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THERMODYNAMIC PROPERTIES OF BINARY ALLOY SYSTEM (FE-V) USING CALPHAD METHOD

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Abstract

This research article shows Thermodynamic calculations and predictions of the Fe-V system using Calphad method, Thermo-Calc package and Pbine database. With different temperature from (1175- 1700)K ranges the said alloy is modeled and corresponding behavior of Gibbs free energy, phase diagram, and activity curve is monitored. As per the calculations the Gibbs energy curve is corresponds to negative era, which shows the actual stability application of the said alloy system. The alloy elements shows strong interaction shows negative deviation from Raoults law and the sigma/Bcc phase combined region is stable one and the ferrite is found most stable one.

Keywords: Thermodynamic Calculations, Predictions, Simulations, Phase diagram, Calphad method

1. INTRODUCTION

Ferric vanadium alloy is a universal hardener, strengthener and anti-corrosive for steels like (High Strength Low Alloy) steel, tool steels, as well as other ferrous-based products. Fe-V alloy has significant advantages over both iron and vanadium individually. Martin Henze discovered Vanadium in hemo-vanadian proteins found in blood cells (coelomic cells) of Ascidiacea (sea squirts) in 1911 [1-2]. Alexander, discussed the solubility behavior of Vanadium in Fe-Nb in the form of C-14 laves and μ phase [3]. Cuiping Guo, observed that the solution phases (liquid, BCC, FCC and HCP) were modeled as substitution solution in Fe–Ti–V system [4]. Anderson studied the Fe-V system using sub regular model and discussed the transition between Phases and Phase boundaries [5]. Byeong, compared the thermodynamic and experimental data of Fe-V and V-C system and discussed the phase diagram and Gibbs energies [6]. Jakub et al, used neutron and x-ray diffraction method and Mossbauer spectroscopy to study the sigma σ phase transition and lattice parameters [7].

2. Phase Diagram of Fe-V system

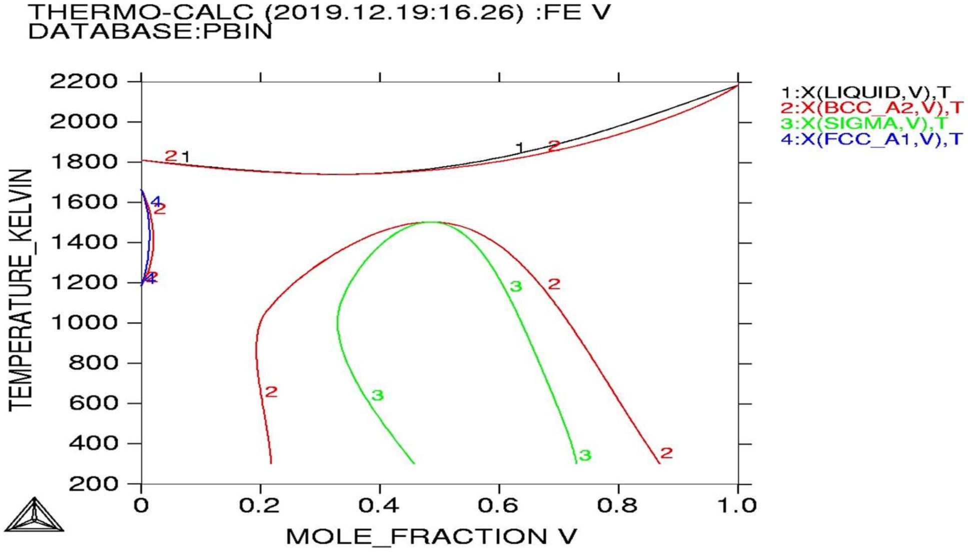


Fig. 1 phase diagram Fe-V system at elevated temperature ≈ 2200K with 106 MPa pressure

Figure: 1 shows phase diagram for particular binary alloy system Fe-V at different elevated temperatures. Different types of phases have been observed as (liquid, BCC_A2, Sigma phase, FCC_A1) as in accordance with literature. The composition ranges for most stable phases are observed as from (0.21-0.31) for BCC_A2 as a ferrite phase, (0.31-0.68) for sigma phase. The observation shows that the alloy composition for (0.26-0.68) mole fraction is most favorable range for solid solution mixing and alloy formation, for peak stability as per the existence of sigma phase here in the form of blanking in the era as in accordance with Jan loaf Anderson [8]. The most likely existing phase is BCC_A2 in the given Fe-V phase diagram as by temperature 1700K, above which the liquid phase becomes dominant. The sigma/ferrite phase is equilibrium phase as reported by thermodynamic assessment. The phase diagram for the Fe-V system has been investigated many time with formulated methods, the thermodynamic evaluation of the alloy reports ferromagnetic ferrite phases as a part of Gibbs energy of the particular alloy system, as per magnetic influences and complexes in the said alloy system, the Redlich-Kister power series is used for mathematical manipulations of the Fe-V alloy.

