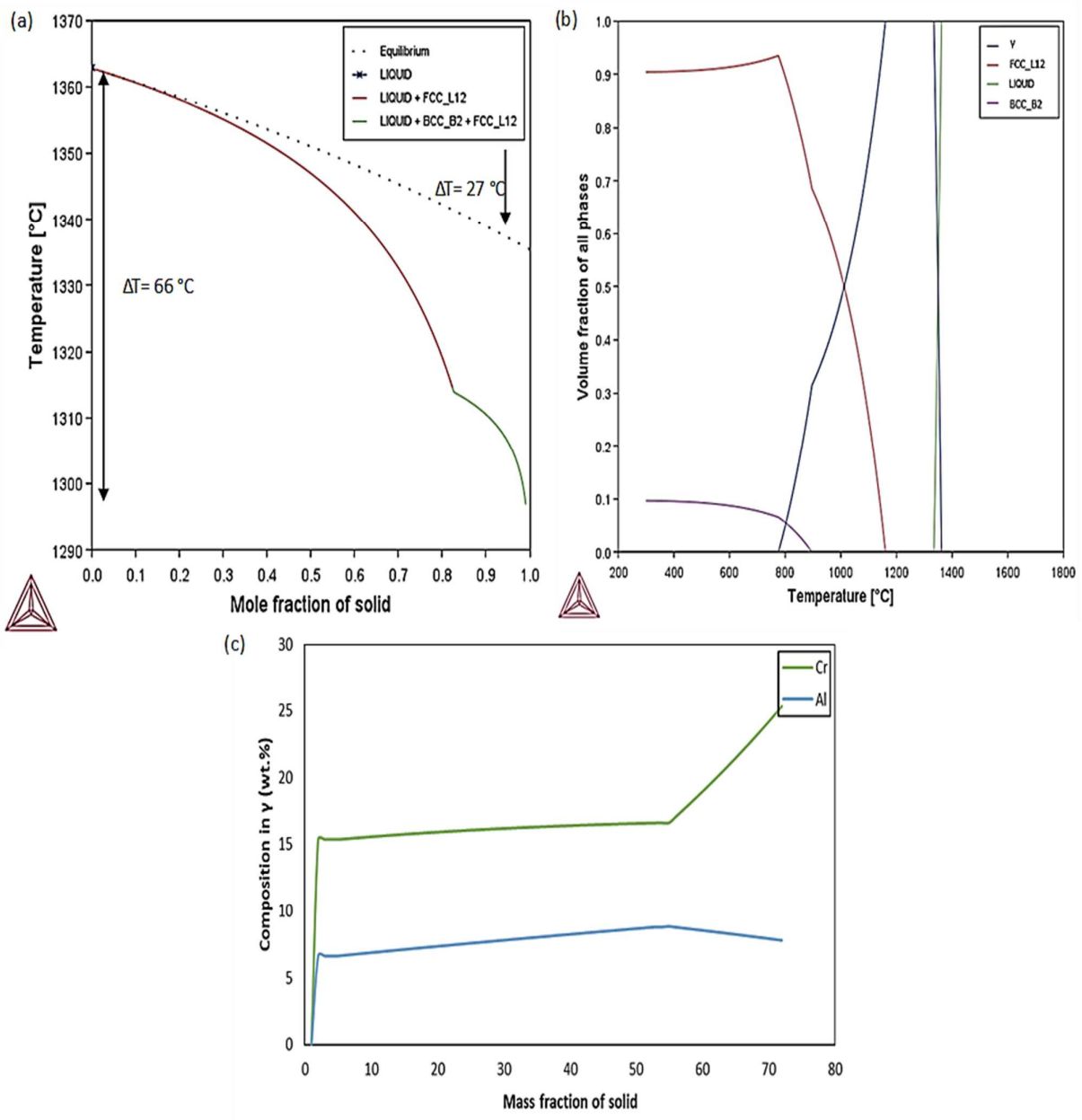

Fig.2. (a) The phase evolution with temperature during the solidification process of Ni-16Cr-8Al (wt.%) was simulated using the Scheil-Gulliver method, (b) fractions of the solid phases as functions of time during solidification and (c) The distribution of Cr and Al within the *γ* phase throughout the solidification path

