

## CHAPTER FIVE

### THERMODYNAMIC MODELLING

#### 5.1 INTRODUCTION

Modelling precipitation in a ferritic stainless steel AISI type 441, requires knowledge of both thermodynamic and kinetic parameters for a variety of possible phases. To obtain these parameters, experimental data are required. The prerequisite thermodynamic information for modelling consists of:

1. the stable phases corresponding to the annealing temperature;
2. the phase fractions corresponding to the annealing temperature;
3. the relative phase stabilities; and
4. the equilibrium chemical compositions of possible phases.

The use of the computer package such as Thermo-Calc® version Q (TCFE3 database [125]) thermodynamic software makes these thermodynamic calculations possible.

#### 5.2 DESCRIPTION OF THERMO-CALC® SOFTWARE

Thermo-Calc® software is a powerful and flexible software package that can perform various kinds of equilibrium thermodynamic and phase diagram calculations by minimising the total Gibbs energy of the system specified [126]. It can handle complex problems involving the interaction of many elements and phases. It is specially designed for the systems and phases that exhibit highly non-ideal behaviour [127,128].

Without an accurate and validated database, any thermodynamic software is useless and misleading. Therefore, a high quality thermodynamic database is essential for conducting reliable thermochemical calculations and simulations. The TCFE3 TCS Steels/Fe-alloys database which covers a complete and critical assessment of binary and some ternary systems as well as the iron rich corner of some higher order systems, was employed in these calculations. It was pointed out that with TCFE1 TCS Steels/Fe-alloys database (version 1.1), data for intermetallics such as  $\sigma$ ,  $\mu$  and Laves phases are less reliable and there is nothing more being said about improvements to the TCFE2

and TCFE3 databases for these phases [129]. This might be the reason why the calculations show the presence of the  $\sigma$ -phase in AISI type 441 stainless steel, whereas it is not expected to be formed in practice in this alloy. Also the recommended temperature range in using the database is from 700 to 2000 °C for the TCFE3. Calculations slightly outside these limits may give reasonable results but it requires experience and skill to correctly extrapolate data and interpret the calculational results. This is particularly so at temperatures of 500 °C and lower where thermodynamic equilibrium is highly unlikely in industrial processes due to slow diffusion. A lower limit of 600°C was, therefore, adopted in the thermodynamic modelling for this study. Note the use of the following phase names in the database; the number symbol # is used to denote different composition sets of the same phase, Table 5.1.

**Table 5.1. The phase names as used in the TCFE3 Steels/Fe-alloys database.**

Phase	database
Austenite	FCC_A1#1
Ferrite	BCC_A2
M(C,N)	FCC_A1#2

### 5.3 EXPERIMENTAL ALLOYS

The purpose of this research is to study the precipitation behaviour of the Laves phase in the ferritic stainless steel AISI type 441. The ternary and quaternary systems of the Fe-Nb-Ti and Fe-Nb-Ti-Mo were therefore, chosen, the latter being more of an experimental alloy. The experimental alloys' compositions were chosen within and outside the recommended Columbus Stainless composition specification for the ferritic stainless steel AISI type 441 (see Steel A & B<sup>†††</sup> in Table 4.1) in order to determine the effect of the Nb, Ti and Mo on the Laves phase formation and its embrittlement effect. Thermo-Calc® software was used in the design of these experimental alloys, with the main emphasis on determining the effect of composition change on the volume fraction and solvus temperature of the Laves phase. The following criteria were used in designing these alloys:

1. lowering the Nb content while keeping Ti content constant;
2. keeping both the Nb and Ti constant and adding 0.5% Mo; and
3. increasing the Nb content to 0.6 wt% and adding about 0.25%Mo.

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<sup>†††</sup> Note that, both steels were supplied by Columbus Stainless for a research purposes. Steel A is the rejected material because it was brittle for further processing, while Steel B was acceptable.

