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Thermodynamic Analysis of Metastable (Ag-Cu) Binary Alloy System Using Calphad Method

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Abstract. This paper shows the thermodynamic analysis and predictions of metastable binary alloy silver-copper (Ag-Cu) system using the Calphad approach. The thermodynamic analysis involves the calculation of phase diagram, Gibbs energy of mixing, excess Gibbs energies, thermodynamic molar activities and coefficient of activities, partial and integral values of enthalpy for (Ag-Cu) alloy system at three elevated temperatures, (1973 K, 2000 K, 2028 K). The given alloys show positive deviation from Vegard's law, Henry's law and corresponding good negative deviation from Raolts's law ideal Gibbs curve. The activity simulation of the adding compositions are seen good attractive interaction for best doping characteristics. The alloy is seen equilibrium fluctuation and good stability.

Keywords: thermodynamic analysis, calphad method, mieddema approach

Introduction

Due to the specific novel structures, geometry, properties, applications and counterparts equilibrium, the metastable alloys are of great interest commercially in industries. Among many amorphous, crystalline, nano-crystalline, and non-equilibrium phases, the metastable alloys have got considerable attention of researcher's because of vast production range and techniques (Babu, 2009). Metastable alloys have contributed many challenges for understanding of phase transformations in the system of alloys. Recently, understanding of stability formation and basic stability, the thermodynamic functions are having primary importance in resolving the challenges easily. Thermodynamic analysis and determination of thermodynamic based functions for alloys system are preceded since many years (Okamoto, 2016).

Material and Methods

The research analysis, simulations and calculations in this resaerch are performed by utilizing the thermo-calc package (based on Calphad method) and the database used is PBIN, which is basic for the Calphad method. Thermo-calc is a worldwide famous software used for thermodynamic analysis and assessments of different alloying materials. The Calphad method is a well established and well-defined method for phase diagram analysis and thermodynamic functions for equilibrium alloys. It is widely used and found suitable in the material zone of industry (Bock *et al*., 2019). The phase diagrams, phase equilibria and figure modules are calculated accordingly through simulations and modeling. The selected database PBIN is much important by providing urgent information about alloy nature and properties just as the phase diagram, thermodynamic calculations, thermodynamic properties and modeling of projection of alloy systems. The Calphad method based on the thermo-calc package is a useful tool for material structure design. The mieddema approach has been used for removing errors in Calphad method to support the results of Calphad calculation in case of a metastable system. Calphade method does not provide clear results in case of a metastable system, so we have used successive mieddema approach. By the Calphad method. Initially we measured the thermodynamic calculations by using an analytical expression describing the formalism of phases and free energy (G) of the binary system as

$$G=G_1X_{Ag}+G_2X_{Cu}+K_BT(X_{Ag}LnX_{Ag}+X_{Cu}Ln_{Cu})+G_{ex}....(1)$$

where;

X_{Ag}, X_{Cu} are the molar concentrations of alloying elements, while G_{ex} is the excess free energy (Li *et al*.,

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2001). The Calphad method is used for the calculation of thermodynamic functions from many years (Delsante *et al*., 2015; Zhu and Pelton, 2015). The Calphad method shows some errors in the case of sigma phase due to the limitation of equilibrium regimes (Miracle, 2006). In this paper, we used the mieddema approach to support Calphad calculations in the case of metastable alloys in accordance shown by (Jian *et al*., 2020). Literature study reveals that the alloys (Ag-Cu) system has limitations at a higher temperature ranges. Some thermodynamic properties just like excess Gibbs free energy, molar thermodynamic activities and enthalpy need to be calculated at higher temperature ranges and used quenching techniques for the production of metastable continue solid solution for (Ag-Cu) eutectic system, a different number of techniques has been utilized for many years for making solutions (Milewski, 2017; Kattner and Cambell, 2009; Gschneidner *et al*., 2003). This research has shown the heterogeneity and enthalpies formation cascades for the (Ag-Cu) system by removing Calphad limitations and calculations. Calphad method has been performed in the sense of fitting to create a phase diagram for the (Ag-Cu) binary system (Ho *et al*., 2008).

