Thermo-mechanical fe-demo based calculations of high entropy alloys (HEAs) (Fe-Ni-Cx $_{(x=0.3-0.5)}$ ternary alloy system using calphad method

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Abstract

The given research shows the thermodynamic analysis and calculation of the basic thermal properties of the high entropy alloy Fe-Ni-Cx $_{(x=0.3-0.5)}$ of concentration. The system is investigated through Thermo-calc package with FEDAT databases and Calphad method. The evaluation of interactions is found maximum at 0.04070 J/m^2 of interfacial energy in the Fe-Ni-C ternary alloy system. The FCC_A_1 phase is found the phase associated with highest molar volume in the Fe-Ni-Cx $_{(x=0.3-0.5)}$ ternary alloy system. The phase FCC_A_1 is having austenite coordination with increasing density and apparent heat capacity. The temperature variation results the composite phases to be disappears with required level. The system is found highest apparent heat capacity 0.39269 J/mol. The density of phases becomes constant and it indicates the rare temperature withstanding phases. The fluctuations in the density of phases are changing with temperature as a result of phase's nature and stability. The better magnetic properties are found for Basic centered cubic structure with highest interfacial energy. The alloy shows better magnetic coordination and thermodynamic properties enhancement for further analysis.

Keywords: Calphad method, fe-demo databases, high entropy alloys, mechanical study, thermodynamic calculations.

1. Introduction

The recent pattern of alloys generated for the quick structural-materials are Fe-Cr-C with remarkable properties of mechanical-based strength and resistance to deformation forces. The alloys adjusted for the fuel cladding and chemical reactors are Fe-based alloys with Ni-C, Cr-C as an alloying element. The annealing properties of the Fe-Cr-C alloys are strongly dependent on the Cr composition percentage above 15%. Increasing composition of chromium may increase the harmful effect in mechanical properties of the given alloy system. The Fe-based alloys are applicable in the generation wise fusion-reactors and super-critical water reactions process. The alloys having more nickel contents are now a day's much important in research fields as to produce the super alloys, high entropy alloys and those alloys having the mechanical properties enhanced toward the positive need of the industry. The Ni contents results the improvement in the wear resistance, strength, and the low thermal expansion capabilities. (Shi Chen, yong sheng

Li *et al,* 2019; Z.K. Liu, Y. Wang *et al*, 2014).For the special types of steels production, the Ni-rich contents are further increased in the alloys systems. The order and disorder transitions in the FCC phase are reported in the research works carried since 1920 s (J. Liu, L.J. Riddiford *et al,* 2016; I. Ohnuma, S. Shimenouchi *et al,* 2019; B.Hallstedt *et al,* 2010).The additions of more carbon concentration in the nickel based alloys are rejected by researchers because of the production of the dislocation motion in the alloy that results the strength and the ductility range of the Ni alloys. The high temperature investigation of the Fe-Ni-C system is still not performed because of the experimental complications. (L.B. Chen, R. Wei *et al,* 2018; Y. Xu, Q. Jin, X. Xiao *et al,* 2011)The pyro-metallurgical process is carried for the developments of the Ni based alloys to recycle the wastes of the industrial products. (J.M. Jeon, S.Y. Kwon *et al,* 2021)The literature shows the thermodynamic modeling assessments of the Ni alloys and Cr alloys with differential scanning calorimetric process for the report of the enthalpy of the mixing of the alloys (Waseem Ullah Shah *et at,* 2022a).

2. Procedure

The computational based techniques are considering famous part of the materials engineering sciences, which makes us possible for the unknown data prediction and simulations. The Quasi-chemical model is developed for the investigation of the properties of the Fe-Ni-C ternary system. The results are again verified and asymmetric N-rich section was developed by Quasi-chemical-parameters. The study is operated for the 1500^0 C-1600^0 C range of carbon composition in the Fe-Ni-C system. The enthalpy of the mixing is found higher ordering in the liquid solution and reproduced successfully. CALPHAD (Calculation of Phase Diagrams) is considered the basic thermodynamic approach based on computational simulations for the calculations of the phase equilibria, for the ternary, binary alloys systems with precise manner (Waseem Ullah Shah *et al,* 2022b; A. Gabriel, P. Gustafson 1987; I. J.H. Weber, encyclopedia *et al,* 2001).