A summary of the Thermo–Calc® predictions is given in Table 5.3, in which the results were obtained in a similar manner as those that are shown in the following sections. Note that a Mo addition increases both the volume fraction and the solvus temperature of the Laves phase precipitates, whilst reducing the Nb content lowers both the volume fraction and the solvus temperature of the Laves phase in the alloy. From this prediction it was then decided to replace 0.6Nb – 0.15Ti – 0.25Mo with a ferritic stainless steel AISI type 444, and cast the other two experimental alloys using AISI type 441 as basis from scrap metal. The chemical composition of the experimental alloys that were physically tested in this study are shown in Table 4.1.

**Table 5.2. Chemical composition (in %wt) of the ferritic stainless steels studied.**

Elements	Supplied by Columbus		Hot rolled experimental alloys		
	Steel A 441 SS <sup>+++</sup>	Steel B 441 SS <sup>sss</sup>	Steel C Nb-Ti	Steel D Nb-Ti-Mo	Steel E 444 SS <sup>****</sup>
C	0.012	0.015	0.023	0.012	0.014
Mn	0.51	0.54	0.46	0.35	0.45
Co	0.03	0.02			0.02
Cr	17.89	17.9	17.9	17.6	18.3
B	0.0004	0.0006			0.0006
V	0.12	0.14			0.12
S	0.001	0.002	0.0073	0.0018	0.003
Si	0.5		0.33	0.31	0.47
Ti	0.153	0.149	0.171	0.171	0.106
Ni	0.19	0.19	0.13	0.12	0.15
N	0.0085	0.021	0.024	0.026	0.016
Al	0.009	0.009	0.011	0.013	0.01
P	0.025	0.023	0.024	0.032	0.024
Cu	0.08	0.09	0.07	0.06	0.12
Nb	0.444	0.445	0.36	0.39	0.251
O	0.0076				
Mo	~0	0.008	< 0.01	0.54	1.942

**Table 5.3. Laves phase’s compositions, volume fractions and solvus temperatures used in designing the optimum chemical composition.**

Alloy	composition	% mole fraction	Solvus temperature (°C)
0.35Nb – 0.15Ti	(FeCr) <sub>2</sub> (Nb,Ti)	0.62	780
0.444Nb – 0.15Ti – 0.5Mo	(FeCr) <sub>2</sub> (Nb,Ti,Mo)	2.40	950
0.6 Nb – 0.15Ti – 0.25Mo	(FeCr) <sub>2</sub> (Nb,Ti,Mo)	1.70	900

<sup>+++</sup> Columbus Stainless MPO Number 3533603- failed during production

<sup>sss</sup> Columbus Stainless MPO Number 3658671 – didn’t fail

<sup>\*\*\*\*</sup> Columbus Stainless MPO Number 3631171

#### 5.4 POSSIBLE STABLE PHASES AT EQUILIBRIUM

The steels in Table 4.1, apart from the primary Fe and Cr alloying elements, also contain carbon, nitrogen, titanium and niobium as common secondary alloying elements. Therefore, the precipitates of Nb(CN) and Ti(CN) and the Laves phase can, in principle, be formed.

Steels A, B and C contain mainly titanium and niobium as the secondary alloying elements; therefore, it is expected that the stable second phases will include the Laves phase  $Fe_2M$  (with M representing mainly Nb) and the carbonitrides Nb(CN)/Ti(CN). The  $M_6C$  carbide (in which, 'M' stands for metallic elements) is not expected to be formed or, alternatively, if present its quantity will be negligible. In steels C and E that contain titanium, niobium and molybdenum as the secondary alloying elements, therefore, it is expected that the stable second phases will be Laves phase, the Nb(CN)/Ti(CN) carbonitrides and possibly the  $M_6C$  carbide. The composition of the Laves phase will change from one alloy to another.

The phases allowed for in these calculations are listed in Table 5.4. The calculations were performed for the temperature range of 600 to 1500 °C. Also, the data for the intermetallic Laves phase are less reliable due to a scarcity of experimentally determined data. It is necessary to consider the existence of the sigma phase even though it is not expected to be formed in practice at the early stages of processing, that is, sigma phase if it happens to be formed in this alloy, is only expected to nucleate at higher service temperatures and after a long service period. The possibility of a miscibility gap for the Cr-rich phases ( $\alpha+\alpha'$ ) was also not introduced in the calculations.