3. Mathematical descriptions

$$G^q = X^0_{Fe}\,G^q_{Fe} + X^0_{v}G^q_{v} + G^q_{m} + G^q_{mag}$$

Where G is the Gibbs free energy of system is for pure element, for V, Fe, Gibbs energy paramagnetic state value is 298.15K. , while the other parameters X, Gq molar fraction, molar Gibbs energy and magnetic based ordering of the system,

$$G^q_m = RT\,[X_{Fe}\,LnX_{Fe} + X_V\,LnX_V] + G^{qs}$$

While R is gas constant with excess molar Gibbs energy. Here the Redlich-Kister power series is used for mathematical manipulations as

$$G_N^{q,s} = X_{Fe} X_V \sum_{V=0}^{n} p\, L^q Fe,\ V (X_{Fe} -)_V^{v}$$

Now by Calphad convention rule

$$^{V}L^q Fe,\ V = a_v^q + b_v^q T + c_v^q T \ln T + d_v^q T^3 + e_v^q T^3 + g_v^q T^{-1} + g_v^q T^7 + h_v^q T^{-9}$$

With “a” and “h” as imperial parameters.

Here the BCC-A_2 of ferromagnetic phase shows magnetic contribution to this particular system, BCC-A_{12}, CPH-A_3, FCC-A_1, while CPH-A_3 shows anti ferromagnetic contributions to this system, as in accordance with Hillert and jar l literature.

$$G_{mag}^q = RT \ln (B^q+1)\, g(t)$$

While for numerical solution, if g (t) <1 then we will observe as

$$g(t) = 1-(79^{t-1}/140\, p + 474/497(1/p - 1)\, (t^3/6 + t^9/135 + t^{15}/600))/D$$

$$G(t) = -(t^{-5}/10 + t^{-15}/315 + t^{-25}/1500)/D \quad \text{if} \quad t > 1$$

While $D = 0.46044 + 0.73189(1/(p-1))$

$t = T/T_{C,N}^q$ that represents a particular curie temperature of q-Th phase during transformation from ferromagnetic to paramagnetic transformation, similarly anti ferromagnetic to paramagnetic ,information about average magnetic moment, as well the crystal structure of That particular alloy system, the value of P is 0.40 for BCC-A_2,while for FCC-A_1,BCC-A_{12}, CPH-A_3 are 0.38.so

$$C_{Pmag}^q = R \ln (B^q+1)\, c(t)$$

$$C(t) = 474/497(1/p - 1)\, (2r^3 + 2t^9/3 + 2t^{15}/5))\, D \quad \text{if } t < 1$$

$$C(t) = (2t^{-5} + 2t^{-15}/3 + 2t^{-25}/5)/D \quad \text{if } t > 1\ [10]$$

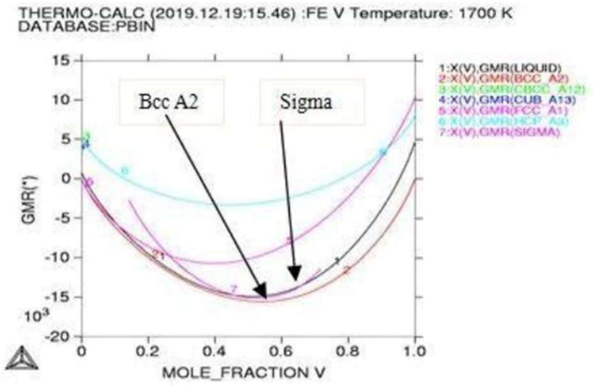
The phase diagram of the said alloy system has been assessed by varying activity and temperature up to 2193K and described the liquid/bcc as an equilibrium one phase at such a high temperature range. The described sigma/bcc and liquid/bcc are sorted as stable one equilibrium phase by evaluating thermodynamic parameters as in accordance with [11]. The given thermodynamic calculations seems that all the thermodynamic phases in system Fe-V including paramagnetic ,ferromagnetic and sigma phases are stable at lower temperature (800-1250)K as by chemical ordering of the alloying. The Gibbs free energy in form of axcees as a part of entropy and sigma phase with parameters of lattice stability for phase BCC boundaries is shown by Hack et al [12]. The magnetic moment of 0.7 at 67K of temperature was seen anti ferromagnetic. By [13] with a very slow value putted for lattice stability by Kaufman et al[14]. At range mention from (0.25-0.44) weight percent in composition of phase diagram, the metastable regime is determined and predicted and shows

Equilibrium among ferromagnetic and paramagnetic BCC for the system Fe-V binary alloysystem.