The solidification condition mapping, simulations, and precipitation nucleation based on the diving forces are the remarkable participation of the CALPHAD method.(Gorsse, S.Tancret, F *et al*, 2018).The interest in the evaluation of phase diagrams are marked important on the basis of the thermodynamic databases for the many multi-components systems, like HEA,s, CCA,s **(I.** Gwalani, B. Gorsse *et al,* 2018; J.-O.Andersson *et al,* 2002).The fully assessed binary and fully assessed ternary systems on the basis of complete thermodynamic assessment are credited by the Calphad method as a set of thermodynamic properties agrees with experimental set ups for the composition and temperature verses (Choudhuri, D. Gwalani *et al,* 2017; Sung- Kwang *et al,* 2015).The Calphad method is based on the following operational correlation cumulant-expansion theorem demonstrated as

$$G = G_{Fe-Cr}x_{Fe-Cr,C} + G_C x_{Fe-Cr} + K_B T\,(x_{Fe-Cr}\mathrm{Ln}x_{Fe-Cr} + x_C Gln_C) + G_{ex} \quad (1)$$

$$(\Delta H_{Fe-Cr,C})\ order = (\Delta H_{Fe-Cr,C})[1 + 8(((\Delta H_{Fe-Cr,C})/f_{Fe-Cr,C} \quad (2)$$

$$\{x_{Fe-Cr}V_{Fe-cr}^{2/3}[1+u_{Fe-Cr}x_C(\Phi_I-\Phi_C)]+x_CV_C^{2/3}[1+u_Cx_{Fe-Cr}(\Phi_C-\Phi_{Fe-Cr})]\})^2 \quad (3)$$

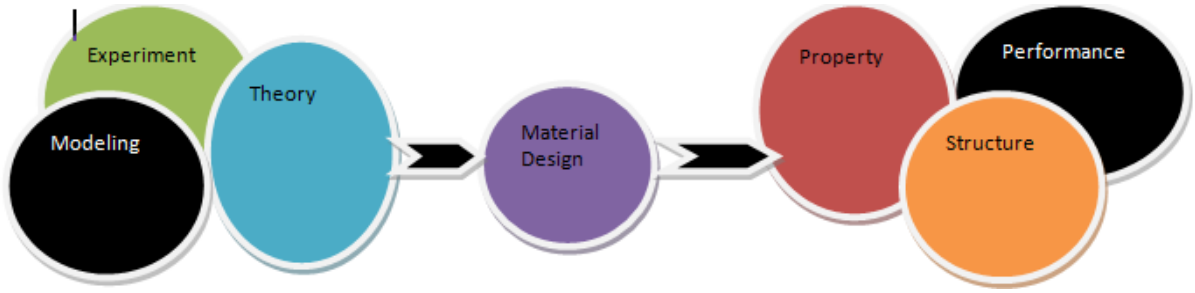
$$f_{Fe-Cr,C}=2pV_{Fe-Cr}^{2/3}V_C^{2/3}[q/p(\Delta n_{ws}^{1/3})^2-(\Delta\Phi)2-\alpha r/p]/(n_{ws}^{1/3})\ a^{-1}+(n_{wa}^{1/3})\ b^{-1} \quad (4)$$

$$G_m^{liquid}=\sum_i x_{Fe-Cr,C}^o G_{Fe-Cr,C}^{liquid}+RT\sum_i x_{Fe-Cr,C}\mathrm{Ln}x_{Fe-Cr,C}+\sum_i\sum_{j>I}x_{Fe-Cr,C}x_{Fe-Cr,C}^oL_{Fe-Cr,C}^{liquid} \quad (5)$$

(Senkov, O.N. Miller ,2015; S Sheibani,S Heshmati-manesh *et al*, 2010; Wei Xiong, *et al*, 2012). The X_{Fe-Cr}, X_C terms in the equations shows the concentrations of alloying elements Fe-Cr, C where the Φ shows the electro-negativity of the system. G shows the total Gibbs energy of the system. $\Delta H_{1,2}$ Is the total change in the enthalpy of formation of alloying elements of Fe-Cr, C portion. Ln is for the logarithmic variation of the X composition of elements. N_{ws} represents Normalized wave function short range correlation coefficient. n_{w1}, n_{w2}, n_{w3}……n_{ws} , It is the electron density correlation cumulant-expansion theorem.