The phase diagram shows three metastable phases with counterpart equilibrium. The high temperature surviving phase is the liquid base phase. Ferrite phase needs lower temperature for survival as the FCC_A1#1 phase is found at temperature ranges (200 K-980 K) with a concentration composition of (0.88-1.0) mole. The FCC_A1#2 phase appeared at a temperature ranges (200 K-1090 K) with a composition of (0.0-0.06) mole. The liquid base phase is the peak one stable up to high temperatures ranges (1090 K-2028 K) with overall composition range as seen by Table 1 and 2.

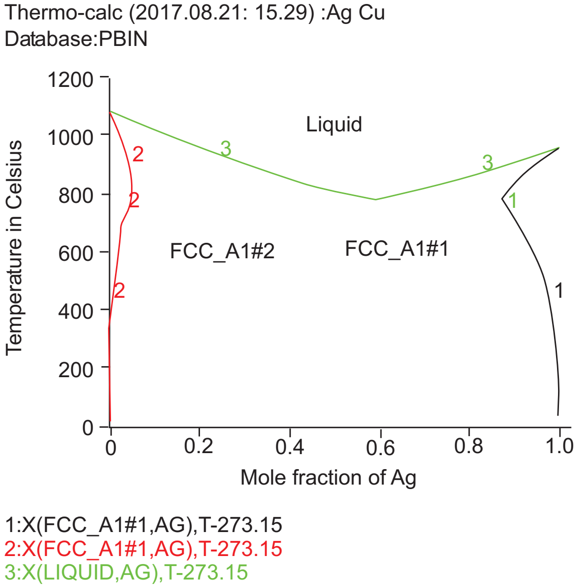

Fig. 1. Phase diagram of Ag-Cu alloy.

The phases have sharp nature and variational heterogeneity up to a higher expend level. At a temperature of 790 K, all the three phases are correlated by peaks and fluctuate to balance counter part equilibrium. To enhance the metastable nature, the alloy starts yielding up to a higher degree of tolerance in the liquid regime.

Mieddema model is useful in removing errors in the Calphad method especally in the case of metastable alloys (Ag-Cu). Due to lack of equilibrium, mieddema approach deals binary alloys composed of Wigner-Seitz cells. The Wigner-Seitz cell geometry change results in pure metal to decompose their boundaries contracts. Influences deals here is electro-negativity deference of elements and electron density between components. By mixing the alloying elements result in the electron density cell disappears, which leaves a positive mixing enthalpy contribution (Li *et al*., 2007). For liquid binary alloys and solid solution, the excess enthalpy disorder is calculated as:

$$(\Delta H_{Ag,Cu})_{disorder} = f_{Ag,Cu}\, X_{Ag}[1 + u_{Ag}X_{Cu}(\Phi_{Ag} - \Phi_{Cu})]X_{Cu}[1 + u_{Cu}X_{Ag}(\Phi_{Cu} - \Phi_{Ag})] / X_{Ag}V_{Ag}^{2/3}[1 + u_{Ag}X_{Cu}(\Phi_{Ag} - \Phi_{Cu})] + X_{Cu}V_{Cu}^{2/3}[1 + u_{Cu}X_{Ag}(\Phi_{Cu} - \Phi_{Ag})]$$

As for order intermetallic components, we have

$$(\Delta H_{Ag,Cu})_{order} = \Delta H_{Ag,Cu}[1 + 8((\Delta H_{Ag,Cu} / f_{Ag,Cu}\, \{X_{Ag}V_{Ag}^{2/3}[1 + u_{Ag}X_{Cu}(\Phi_{Ag} - \Phi_{Cu})] + X_{Cu}V_{Cu}^{2/3}[1 + u_{Cu}X_{Ag}(\Phi_{Cu} - \Phi_{Ag})]))^2$$