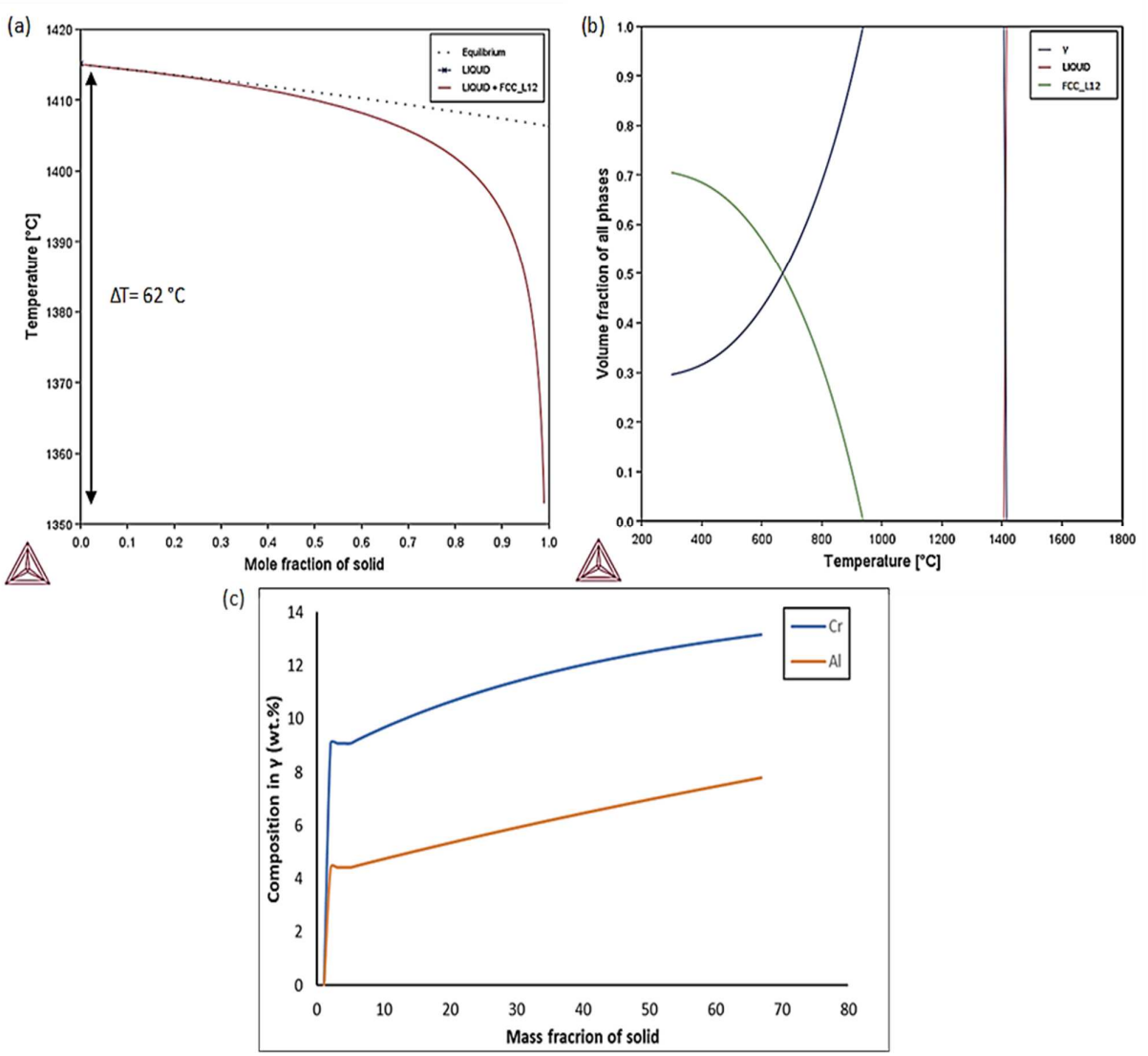

Fig.3. (a) The phase evolution with temperature during the solidification process of Ni-10Cr-5Al (wt.%) was simulated using the Scheil-Gulliver method, (b) fractions of the solid phases as functions of time during solidification and (c) The distribution of Cr and Al within the γ phase throughout the solidification path