3. Flow Chart of modeling

For the process of material designing, the material microstructure is determined as result of phase equilibria and phase distribution. In current research fields the phase transformation is vitally used (Waseem Ullah shah *et al,* 2022c; Sumaryada, T.Sofyan *et al,* 2019).



The Thermo -Calc database software used in order to approach and investigate quantitatively the basic effects of alloying elements particularly the effect of Fe-Ni-C systems by alloying. Thermodynamic calculations and predictions of Meta stable ternary alloys Fe-Ni-C alloys system involves calculation of energies of mixing of the alloying system, excess Gibbs energies, thermodynamic molar activities, coefficient of activities, partial and integral values of enthalpy for the said alloy system at elevated temperatures (1900-2000) K. Obtaining optimal set of thermodynamic parameters for over the whole range compositions of binary systems Fe-Ni, while the carbon mole fraction is maintained at 0.3,0.4,0.5 mass % with temperature investigation for selected alloys. The mode of operation follows the tabulated procedure as given below,

The database selection from main TC window	Sorting Require calculator for calculation	Assessment of results from TC-Prisma
The inserting of alloys from the databases	Adjustment of Ratio of elements	Adjustment of Data with literature
Adjustment of alloying composition on TC databases	Plotting of results on main window	Analysis of the final outcomes

The results are obtained for the complete thermodynamic description of the system for assessment of the properties and applications. The results obtained are novel and prediction basis for the certain thermodynamic and mechanical parameters enhancing properties for the need.

4. Input for methodology.

Composition	Mass %	Flow thermal mode	Flow heat $1/t^2$
Annealing range	1901-2001 K	Relaxation fraction value	0.59
Pressure	10^6 Pascal	Vulnerability transition	0.01-0.1
Fe-region comp	99.50 mass %	Type of execution	Grid
Cr-region comp	0.01 mass %	C-range/steps adopted	0.0-1 /10
C-region comp	0.3-0.4 mass %	Proceeding temp	500-3000 /10
Duration of process	30 minutes	Distribution-truncate	3-std
Scheill based temp	2501.15 K	Distribution of total sample	200 Gauss D
Least fraction	$1*10^{-12}$	Density of dislocation	$5.01*10^{12}$
Term-phase amount	0.01	Phase energy addition	0.01 J/mol
Morphology seen	sphere	mobility of phase boundary	10 m^4/Js
Sites of nucleation	Grains/bulks	Phase to deform	FCC_A1
Molar volume	$7.0*10^{-6}$	Matrix phase	FCC_A1
Sol solid strength	293.20 K	Precipitate phase	FCC_A1
Mean-radius	$1.10*10^{-8}$	Critical-radius	$2.88*10^{-9}$

The simulation parameters varied during calculation are tabulated and given for the note. The data represents the input heads for the execution of the results of the alloy system are systematic paths for the execution. The sections of the parameters are adjusted for the better results desired. The pressure of the alloy Fe-Ni-C is kept constant of 10^6 Pascal to avoid secondary phases in the given ternary system. The bulk properties are adjusted for Ni-site nucleation of the given system. The dislocation density of the alloy shows the symmetric parameters for the response to the phase transition in the given alloy system. The dislocation density is maintained $5.01*10^{12}$ values for smooth alloying. The Gaussian distribution density of the total sample is kept 200 points for the alloy response to demagnetization forces. The critical radius and mean radius of the sample Are maintained $2.88*10^{-9,}$ $1.10*10^{-8}$ nm for the sample sintering through computational analysis and execution. The duration of the process are taken 30 minutes with critical radius of $2.88*10^{-9}$mm with morphology seen as a sphere based orientation. The distribution of the sample is 200 Gaussian D with the density of dislocation as $5.01*10^{12}mm^3$ and the phase form to deform is

FCC with austenitic orientation and properties. The mobility of the phase boundaries in the grains are kept as 10 m^4/Js with phase energy addition as 0.01 J/mol. The Vulnerability transition formation is executed of the numerical standards as 0.01-0.1mm with relaxation fraction value of the 0.59. The required Distribution-truncate for the process are maintained 3-std with annealing range of 1901-2001K. The Fe-region composition is maintained as 99.50 mass %, the Cr-region composition is tackled as 0.01 mass% and C region composition is maintained in the range0.3-0.4 mass % during the process nucleation.