Now;

$$f_{Ag,Cu} = 2p\, V_{Ag}^{2/3} V_{Cu}^{2/3}[q/p\, (\Delta n_{ws}^{1/3})^2 - (\Delta\Phi)^2 - \alpha\, r/p] / (n_{ws}^{1/3})_A^{-1} + (N_{wa}^{1/3})_b^{-1}$$

where;

n_{WS} is the electron density; Φ is the electronegativity, u, q, p, α are the empirical parameters q/p is by p-d hybridization, q/p is equal to 9.4, p is 14.4, 10.6, 12.3 for solid alloy, for non-transition metal phases α is 0.73 and 1 for solid and liquid, parameters obtained from reference (Sheibani *et al*., 2010).

Table 1. Thermodynamic phase calculation at different temperature ranges for the system: Ag-Cu

Temperature	Pressure (Pascal)	Number of moles	ACR (X) (activity of a component relative ratio Ag)	Mass (g)	Total Gibbs energy (J/mol, Cal)	Vol (cm^3)	Enthalpy (J/mol, Cal)	Activity Ag. SER(stable element reference)state	Activity Cu. SER (stable element reference) state
300K-600K	1.000000E+05 1.000000E+05	1.00000E+0 1.00000E+0	1E-2 1E-2	6.38082E+01 6.38082E+01	-9.91241E+03 -1.79894E+04	0.0E+0	1.10825E+02 5.22704E+03	5.9153E-03 1.0000E-02 1.7086E-01 -4.4073E+03 5.9153E-03 1.0000E-02 2.0509E-02 -1.6159E+04	9.9408E-01 9.9000E-01 1.8554E-02 -9.9452E+03 9.9408E-01 9.9000E-01 1.3169E-02 -1.8000E+04
Liquid #1		5.9032E-03 4.7502E-03		6.3678E-01 5.1187E-01				9.99993E-01 9.98495E-01	7.10249E-06 1.50450E-03
FCC_A1 #1		9.9410E-01 9.9525E-01		6.3171E+01 6.3296E+01				2.06740E-05 2.00622E-03	9.99979E-01 9.97994E-01
700K-1800K	1.000000E+05	1.00000E+00	1E-2	6.38082E+01 6.38082E+01 6.38082E+01 6.38082E+01 6.38082E+01 6.38082E+01	-2.82447E+04 -4.00938E+04 -5.32024E+04 -6.73683E+04 -8.39266E+04 -9.27650E+04	0.00000E+0	1.07035E+04 1.62438E+04 2.19538E+04 2.78158E+04 4.71139E+04 5.02532E+04	5.9153E-03 1.0000E-02 3.8192E-03 -3.2405E+04 5.9153E-03 1.0000E-02 5.2460E-04 -5.6519E+04 5.9153E-03 1.0000E-02 1.2867E-04 -8.1932E+04 5.9153E-03 1.0000E-02 4.3842E-05 -1.0847E+05 5.9153E-03 1.0000E-02 5.7815E-06 -1.5042E+05 5.9153E-03 1.0000E-02 4.1977E-06 -1.6471E+05	9.9408E-01 9.9000E-01 7.8389E-03 -2.8220E+04 9.9408E-01 9.9000E-01 4.7725E-03 -3.9996E+04 9.9408E-01 9.9000E-01 3.0326E-03 -5.3031E+04 9.9408E-01 9.9000E-01 2.0091E-03 -6.7124E+04 9.9408E-01 9.9000E-01 1.2339E-03 -8.3531E+04 9.9408E-01 9.9000E-01 9.6735E-04 -9.2337E+04

Now, by using four species association model, Gibbs free energy of liquid phase will become $G_m^{liquid} = \Sigma_i X_{AgCu} {}^\circ G_{AgCu}^{liquid} + RT\ \Sigma_i X_{AgCu} Ln X_{AgCu} + \Sigma_i \Sigma_{j>i} X_{AgCu} X_{CuAg} {}^\circ L_{AgCu}^{liquid}$

G_m^{liquid} shows molar Gibbs free energy of liquid phase; X_{AgCu} is the molar fraction by only considering pairwise interaction between species, the Gibbs energy of Ag-Cu atoms will become as

$$G_{AgCu}^{liquid} = m^\circ G_{Ag}^{liquid} + n^\circ G_{Cu}^{liquid} + \Delta G_{AgCu}^{liquid},$$

ΔG_{AgCu}^{liquid} shows liquid Gibbs free energy of alloy formation.