**Table 5.4. Prospective phases for equilibrium calculations using Thermo-Calc® with a TCFE3 database for steels.**

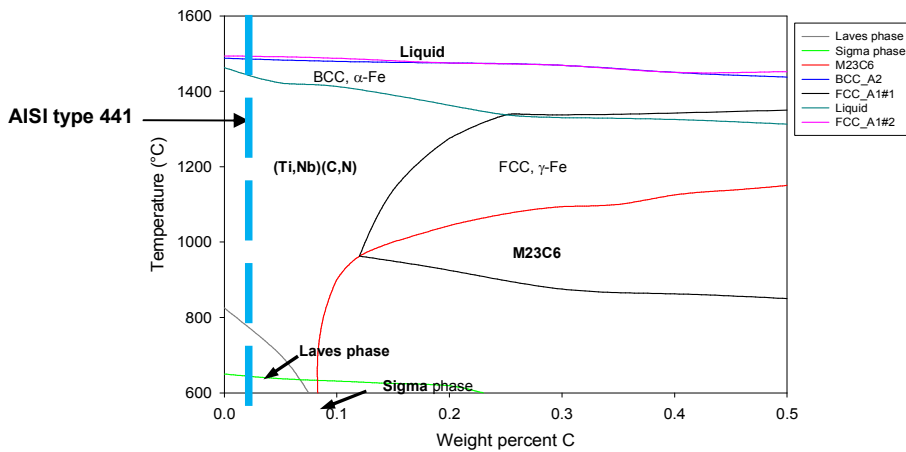
Steel	Alloy	Phases
A	Type 441	Liquid, ferrite, carbo-nitrides, sigma, Laves phase, $M_6C$
B	Type 441	Liquid, ferrite, carbo-nitrides, sigma, Laves phase, $M_6C$
C	Nb-Ti	Liquid, ferrite, carbo-nitrides, sigma, Laves phase, $M_6C$
D	Nb-Ti- Mo	Liquid, ferrite, carbo-nitrides, sigma, Laves phase, $M_6C$
E	Type 444	Liquid, ferrite, carbo-nitrides, sigma, Laves phase, $M_6C$



## 5.5 PHASE DIAGRAMS

The isopleth diagrams for the phases that were expected to be stable and at equilibrium over a wide range of carbon content in these types of materials, are shown in Figure 5.1. These calculations are based on the fixed chemical composition of the steels studied in this work. A line illustrates where a new phase appears or disappears, and a number representing a phase is located on the side of the line where the phase is expected to be unstable.

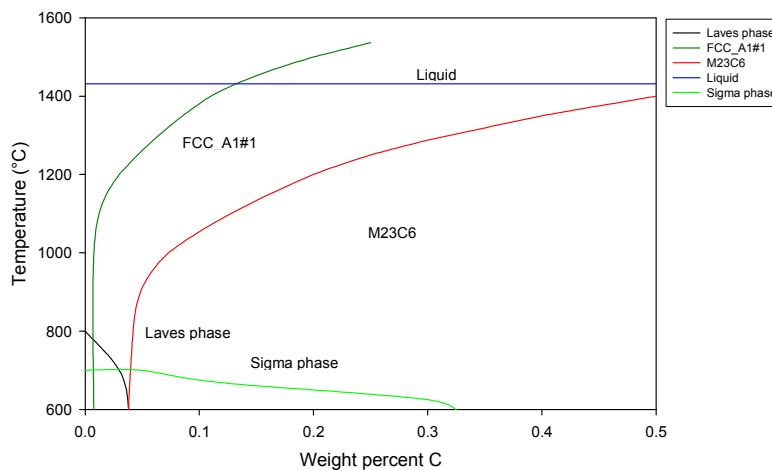
With type 441 stainless steel (marked with an arrow in Figure 5.1); the equilibrium phases that are formed over a wide range of temperatures are the Laves phase, titanium and niobium carbo-nitrides (FCC\_A1#2) and the sigma phase. The sigma phase should not be given much consideration in this particular work since it has often been reported that this phase only precipitates after a very long period at a high service temperature [25,26,27]. Note that the carbonitrides Ti(CN)/Nb(CN) are precipitated from the melt, that is their solvus temperatures are higher than the liquidus temperature in these alloys. This result predicts that the steel is fully ferritic (BCC\_A1#1) up to the liquidus temperature (line 6, Liquid). The austenitic phase will only be formed at carbon contents above 0.09 wt%C (FCC\_A1 #1). Both the solvus temperature and the volume fraction of each phase in these alloys are dependent on their respective chemical compositions. Thermo-Calc® calculations show that the formation of Laves phase is more favourable at a lower carbon content, that is below 0.1 wt.%; and that above this level of carbon and based on the fixed chemical composition of these alloys, the Laves phase will not be formed. Also, note that the  $M_{23}C_6$  carbide is not formed in the presence of the Laves phase, that is, in these alloys the precipitation of the  $M_{23}C_6$  carbide is only limited to an alloy with a high carbon content where the Laves phase does not exist.