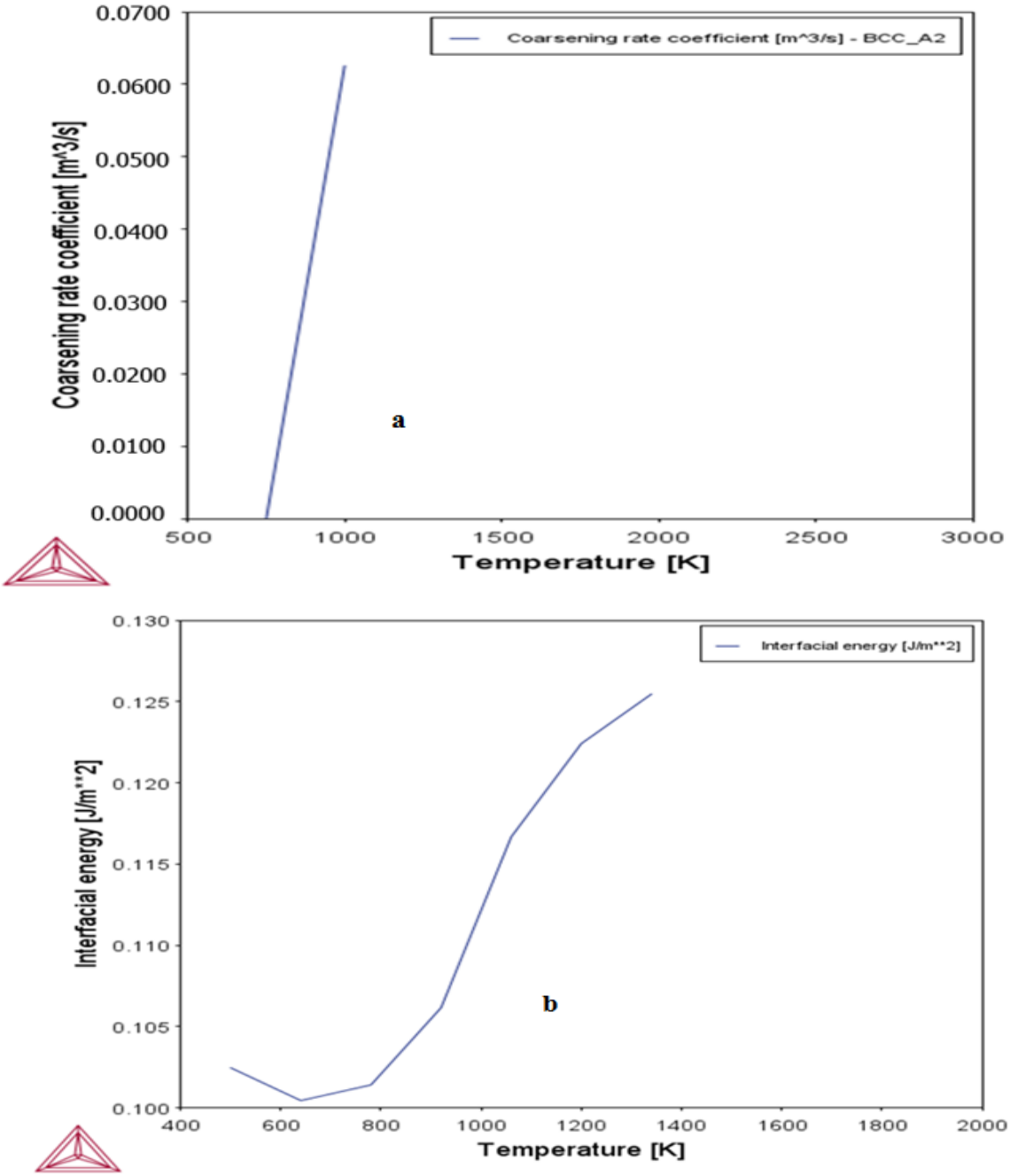


Fig. 1. (a) Coarsening energy rate coefficient (b) Interfacial energy analysis at 1900K.