Table 2. Thermodynamic phase scalculationat temperature ranges: 1973K, 2000 K, 2028 K for Ag-Cu binary system

Temperature	Pressure (Pascal)	Number of moles	ACR (X) (activity of a component relative ratio Cu)	Mass (g)	Total Gibbs energy/mol, Cal	Volume (cm^3)	Enthalpy (J/mol, Cal)	Activity Ag. SER(stable element reference)state	Activity Cu. SER (stable element reference) state
1973K	1.00000 E+05	1.00000 E+00	1E-02	6.38082 E+01	-1.27376E+05	0.00000 E+00	6.19625E +04	5.9153E-03	9.9408E-01
								1.0000E-02	9.9000E-01
								1.5219E-06	4.3893E-04
								-2.1975E+05	-1.2683E+05
Liquid#1		1.0000 E+00		6.3808 E+01					
								9.90000E-01	1.00000E-02
2000K	1.000000 E+05	1.00000 E+00	1E-2	6.38082 E+01	-1.29973E+05	0.00000 E+00	6.28101E +04	5.9153E-03	9.9408E-01
								1.0000E-02	9.9000E-01
								1.4267E-06	4.1700E-04
								-2.2383E+05	-1.2941E+05
Liquid#1		1.0000 E+00		6.3808 E+01				9.90000E-01	1.00000E-02
2028K	1.000000 E+05	1.00000 E+00		6.38082 E+01	-1.32678E+05	0.00000 E+00	6.36891 E+04	5.9153E-03	9.9408E-01
								1.0000E-02	9.9000E-01
								1.3356E-06	3.9570E-04
								-2.2808E+05	-1.3211E+05
Liquid#1		1.0000 E+00		6.3808 E+01				9.90000E-01	1.00000E-02

$G_m^{liquid} = (X_{Ag} + 2X_{AgCu} + X_{AgCu})^\circ G_{Ag}^{liquid} + (X_{Cu} + X_{AgCu} + 2X_{AgCu})^\circ G_{Cu}^{liquid} + X_{AgCu}\Delta G_{AgCu}^{liquid} + X_{AgCu}\Delta G_{AgCu}^{liquid} + RT$

$(X_{Ag}LnX_{Ag} + X_{AgCu}lnX_{AgCu} + X_{AgCu}lnX_{AgCu} + X_{Cu}lnX_{Cu})X_{Ag}X_{AgCu}{}^\circ L_{AgCu}^{liquid} + X_{Ag}X_{AgCu}{}^\circ L_{AgCu}^{liquid} + X_{Ag}X_{Cu}{}^\circ L_{AgCu}^{liquid} + X_{AgCu}X_{AgCu}{}^\circ L_{CuCu}^{liquid} + X_{Cu}X_{Ag}{}^\circ L_{CuAg}^{liquid} + X_{Cu}X_{AgCu}{}^\circ L_{AgCu}^{liquid}$

As ${}^\circ L_{CuAg}^{liquid}$ is the interaction Gibbs energy of alloy formation.

The FCC phases are found by using the substitution solution model and treating it as a simple binary alloy.

${}^\circ G_m^{\Phi} = \Sigma_{i=AgCu} X_{AgCu}{}^\circ G_{AgCu}^{\Phi} + RT\, \Sigma_{i=CuAg} X_{AgCu} lnX_{AgCu} + {}^{xs}G_m^{\Phi}$, (Turchanin *et al*., 2020; Ozturk *et al*., 2002). Where Φ shows FCC structure and ${}^\circ G_m^{\Phi}$ is for molar Gibbs free energy, so${}^{xs}G_m^{\Phi} = X_{AgCu}\Sigma_{i=0}^{j} L_{AgCu}^{\Phi} (X_{Ag} - X_{Cu})$, where L_{AgCu} coefficient of regular solution model.