**Figure 5.1. Thermo-Calc® calculation of the isopleth diagram for type 441 stainless steel with a constant amount of alloying elements and 0 to 0.5 wt.% of carbon. Below any line, these represents the stable region for the phase.**

The isopleth diagram for the stable phases at equilibrium in the high Mo-containing AISI type 444 ferritic stainless steel is shown in Figure 5.2. According to Fujita et al [5], they have observed that Mo additions to these alloys do slow down the diffusivity of Nb. Therefore, the precipitation kinetics of  $Fe_2Nb$  will be expected to be slower if molybdenum is present.

There are certain aspects from these calculations that do not make sense, that is, Thermo-Calc® calculations predict the presence of austenite phase even at room temperature, but using the Fe-Cr phase diagram, and this steel is fully ferritic up to the liquidus temperature. The more useful information about phases present in this alloy can be obtained from the Thermo-Calc® “property diagram”, see Section 5.6 below.

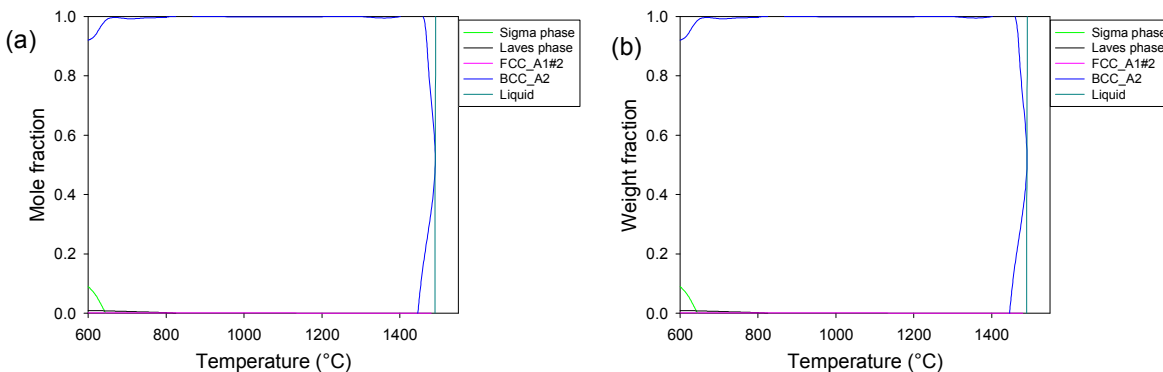


**Figure 5.2. Thermo-Calc® calculation of the isopleth diagram for the high Mo-containing type 444 ferritic stainless steel E with a constant amount of alloying elements and 0 to 0.5wt.% of carbon.**

## 5.6 PROPERTY DIAGRAMS

Some of the results obtained from these calculations are shown in Figure 5.3. in the form of a “property diagram”, which shows the dependence of the phase proportions on temperature. This diagram shows which phase has nucleated and grown at a specific temperature under equilibrium conditions. In multicomponent systems, property diagrams are often more useful than phase diagrams, as they give information within the phase region whereas phase diagrams give only the information of when the set of stable phases changes. One of the good examples of the problems of Thermo-Calc® at low temperature is that it predicts a weight fraction of 25% for sigma phase, which is just impossible.