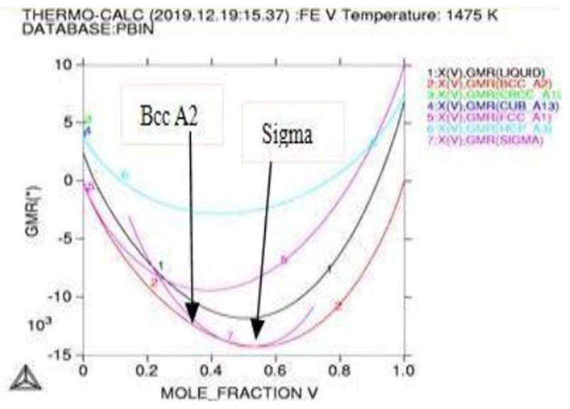
4. Calphad method and thermodynamic calculations

It is the most important computational based method as a base for thermo-calc package for the precise calculations of phase diagrams, thermodynamic parameters of different binary and ternary alloy systems in the term of phase equilibria. It is based on many modules to use for thermodynamic calculations, modeling and activity simulations. The recent modules are more polished for quick calculations of molar volume, elastic modules, with phase equilibria properties with composition of molar activities, Gibbs energy, enthalpy, entropy.

5. Thermodynamic Simulations



a)



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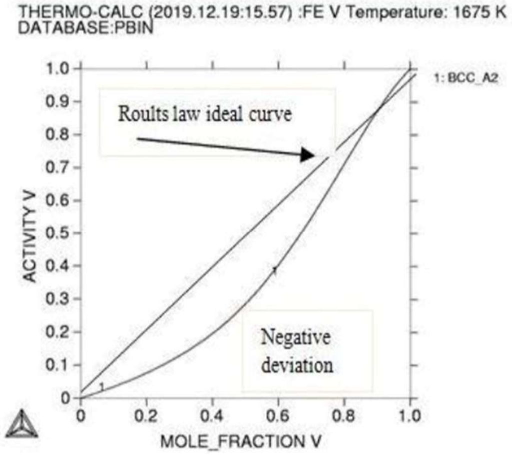

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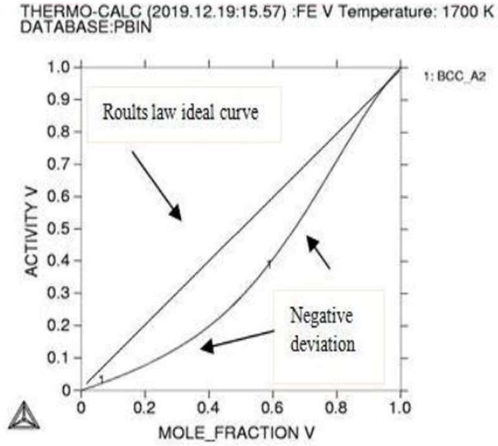

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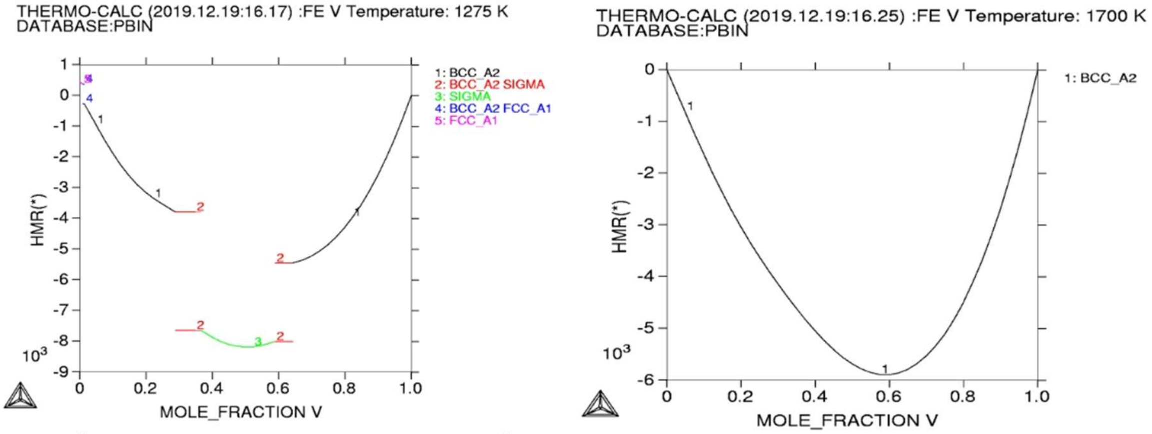