Results and Discussion

Figure 2(a,b,c) shows the Gibbs free energy of the (Ag-Cu) binary alloy system as calculated through simulations at temperatures 1973 K, 2000 K and 2028 K. The analysis shows that the liquid phase is having more decrease in Gibbs energy at elevated temperatures. It seems that the liquid regime is the most temperature with standing and stable one in the (Ag-Cu) binary system. FCC_A1#1, FCC_A1#2 predicted the austenite and ferrite phase seems less stable with a variety of fluctuation and less Gibbs energy.

Figure 3(a,b,c) shows activity of Ag and Cu in (Ag-Cu) binary system at different temperature ranges 1973 K, 2000 K, 2028 K. The activity shows a positive deviation from Vegard's law which shows increasing enthalpy of (Ag-Cu) system, which result increasing heat contents of the system. Corresponding positive deviation from Roalts law ideal curve is seen, which indicates repulsive interaction among alloying elements

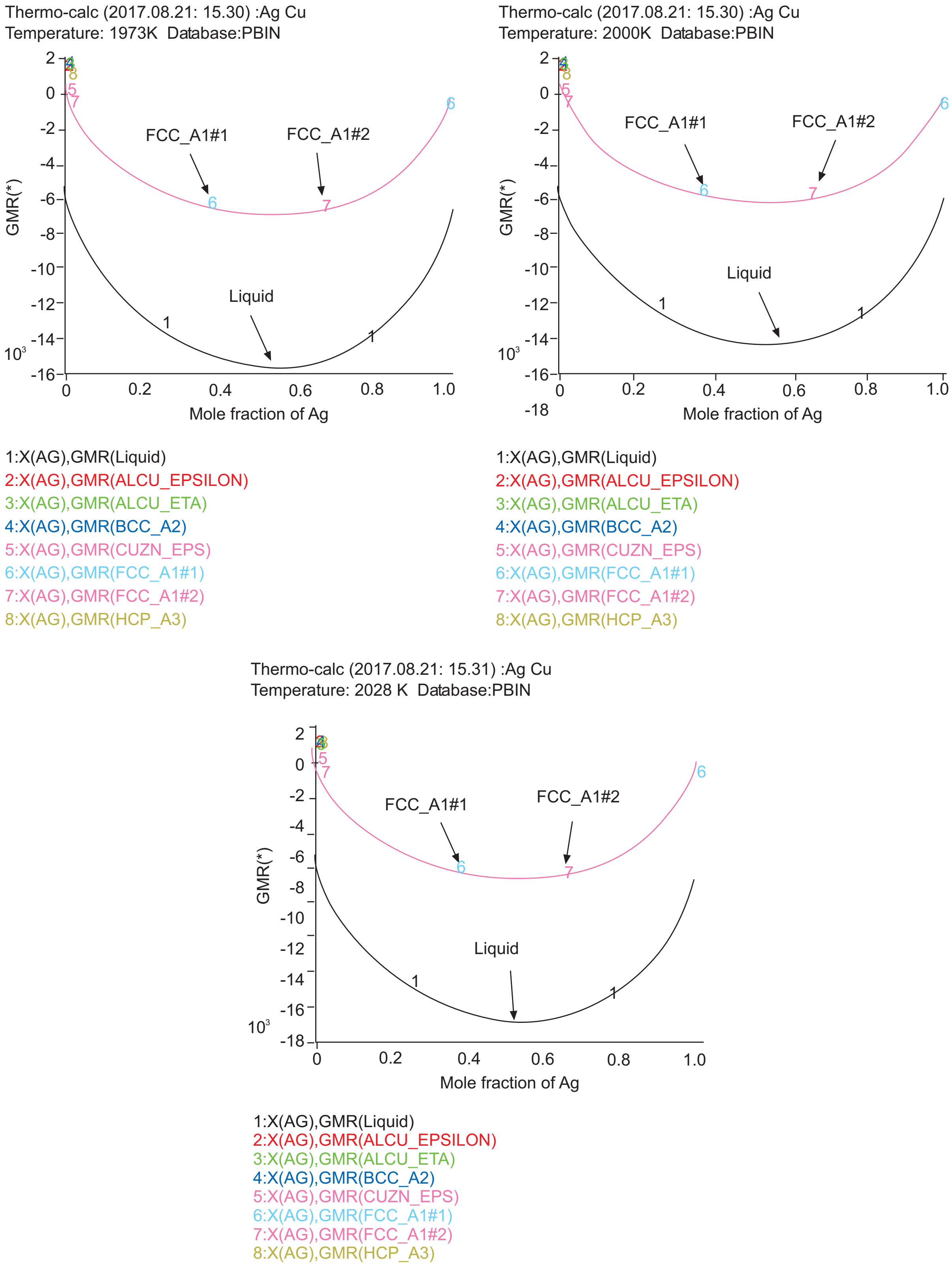

Fig. 2(a,b,c). The Gibbs free energy of the (Ag-Cu) shows the binary alloy system as calculated through simulations at temperatures 1973 K, 2000 K, 2028 K.

of the (Ag-Cu) system and shows less epitaxial growth of the alloying system. Figure 2 shows that the alloy still shows stability by decreasing their Gibbs energy value regularly with increasing enthalpy, which shows a negative deviation from Raolts's law ideal curve. The total Gibbs energy of the (Ag-Cu) system decreases with increasing temperature, which shows the stability of the (Ag-Cu) system. These tremendous behaviours of stability are much important for industrial zones and research fields.

Table 1 and 2 shows the activity of alloying elements (Ag, Cu) during alloying and justifying the phase diagram of Ag-Cu binary alloy system. At temperature