These diagrams are similar for Steels A – E, the only difference is the phase proportion as a function of temperature in these different steels. From this diagram the composition of each phase over its respective existence temperature range can be calculated.



**Figure 5.3. The property diagram that shows the dependence of phase proportion on temperature; (a) mole fraction of stable phase and (b) weight fraction of stable phase.**

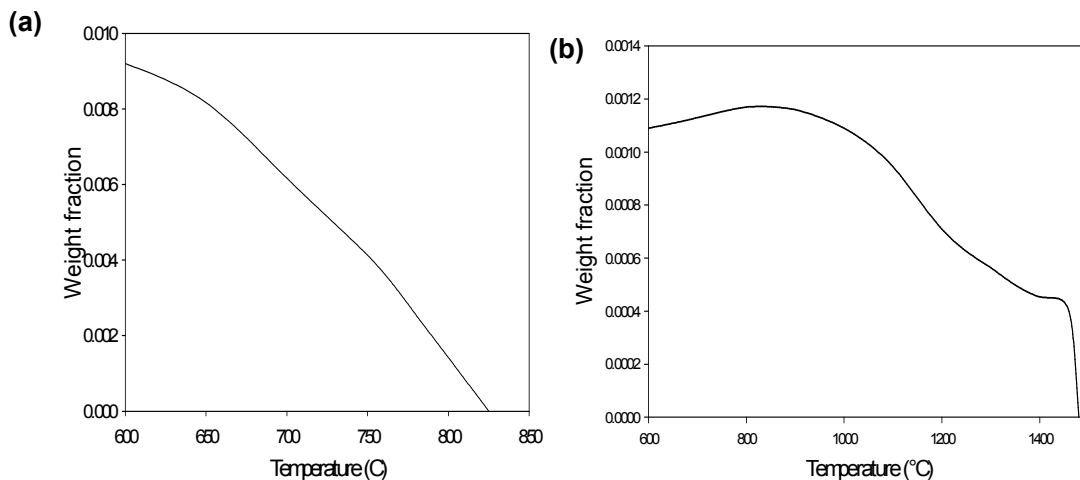
## 5.7 RELATIVE PHASE STABILITIES

The relative stability of a phase can be deduced by removing existing phases one by one in the equilibrium calculations. Thermo-Calc® predicts that the phase proportion of each existing secondary phase in type 441 stainless steel is independent from one to another, that is, removing one phase from the calculation won't affect the amount of the other phase. Therefore, the removal of the sigma phase from the calculations will not affect the proportion of the carbo-nitrides or Laves phases. The temperature range of

interest will be from 600 °C to 950 °C, whereby it was previously determined that this is the stable region for Laves phase precipitation in these steels.

### **AISI Type 441: Steel A**

Figure 5.4 shows the weight fraction of the equilibrium phases in steel A with composition 0.444Nb-0.153Ti. Figure 5.4 (a) shows the Laves phase weight fraction, which is estimated to be about 0.92 wt% at 600 °C and this fraction decreases with increasing temperature. The solvus temperature of Laves phase is estimated to be about 825 °C in this steel, and this is in broad agreement with results from the literature for this type of 441 stainless steel [3,9,99]. Figure 5.4 (b) is the weight fraction of the (Ti,Nb)(C,N), which is estimated to be less than 0.12 wt%. The solvus temperature of the (Ti,Nb)(NC) is predicted to be about 1480 °C. Note that the weight fraction of the (Ti,Nb)(NC) first increases with temperature up to about 825 °C before it decreases down to zero at 1480 °C. This increase below 825 °C is most likely due to the release of Nb from the dissolving Laves phase with the released Nb increasing the thermodynamic driving force for more (Ti,Nb)(C,N) to form. In this sense, there seems to be an indirect dependence between the two separate phases.