The coarsening energy analysis and interfacial energy calculations of Fe-Ni-C alloys system is given by Figure 1(a, b). The active phase found for coarsening rate coefficient is BCC_A_2 with different composition of alloying elements. The interfacial energy of the BCC_A_2 is found activated for 500 K, 750 K and 1000 K. the Fe, Ni, C mass percents are found 99.59, 0.01, 0.4 with interfacial energy calculations of (0.04070, 0.02905, 0.01759) J/m^2.The highest value of coarsening energy is found 0.04070 J/m^2 indicates the ability of the alloying material to withstand an external magnetic field without demagnetization process and metallurgical fields.

Table. 1 interfacial energy analysis of Fe-Ni-C system.

Coarsening rate coefficient, BCC_A_2	Temperature [K]	Interfacial energy	Mass % Ni	Mass % C
0.04070	500	0.1025J/m^2,500K	0.01	0.5
0.02905	750	0.1008, 640K	0.01	0.5
0.01759	1000	0.102, 790K	0.01	0.5
0.01759	--	0.1125,1000K	0.01	0.5
--	1330	0.125	0.01	0.5

The evaluations of interaction of activity components in the alloy are found more 0.04070 times at 500 K. The magnetic properties of the alloy are recorded better at low temperature in Fe-Ni-C system with activated phase of BCC_A_2. Coercive energy calculations of Fe-Ni-C ternary alloy system as per result. The alloy shows increasing coarsening rate at low temperature for Ni contents alloying. At higher temperature, the progress of material to remove grains of carbides and refining the grains are low. interfacial energy increases with increasing temperature as it indicates the imbalanced molecular forces of carbides in the alloying elements. The alloy still shows the stability and performance by lowering its coarsening at higher temperature ranges