Comparing these two alloys, it is clear how different concentrations of Cr and Al in Ni-based alloys affect solidification temperature range. It appears that the theoretical solidification temperature range decreases slightly as the content of alloying elements decreases. In the first alloy, it is anticipated that the final liquid to solidify will undergo solidification through a peritectic reaction. Conversely, in the second alloy, solidification is expected to occur via eutectic reaction. From a thermodynamic point of view, the formation of the thermodynamically stable phase is favored, i.e., the one with the most negative Gibbs energy, due to the micro-segregation of the components. Consequently, based on the above equations, the alloying elements' contents and the temperature contribute to the formation of the final microstructure.

4. CONCLUTIONS

In the present study, thermodynamic calculations based on the CALPHAD method were performed for Ni-Cr-Al system. The solidification microstructure and the volume fractions for the major solidified phases for two Ni-Al-Cr alloys with a Cr/Al ratio of 2:1, Ni-

10Cr-5Al, and Ni-16Cr-8Al (wt.%) at non-equilibrium conditions, were studied. Furthermore, micro-segregation of the alloys during rapid solidification was simulated via Thermo-Calc using classic Scheil–Gulliver model. The main conclusions that can be drawn are:

- In the alloys studied, the formation of the γ' phase was observed, known to contribute to the mechanical properties of the alloys.
- The different concentrations of the alloying elements affect the final microstructure of the alloys, leading to two alloys with different solidification microstructure. Furthermore, the solidification temperatures are also affected by the concentration of the alloying elements.
- The final microstructure of the alloys is directly influenced by the Gibbs energy.
- For both of the alloys the micro-segregation occurs.

5. REFERENCES

[1] Jin, S., Li, Y., Shi, S., Yan, Z., Chen, S. "Effects of Cr content on compositional evolution and precipitation kinetics of γ′ phase in Ni–Al–Cr alloy: 2D phase-field simulation," Journal of Materials Research and Technology, vol. 9, no. 4, pp. 7499–7507, Jul. 2020, doi: 10.1016/j.jmrt.2020.05.065.

[2] Kim, D.E., Shang, S.L., Liu, Z.K. "Effects of alloying elements on elastic properties of Ni3Al by first-principles calculations," Intermetallics (Barking), vol. 18, no. 6, pp. 1163–1171, Jun. 2010, doi: 10.1016/j.intermet.2010.02.024.

[3] Long, H., Mao, S., Liu, Y., Zhang, Z., Han, X. "Microstructural and compositional design of Ni-based single crystalline superalloys — A review," Journal of Alloys and Compounds, vol. 743. Elsevier Ltd, pp. 203–220, Apr. 30, 2018. doi: 10.1016/j.jallcom.2018.01.224.

[4] Shi, R., Luo, A.A. "Applications of CALPHAD modeling and databases in advanced lightweight metallic materials," CALPHAD, vol. 62, pp. 1–17, Sep. 2018, doi: 10.1016/j.calphad.2018.04.009.

[5] Luo, A.A. "Material design and development: From classical thermodynamics to CALPHAD and ICME approaches," CALPHAD, vol. 50, pp. 6–22, Sep. 2015, doi: 10.1016/j.calphad.2015.04.002.

[6] Kroupa, A. "Modelling of phase diagrams and thermodynamic properties using Calphad method - Development of thermodynamic databases," Comput Mater Sci, vol. 66, pp. 3–13, Jan. 2013, doi: 10.1016/j.commatsci.2012.02.003.

[7] Chang, Y.A. et al., "Phase diagram calculation: Past, present and future," in Progress in Materials Science, 2004, pp. 313–345. doi: 10.1016/S0079-6425(03)00025-2.

[8] Zhang, C., Miao, J., Chen, S., Zhang, F., Luo, A.A. "CALPHAD-Based Modeling and Experimental Validation of Microstructural Evolution and Microsegregation in Magnesium Alloys During Solidification," J Phase Equilibria Diffus, vol. 40, no. 4, pp. 495–507, Aug. 2019, doi: 10.1007/s11669-019-00732-0.