e) f)

Fig. 2 a) Gibbs energy of Fe-V system at 1700K b) Gibbs energy of Fe-V system at 1475K c) Thermodynamic molar activity of Fe-V system at 1675K d) Thermodynamic activity of Fe-V system at 1700K e) Enthalpy of formation of Fe-V binary system at 1275K f) Enthalpy of Formation of Fe-V system at 1700K

The modeled figures shows simulation and modeled simulations for Gibbs energy, Activity curves and enthalpy formation curves by Calphad method with P-bin database. The elevated temperature ranges from 1175K-1700K. The alloy is showing stability between regions of (0.25-0.44) compositions range as in that era the Para and Ferro magnetic phase are in equilibrium and the alloy retained its stable phase in accordance with Meta stable regime with prescribed phase's bcc/sigma. The most stable phase is the combined boundary grain region of bcc/sigma and the bcc is most stable side in the form of ferrite phase with magnetic contributions most. The activity increases with temperature shows accordance with Raoults law. [15]. The flexible tool for solving interactions among various thermodynamic calculations and predictions with ideal and non-ideal behavior in 1981 is Thermo-Calc package with revised version of their modules in 2002 with many databases in 1985 by [16-17].

Table.1: Thermodynamic phase's calculation at temperature zone (**1100K- 1700K**) for Fe-V binary alloy system:

T^O/K: Degree Kelvin.	Pressure: pascal	Number of moles	ACRX : (activity of component relative ratio (Fe,V)	Mass: gram	Gibbs energy : J/mol	Volume :cm3	Enthalpy: J/K	Activity Fe. SER:stable element reference state	Activity V. SER: stable element reference state
1100K	1.00×10^5	1.00	2×10^{-3}	5.58×10^1	-4×10^4	7.32×10^6	2.98×10^4	9.97×10^{-1} 9.98×10^{-1} 4.58×10^{-3} -4.92×10^4	2.19×10^{-3} 2.00×10^{-3} 1.44×10^{-6} -1.23×10^5
BCC_		1.00		5.58×10^1				9.98×10^{-1}	2.00×10^{-3}

A2#1									
1200K	1.00×10^{5}	1.00	2×10^{-3}	5.58×10^{1}	-5×10^{4}	7.31×10^{6}	3.47×10^{4}	9.97×10^{-1}	2.19×10^{-3}
								9.89×10^{-1}	2.00×10^{-3}
								3.42×10^{-3}	1.97×10^{-6}
								-5.66×10^{4}	-1.31×10^{5}
									2.79×10^{-3}
									1.66×10^{-3}
BCC		3.00×10^{-1}		1.00×10^{-1}				9.97×10^{-1}	2.0157×10^{-1}
_A2#1		6.99×10^{-1}		3.90×10^{1}				9.98×10^{-1}	
1300K	1.00×10^{5}	1.00	2×10^{-3}	5.58×10^{1}	-6×10^{4}		3.851×10^{4}	9.97×10^{-1}	2.19×10^{-3}
						7.33×10^{6}		9.98×10^{-1}	2.00×10^{-3}
								2.57×10^{-3}	2.05×10^{-6}
								-6.44×10^{4}	-1.41×10^{5}
FCC_A1#1		1.00		5.58×10^{1}				9.98×10^{-1}	2.00×10^{-3}
	1.00×10^{5}		2×10^{-3}	5.58×10^{1}	-7×10^{4}	7.39×10^{6}	4.205×10^{4}	9.97×10^{-1}	
1400K		1.00						9.98×10^{-1}	9.97×10^{-1}
								1.97×10^{-3}	9.98×10^{-1}
		1.00						-7.24×10^{4}	1.97×10^{-3}
FCC_A1#				5.58×10^{1}				9.98×10^{-1}	-7.24×10^{4}
1					-8×10^{4}		4.567×10^{4}	9.97×10^{-1}	9.98×10^{-1}
	1.00×10^{5}	1.00		5.58×10^{1}		7.44×10^{6}		9.98×10^{-1}	
			2×10^{-3}	6.38×10^{1}				1.53×10^{-3}	2.19×10^{-3}
					-8×10^{4}		4.938×10^{4}	-8.08×10^{4}	2.00×10^{-3}
1500K	1.00×10^{5}	1.00		5.58×10^{1}		7.50×10^{6}		9.98×10^{-1}	1.52×10^{-6}
					-9×10^{4}		5.405×10^{4}		-1.67×10^{5}
FCC_A1#		1.00	2×10^{-3}	5.58×10^{1}		7.59×10^{6}		9.97×10^{-1}	2.00×10^{-3}
1	1.00×10^{5}							9.98×10^{-1}	
		1.00		5.58×10^{1}				1.21×10^{-3}	2.19×10^{-3}
1600K								-8.93×10^{4}	2.00×10^{-3}
			2×10^{-3}	5.58×10^{1}				9.98×10^{-1}	1.31×10^{-6}
FCC_A1#									-1.80×10^{5}
1								9.97×10^{-1}	2.00×10^{-3}
								9.98×10^{-1}	
1700K								9.63×10^{-4}	2.19×10^{-3}
								-9.81×10^{4}	2.00×10^{-3}
BCC_A2#								9.98×10^{-1}	9.21×10^{-7}
1									-1.96×10^{-5}
									2.00×10^{-3}