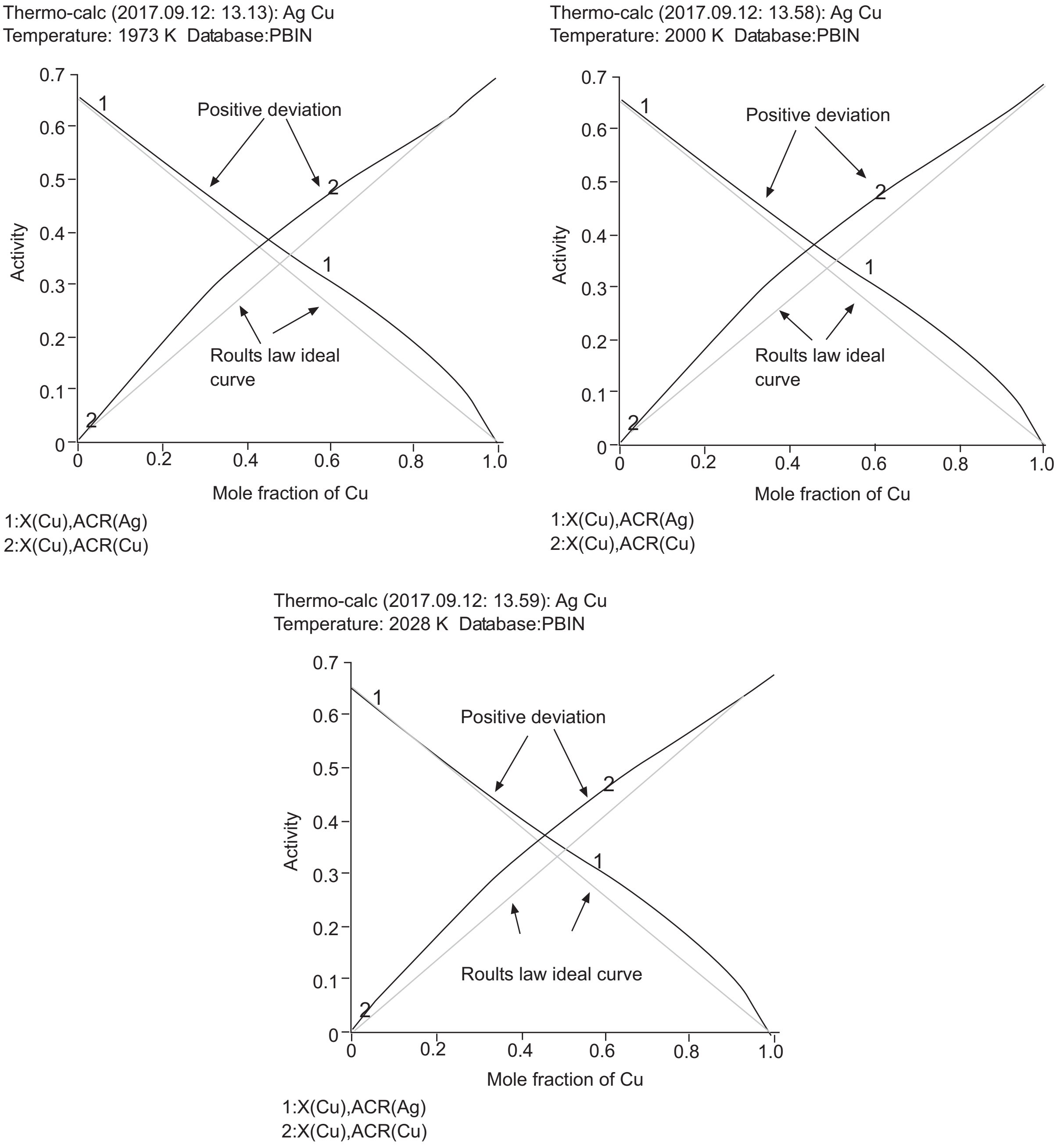

Fig. 3(a,b,c). The activity of Ag and Cu shows in (Ag-Cu) binary system at different temperature ranges 1973 K, 2000 K, 2028 K.