[9] Bocklund, B., Bobbio, L.D., Otis, R.A., Beese, A.M., Liu, Z.K. "Experimental validation of Scheil–Gulliver simulations for gradient path planning in additively manufactured functionally graded materials," Materialia (Oxf), vol. 11, Jun. 2020, doi: 10.1016/j.mtla.2020.100689.

[10] Wen, Y.H., Lill, J.V., Chen, S.L., Simmons, J. P. "A ternary phase-field model incorporating commercial CALPHAD software and its application to precipitation in superalloys," Acta Mater, vol. 58, no. 3, pp. 875–885, Feb. 2010, doi: 10.1016/j.actamat.2009.10.002.

[11] Wang, Y., Cacciamani, G. "Thermodynamic modeling of the Al-Cr-Ni system over the entire composition and temperature range," J Alloys Compd, vol. 688, pp. 422–435, 2016, doi: 10.1016/j.jallcom.2016.07.130.

[12] Keller, T. et al., "Application of finite element, phase-field, and CALPHAD-based methods to additive manufacturing of Ni-based superalloys," Acta Mater, vol. 139, pp.

244–253, Oct. 2017, doi: 10.1016/j.actamat.2017.05.003.
[13] De Luca, A., Kenel, C., Griffiths, S., Joglekar, S.S., Leinenbach, C., Dunand, D. C. "Microstructure and defects in a Ni-Cr-Al-Ti γ/γ' model superalloy processed by laser powder bed fusion," Mater Des, vol. 201, Mar. 2021, doi: 10.1016/j.matdes.2021.109531.
[14] Mohammadpour, P., Yuan, H., Phillion, A. B. "Microstructure evolution of Inconel 625 alloy during single-track Laser Powder Bed Fusion," Addit Manuf, vol. 55, Jul. 2022, doi: 10.1016/j.addma.2022.102824.
[15] Xu, B. et al., "CALPHAD design and high-throughput search of novel Ni-based superalloys that are reinforced by γ' + γ''," Mater Today Commun, vol. 30, Mar. 2022, doi: 10.1016/j.mtcomm.2022.103164.
[16] Kroupa, A. "Modelling of phase diagrams and thermodynamic properties using Calphad method - Development of thermodynamic databases," Comput Mater Sci, vol. 66, pp. 3–13, Jan. 2013, doi: 10.1016/j.commatsci.2012.02.003.
[17] Thermo-Calc software, Ni-based Database, Version 2.0. June 2020. https://thermocalc.com/products/databases/nickel-based-alloys/.

Cercetarea termodinamică computațională pentru predicția de fază a aliajului pe bază de Ni

CALPHAD (Calculation of Phase Diagrams) este o metodă de calcul pentru prezicerea proprietăților termodinamice și a comportamentului de fază a materialelor pe baza compoziției lor chimice. A fost aplicat pe scară largă în dezvoltarea materialelor metalice ușoare avansate. În studiul de față, a fost utilizată o abordare termodinamică computațională pentru a investiga aspectele microstructurii în timpul solidificării rapide a aliajului pe bază de Ni. Mai precis, a fost studiat aliajul Ni-Al-Cr cu un raport Cr/Al de 2:1. Modelarea CALPHAD a fost utilizată pentru a prezice comportamentul de solidificare folosind modelul de solidificare Scheil-Gulliver și au fost, de asemenea, prezise fracțiile de volum pentru fazele/structurile majore solidificate. Din calculele termodinamice, au fost prezise microstructurile γ, FCC_ L12 (γ'), și BCC_B2 ca faze predominante.

Maria BALANOU, PhD student, Laboratory of Manufacturing Technology, School of Mechanical Engineering, National Technical University of Athens, Heroon Polytecniou 9, 157 80 Athens, Greece, mpalanoumaria.23@hotmail.com
Angelos P. MARKOPOULOS, Associate Professor, Laboratory of Manufacturing Technology, School of Mechanical Engineering, National Technical University of Athens, Heroon Polytecniou 9, 157 80 Athens, Greece, amark@mail.ntua.gr