Table: 1 shows thermodynamic parameters variation verses temperature ranges for the binary eutectoid system. The system is showing thoroughly fluctuation and result are significant for linear ideal behavior at some extent. At 1100K the thermodynamic parameters starts precipitation behavior decreases and integral Gibbs energy achieves -4.94134×10^{4} of range, enthalpy achieves at

2.98347×10^{4} of range both at the cost of pressure 1.000000×10^{5} and volume of the sample alloying extend up to 7.32753×10^{-6} at that level of temperature the mass fluctuation of the system expends up to 5.58362×10^{1},the sample of alloying elements Fe and V shows following molar activity behaviors during growth of alloying at 1100k temperature range as 9.9781×10^{-1},9.9800×10^{-1},4.5845×10^{-3},-4.9252×10^{4} for Fe participants and 2.1922×10^{-3},2.0000×10^{-3},1.4415×10^{-6},-1.2301×10^{5} for V participants during alloying. The result of alloying at 1100K shows that the precipitation and alloying behavior of Fe is more impressive than V participants. The dominant phase here at 1100K of alloying arises BCC_A2 which is ferrite nature phase. The temperature range 1200K at same pressure 1.000×10^{5} with varying nature of moles of the sample from 3.0026×10^{-1} to 6.9974×10^{-1}, the Gibbs energy achieves the value of -5.68124×10^{4} with enthalpy 3.47850×10^{4} at extended volume varies 7.31021×10^{-6} the mass of the alloying constituents varies as 1.6764×10^{1},3.9072×10^{1}which results the molar activity fluctuation as 9.9781×10^{-1},9.8900×10^{-1},3.4212×10^{-3},-5.6649×10^{4} for Fe participants and 2.1922×10^{-3},2.0000×10^{-3},1.9757×10^{-6},-1.3105×10^{5} for V constituents of the said alloying system. The result at 1200K shows that the activity of Fe participants is still dominant in precipitation basis and shows good alloying base for the system. The two types of phases seen at 1200K as BCC_A2 and FCC_A1, which indicate ferrite and austenite coordination behaviors, The FCC_A1 here as austenite is dominant as the activity of alloying in sample is maximum for Fe alloying participants. At 1300K the pressure maintained at 1.000000×10^{5}, the mass extend is up to 5.58362×10^{1}, the Gibbs energy seen at that level is -6.46080×10^{4}, where enthalpy is 3.85168×10^{4}, of value with extend volume of the alloying sample as 7.33938×10^{-6}. The molar activity of the alloying element is seen following fluctuation at 1300K as 9.9781×10^{-1},9.9800×10^{-1},2.5756×10^{-3},6.4439×10^{4} for Fe participants and 2.1922×10^{-3},2.0000×10^{-3},2.0546×10^{-6}, -1.4155×10^{5} for V participants, the result of alloying at 1300K shows that the dominant participants is Fe, and the precipitation as a base is more of Fe constituents in alloying. The FCC_A1 phase is seen only at 1300K, while the other phases disappear because of less stability. At 1400K the activated pressure is maintained same as 1.000000×10^{5} with extended volume 7.39322×10^{-6}, at mass extend 5.58362×10^{1}, shows Gibbs energy variation here -7.26727×10^{4}J/mol, with enthalpy 7.39322×10^{-6}J/K, of significant value, the activity behavior of participants is seen here as 9.9781×10^{-1},9.9800×10^{-1},1.9738×10^{-3},-7.2494×10^{4} for Fe participants and 2.1922×10^{-3},2.0000×10^{-3},1.7711×10^{-6},-1.5416×10^{5} for V constituents of the said alloying