(300-600) K, the Gibbs energy value is –9.91241E+03 j/mol –1.79894E+04 j/mol. The enthalpy is 1.10825E+02 j/mol, 5.22704E+03 j/mol. The fluctuation of Ag elements is seen as 5.9153E-03, 1.0000E-02, 1.7086E-01, –4.4073E+03, 5.9153E-03, 1.0000E-02, 2.0509E-02, –1.6159E+04 during alloying, while for Cu elements is 9.9408E-01, 9.9000E-01, 1.8554E-02, –9.9452E+03, 9.9408E-01, 9.9000E-01, 1.3169E-02, –1.8000E+04. The liquid phase (Liquid#1) achieved at activity ranges 9.99993E-01, 9.98495E-01, while the FCC_A1 is achieved at molar activity ranges 2.06740E-05 for Ag elements. 9.99979E-01 is seen for Cu elements. Observation at temperature range of 700 K-1800 K seems the following values for Gibbs energy –2.82447E+04, –4.00938E+04, –5.32024E+04, –6.73683E+04, –8.39266E+04, –9.27650E+04. The enthalpy value achieved here is 1.07035E+04, 1.62438E+04, 2.19538E+04, 2.78158E+04, 4.71139E+04, 5.02532E+04. The activity Ag SER (stable element reference) state is 5.9153E-03, 1.0000E-02, 3.8192E-03, –3.2405E+04, 5.9153E-03, 1.0000E-02, 5.2460E-04, –5.6519E+04, 5.9153E-03, 1.0000E-02, 1.2867E-04, –8.1932E+04, 5.9153E-03, 1.0000E-02, 4.3842E-05, –1.0847E+05, 5.9153E-03, 1.0000E-02, 5.7815E-06, –1.5042E+05, 5.9153E-03, 1.0000E-02, 4.1977E-06 , –1.6471E+05. The activity Cu SER (stable element reference) state shows the following fluctuation during alloying, 9.9408E-01, 9.9000E-01, 7.8389E-03, –2.8220E+04, 9.9408E-01, 9.9000E-01, 4.7725E-03, –3.9996E+04, 9.9408E-01, 9.9000E-01, 3.0326E-03, –5.3031E+04, 9.9408E-01, 9.9000E-01, 2.0091E-03, –6.7124E+04, 9.9408E-01, 9.9000E-01, 1.2339E-03, –8.3531E+04, 9.9408E-01, 9.9000E-01, 9.6735E-04, –9.2337E+04. Further increasing temperature of alloying up to 1973 K, the Gibbs energy if further decrease its value as seen 6.19625E+04 j/mol, with enthalpy of further increasing with temperature 6.19625E+04 j/mol. 5.9153E-03, –2.1975E+05, 1.5219E-06, 1.0000E-02 is Ag elements molar activity, while 9.9408E-01, 9.9000E-01, –1.2683E+05, 4.3893E-04 is molar activity for Cu elements during alloying. The Liquid#1 is the stable phase here with activity of Ag 9.90000E-01 and 1.00000E-02 for Cu elements configuration. At 2000 K, the total Gibbs energy acquires a value -1.29973E+05 j/mol. The enthalpy is 6.28101E+04 j/mol. Activity of Ag SER (stable element reference) state is 5.9153E-03, –2.2383E+05, 1.4267E-06, 9.90000E-01. Activity of Cu SER (stable element reference) state is 9.9408E-01, 9.9000E-01, 4.1700E-04, 1.00000E-02, –1.2941E+05 at 2028 K of peak temperature the Gibbs energy reaches highest value of –1.32678E+05 j/mol. Enthalpy with highest value 