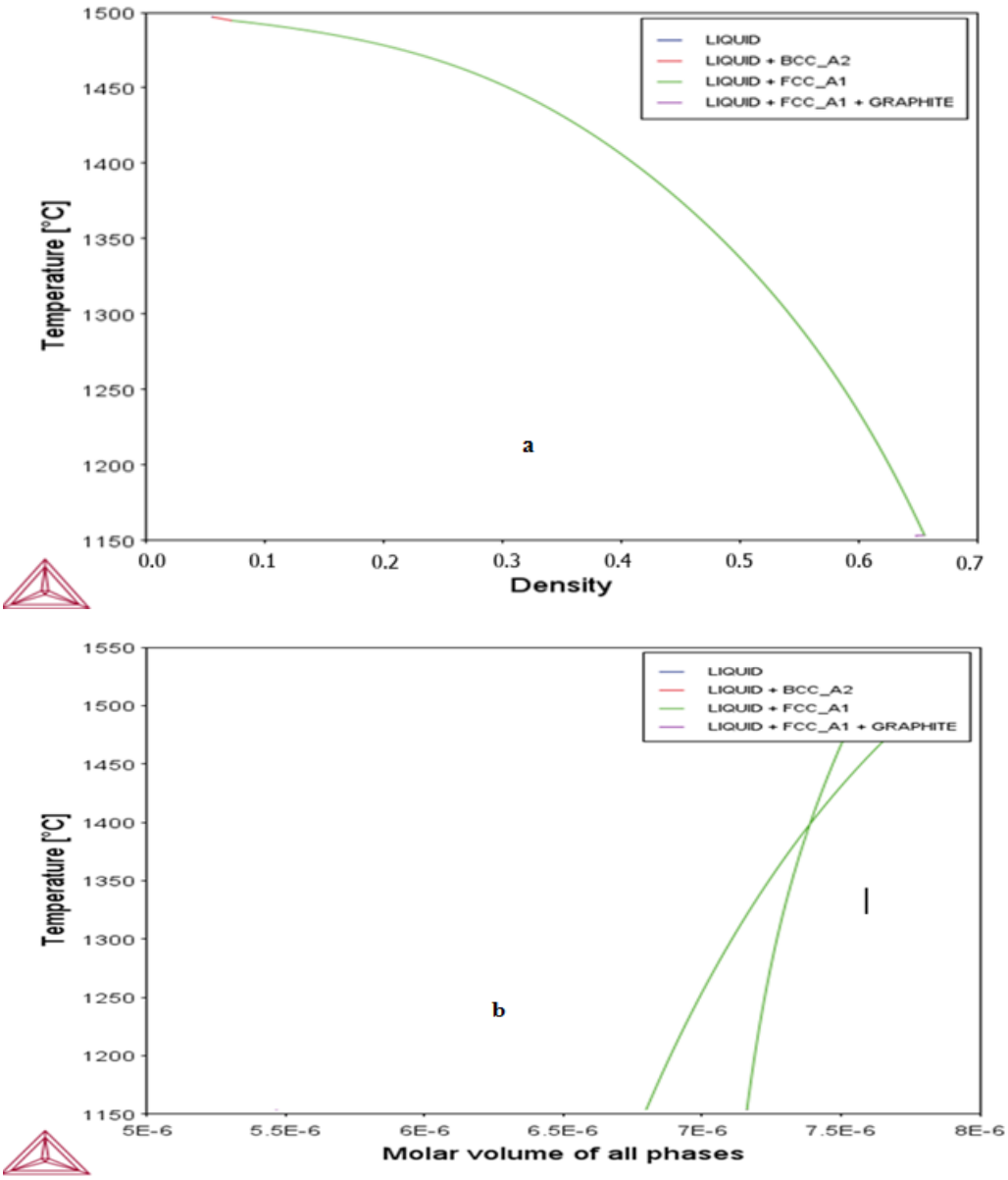


Fig. 2. (a) Fe-Ni-C density analysis (b) Fe-Ni-C Molar Volume analysis profile.

As seen from the simulations that the density of BCC_A_2 is seen constant 0.22-0.32 mole fraction by figure 2 (a, b). The alloying order is found magnetically activated for Ni-rich portion. At low temperature range 1497 K. the density of system is found maximum value of 0.056 gm/m^3,which indicated the majority phases composition in the given alloy system. With the decrease in temperature the composite nature phases overcomes and the most withstanding phases retained with increasing density. At the highest temperature from 1505.72 K, the density of phases becomes peak and it indicates the rare temperature withstanding phases. The fluctuations in the densities of phases are changing with temperature as a result of phase's nature and stability.