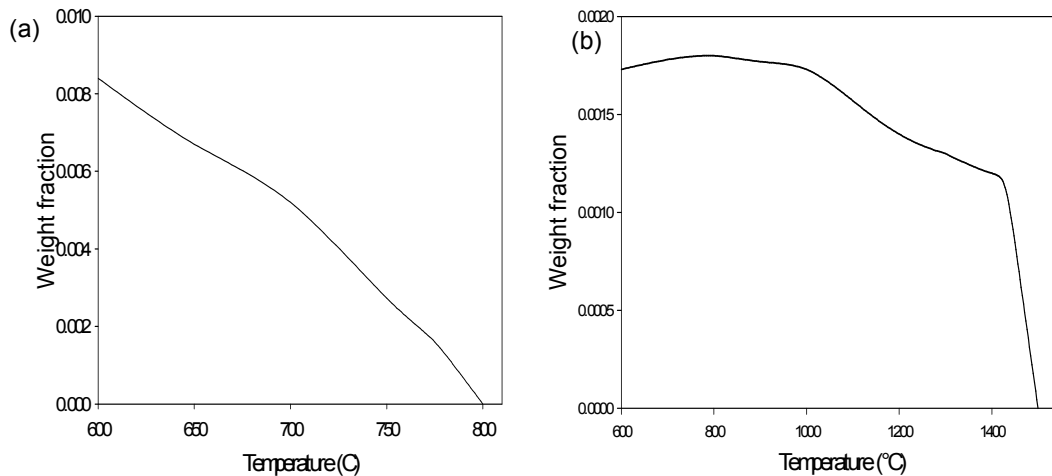
**Figure 5.4. Thermo-calc® plots of weight fraction of the stable phases as a function of the temperature in the Steel A with composition 0.444Nb-0.153Ti; (a) Laves phase and (b) (Ti,Nb)(CN).**

### **AISI type 441: Steel B**

Figure 5.5 shows the weight fraction of the equilibrium phases in Steel B with composition 0.445Nb-0.149Ti. This steel is very similar to Steel A except for more than



double nitrogen content, i.e. 0.021%N versus the lower 0.0085%N in Steel A. Figure 5.5 (a) shows the Laves phase's weight fraction, which is estimated to be about 0.84 wt% at lower temperatures and this decreases with increasing temperature. The solvus temperature of the Laves phase in this steel is about 800 °C, i.e. about 25°C lower than in Steel A. Figure 5.5 (b) shows the weight fraction of the (Ti,Nb)(C,N), and it is estimated to reach a maximum of 0.18 wt% at about 800 – 850 °C. This weight fraction is higher than the 0.12 wt% of steel A for this carbo-nitride, most likely due to the higher nitrogen content in steel B. The solvus temperature of the TiNb (NC) is about 1550 °C. According to Thermo-Calc®, there is not much difference in the Laves phase weight fractions between Steels A and B, but the major difference is in the weight fraction of (Ti,Nb)(C,N), which is dictated by the carbon and increased nitrogen content level.



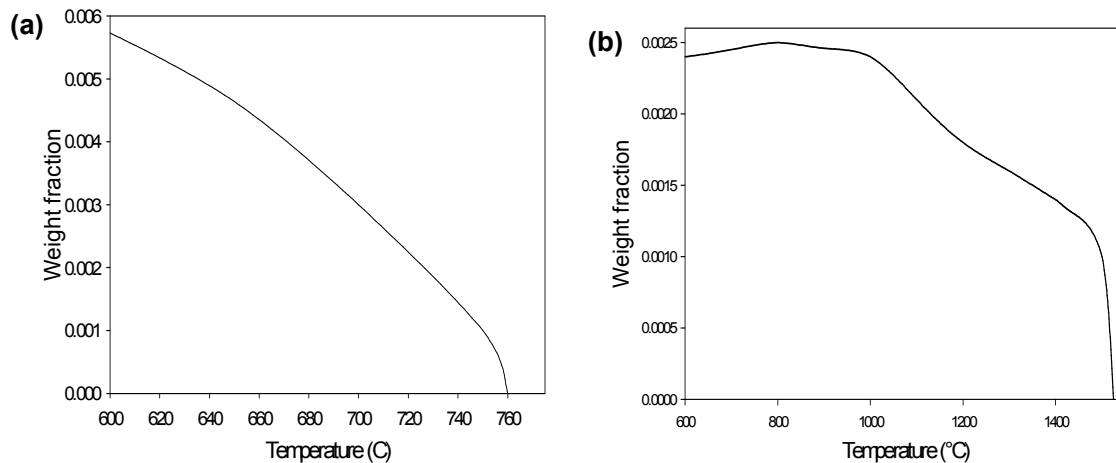
**Figure 5.5. Thermo-calc® plots of weight fraction of the stable phases as a function of the temperature in the Steel B with composition 0.445Nb-0.149Ti; (a) Laves phase and (b) (Ti,Nb)(CN)).**