6.36891E+04 j/mol at that peak temperature. Activity of Ag SER (stable element reference) state is 5.9153E-03, 1.0000E-02, 1.3356E-06, 9.90000E-01, –2.2808E+05. Activity of CuSER (stable element reference) state is 9.9408E-01, 9.9000E-01, 1.00000E-02, –1.3211E+05, 3.9570E-04 at peak temperature range. The overall fluctuation of alloying shows stability of the liquid phase at 2028 K. The Gibbs energy acquire its maximum deviated negative value (–1.32678E+05) j/mol, Cal at 2028 K, which shows the system goes toward stability and obeying Raolts's Law. The enthalpy value at 2028 K is maximum (6.36891E+04) j/mol, Cal which show non ideal mixing and repulsive forces in the said alloy system to avoid equilibrium, which obeys Henry's and Vegard's law. The activity of Ag is maximum as (9.90000E-01), while smaller for Cu elements. The system shows non equilibrium and stable state at highest given temperature.

Conclusion

The thermodynamic analysis is shown using the Calphad method and mieddema approach, all thermodynamic optimization shows compositional heterogeneity. No equilibrium is found in the (Ag-Cu) binary alloy system and shows metastable nature accordance. Increasing temperature in (Ag-Cu) binary alloy system results in the enthalpy of the system increase gradually as by existing repulsion forces among alloying elements. This shows a positive deviation from Vegard's law that is found in accordance with previous results. The alloy shows stability by decreasing their Gibbs energy value regularly with increasing enthalpy, which shows a negative deviation from Raolts's law. Total Gibbs energy of (Ag-Cu) system decreases with increasing temperature, which shows the stability of the (Ag-Cu) system. The peak negative deviation is observed (2028 K) shows a strong negative deviation in (Ag-Cu) system and by increasing the stability level means hardening, wear resistance, corrosion resistance and other doping characteristics of the (Ag-Cu) alloy. The enthalpy proportion with temperature shows the increase in the heat contents of the said alloy system and observed maximum enthalpy at 2028 K, which is responsible for the withstanding and surviving high temperature and high heat-absorbing capacity of (Ag-Cu) alloy system. Activity shows throughout fluctuation from Vegard's law in a positive sense, which shows the system complex nature with rare doping and shows its greater validity for industrial applications in the system of interests and research areas.

Conflict of Interest. The authors declare no conflict of interest.

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