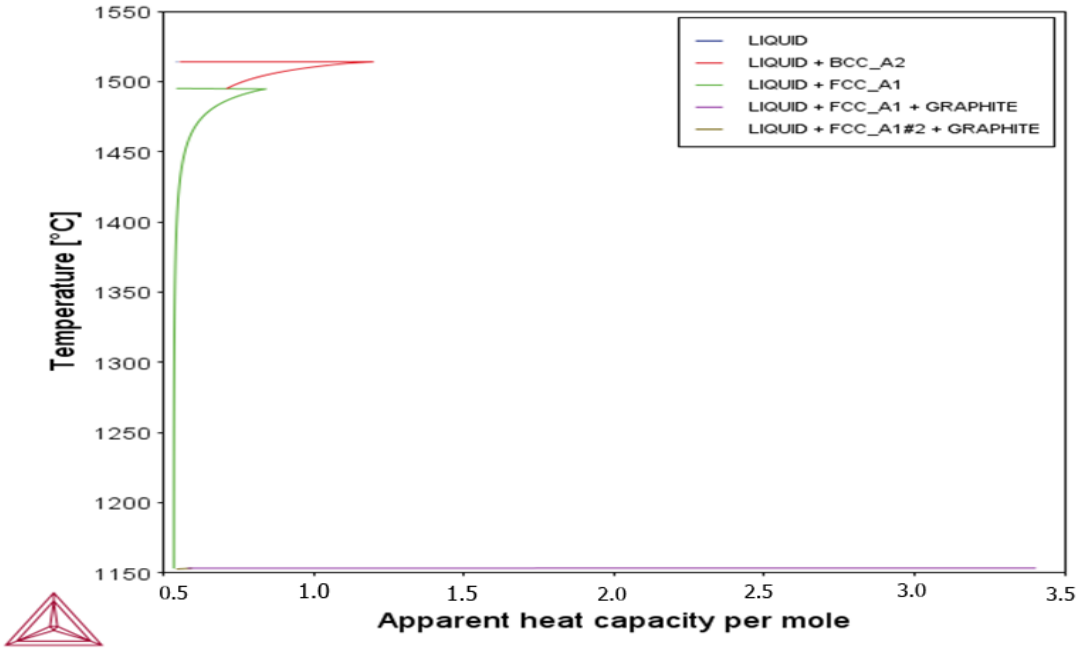


Fig. 3. Apparent heat capacity per mole in Fe-Ni-C system

Table. 2 apparent heat capacity of Fe-Ni-C system.

Apparent Heat Capacity	Temperature [°K]
0.03435	1503.6000
0.06631	1502.6000
0.09628	1501.6000
0.17589	1498.6000
0.19946	1497.6000
0.22174	1496.6000
0.24285	1495.6000
0.26285	1494.6800
0.28044	1494.6800
0.28130	1493.6500
0.31070	1492.6500
0.33807	1492.6500

The given result shows the apparent heat capacity of the carbon elements in the Fe-Ni-C System. The solid phases retained up to 1505.7 K. The highest apparent heat capacity is noted 0.33807 for 1492.6500 K. the increase in temperature results the increase in the apparent heat capacity of phases. The FCC_A_1 phase is found the phase associated with highest molar volume in the Fe-Ni-C ternary alloy system with highest apparent heat capacity. The temperature variation results the composite phases to be disappears with required level of annealing. The system is found lowest apparent heat capacity 0.03435 with temperature of 1503.6000 K. The apparent heat capacity of FCC is found more responsive and found in austenite coordination.

5. Conclusion

The thermodynamic properties analysis of the Fe-Ni-$C_{X\ (X=0.3\text{-}0.5)}$ ternary alloys is investigated through the Thermo-Calc package with FEDAT databases and Calphad method. The Fe-Ni, binary alloy are kept base component, while the Carbon composition is maintained 0.3, 0.4, and 0.5 mass percent for alloying. The interfacial energy fluctuation values are found (0.04070, 0.02905, 0.01759) J/m^2. The magnetic properties are found activated at low temperature 500 K which shows the maximum withstanding power of the alloy toward demagnetization. The evaluation of interactions is found maximum at 0.04070 J/m^2 in the Fe-Ni-C ternary alloy system. The system shows more phase's arrangements and compositions at low temperature and at high temperature, the phases arrangements decreases and the vitality range of the alloy decreases. The Fe-Ni-C system shows FCC_A1 phase is stable at temperature variation in the system. At low temperature 1492 K , the density of system is maximum value of 0.33945 gm/m^3,which indicated the majority phases composition in the given alloy system. With the increase in temperature the composite nature phases overcomes and the most withstanding phases retained. At the highest temperature from 1505.72 K, the density of phases becomes constant and it indicates the rare temperature withstanding phases. The alloy shows increasing coarsening rate at low temperature for Ni contents alloying. At higher temperature, the progress of material to remove grains of carbides and refining the grains are low. interfacial energy increases with increasing temperature as it indicates the imbalanced molecular forces of carbides in the alloying elements. The fluctuations in the density of phases are changing with temperature as a result of phase's nature and stability. The highest mole fraction is seen at 1484.65 K with 0.35044 of value. The FCC_A1 phase is found the phase associated with highest molar volume in the Fe-Ni-C ternary alloy system. The temperature variation results the composite phases to be disappears with required level. The system is found highest apparent heat capacity 0.39269 with temperature of 1501.02 K. the apparent heat capacity is found maximum in the Ni-rich portion of alloy, indicating the more heat resistive properties of the system. The alloy shows better industrial and research applications.

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