### ***Nb-Ti Alloy: Steel C***

Figure 5.6 shows the weight fraction of the equilibrium phases in steel C with a composition of 0.36Nb-0.171Ti. Figure 5.6 (a) shows the Laves phase weight fraction, which is estimated to be about 0.57 wt% at 600 °C, and the weight proportion decreases with increasing temperature. The solvus temperature of the Laves phase is estimated to be about 760°C in this case. This predicts that the phase proportion and the solvus temperature of the Laves phase are dependent on the niobium content, that is, by lowering the niobium content to 0.36 %wt as compared to 0.444 %wtNb in Steel A, both

the solvus temperature and the weight fraction will decrease, with the Laves phase's solvus temperature now as low as about 760°C.

Figure 5.6 (b) shows the weight fraction of the (Ti,Nb)(C,N), which is estimated to be about 0.24 wt% maximum at the temperatures of about 800 – 850 °C and its solvus temperature is predicted to be about 1525°C. From Table 4.1, it can be seen that this steel has a higher carbon and nitrogen content of 0.023wt% and 0.024wt% respectively than for any of the other steels studied. This means that most of the carbon and nitrogen had precipitated out as carbo-nitrides, resulting in a high content of (Ti,Nb)(C,N). Both carbon and nitrogen have a significant impact on the fraction of (Ti,Nb)(C,N), and this reduces the amount of Nb available to have contributed to the solid solution strengthening of the steel at high temperatures and also the weight fraction of Laves phase at lower temperatures. Comparing Figure 5.4(a) and Figure 5.5(a), it can be seen that by lowering the Nb content from 0.444wt% as in Steel A to 0.36wt% as in Steel C, this also lowers both the Laves phase content and its solvus temperature. This shows that the Nb content in this steel plays a more significant role in the precipitation of Laves phase than the Ti does.



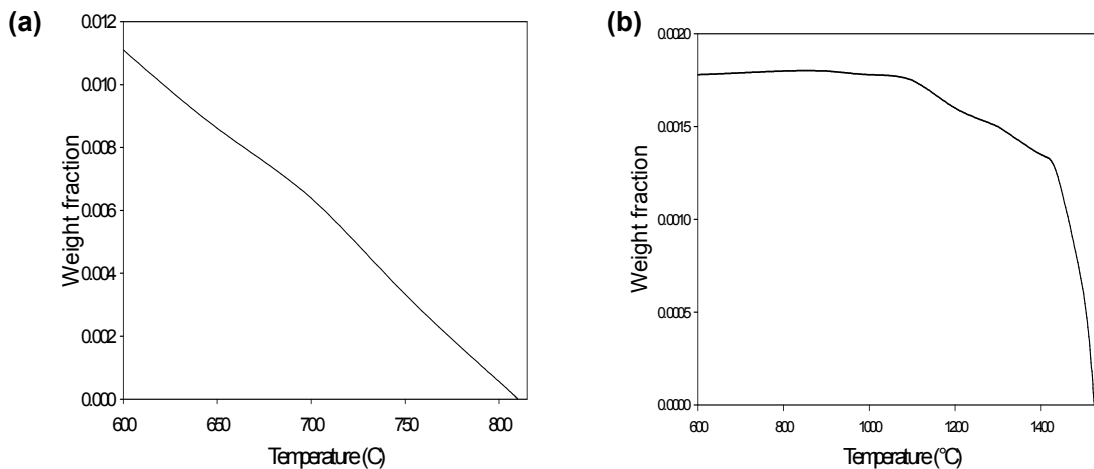
**Figure 5.6. Thermo-calc® plots of weight fraction of the stable phases as a function of the temperature in the Steel C with composition 0.36Nb-0.171Ti; (a) Laves phase and (b) (Ti,Nb)(C,N).**