System. Here the activity of Fe system is still dominant for 1400K and here the FCC_A1 phase is still dominant as an austenite contribution to the alloying system. At 1500K the sample of alloying is again simulated for Fe-V binary system. The pressure is constant as 1.000000×10^{5}, the mass of sample here extended as 5.58362×10^{1}, while volume expansion as 7.44747×10^{-6}, so as the resultant Gibbs energy is -8.09933×10^{4} with enthalpy 4.56760×10^{4}J/K, the activity behavior of participants is seen here as 9.9781×10^{-1},9.9800×10^{-1} 1.5354×10^{-3},-8.0804×10^{4} for Fe participants and 2.1922×10^{-3},2.0000×10^{-3},1.5274×10^{-6},-1.6702×10^{5} for V participants, the phase here seen is FCC_A1 as austenite coordination, shows dominancy and good precipitation behavior of Fe in the prescribed sample of Fe-V binary alloying system. At temperature range 1600K at same pressure 1.000×10^{5} with varying nature of moles 1.00000,the Gibbs energy achieves the value of -8.95585×10^{4} , with enthalpy 4.93854×10^{4} at extended volume varies 7.50210×10^{-6} the mass of the alloying constituents varies as 5.58362×10^{1}which results the molar activity fluctuation as 9.9781×10^{-1},$9.9800\times10^{-1,}$$1.2100\times10^{-3}$,$-8.9360\times10^{4}$ for Fe participants and 2.1922×10^{-3},2.0000×10^{-3},1.3186×10^{-6},-1.8011×10^{5} for V participants, the growth is showing best for Fe constituents as a good precipitation element in Fe-V system and FCC_A1 is still dominant as austenite coordination phase here. At 1700K the Gibbs energy is seen as -9.83815×10^{4}, with showing good stability of the alloy at a more heat content and alloys value of 5.40565×10^{4}, the molar activity for Fe is 9.98000×10^{-1}while $2.00000\times10^{-3}$for V system shows still good dominancy of Fe constituents in Fe-V alloying system. The BCC_A2 phase is found here most stable phase at 1700k and it shows ferrite coordination and FCC_A1 phase with austenite coordination vanishes here because of less stability at peak 1700K.

6. Conclusions

All the modeled figures and calculations are carried out by thermodynamic based parameters. The behavior of Gibbs free energy is monitored well. The Gibbs free energy curve is approaching toward more stability at 1575K with molar concentration of (0.44-0.61) as concern with stability here the sigma phase is the peak stable at that curie temperature and show greatest negative deviation and most attractive force among the alloying elements at that described concentration. Correspondence of the activity is showing negative deviation from ideality at 1475K the two phase activity is dominant at the molar concentration of (0.1-0.6) with sigma/bcc phases. At 1675K the most active elemental phase is BCC_A2 with highest stable activity as ferrite nature phase .The peak activity of BCC_A2 range is at concentration (0.2-0.6).the value of activity is increasing with the increase of temperature range 1700K but the Related Gibbs energy is conversely behavior as after 1575K it goes further decreasing so shows

The binding nature of the alloying elements with good negative deviation from Roults law .The vegard, s law cannot be applied here as with less enthalpy and no positive deviation of the system. The enthalpy of the system show maximum peak value at 1700K with highest number of heat contents of the system at concentration range of (0.48-0.63). The alloy shows good magnetic and paramagnetic transformations regions in grains as calculated by many researchers. The magnetic property of the alloy is due to the ferrite phase and due to the equilibrium region of sigma/Bcc at some particular concentration shown above. The Gibbs free energy and the excess Gibbs free energy retain its negative value to employee good stability of the said alloy. The alloys are valid for best industrial and research interest for upcoming inventions and updates in material science, modeling and simulation technologies.

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