### ***Nb-Ti-Mo Alloy: Steel D***

Figure 5.7 shows the weight fractions of the equilibrium phases in steel D with composition 0.39Nb-0.171Ti-0.54Mo. Figure 5.7 (a) shows the Laves phase weight fraction, which is estimated to be about 1.11 wt% at 600 °C, and this weight fraction

decreases with increasing temperature. The solvus temperature of the Laves phase in this steel is estimated to be about 810 °C. The addition of 0.54%wt molybdenum has a significant impact on the predicted weight fraction of the Laves phase, that is, Mo additions increase the weight fraction of the Laves phase, but do not have a significant impact on the solvus temperature of the Laves phase.

Figure 5.7 (b) shows the weight fraction of the (Ti,Nb)(C,N) phase, which is estimated to reach a maximum of 0.18 wt% at about 800 to 850 °C, and its solvus temperature is about 1520 °C. Also, the increase in both carbon and nitrogen levels has a significant impact on the (T,N)(CN) weight fraction whereas the level of titanium and niobium have no major impact on this value.



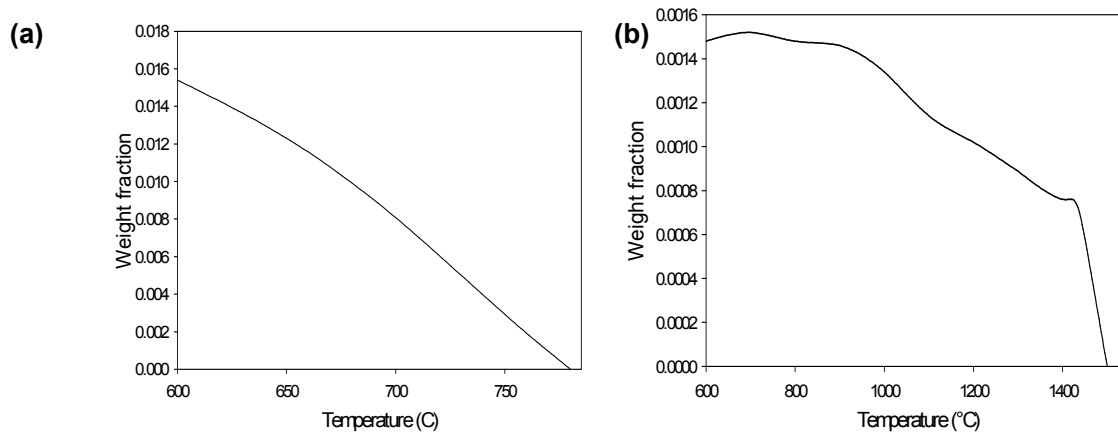
**Figure 5.7. Thermo-calc® plots of weight fraction of the stable phases as a function of the temperature in the Steel D with composition 0.36Nb-0.171Ti-0.54Mo; (a) Laves phase and (b) (Ti,Nb)(C,N).**

### ***AISI type 444: Steel E***

Figure 5.8 shows the weight fraction of the equilibrium phases in steel E with composition 0.251Nb-0.106Ti-1.942Mo and this steel falls under the category of a steel commonly referred to as a high molybdenum, high chromium steel; usually with a composition of 19Cr-2Mo. Figure 5.8 (a) shows the weight fraction of Laves phase expected to be about 1.54 wt% at 600 °C, and this also decreases with increasing temperature. The solvus temperature of the Laves phase in this steel is estimated to be about 780 °C. The addition of 1.942%wt molybdenum is predicted to have a significant impact on the weight fraction of the Laves phase, that is, Mo additions increase the weight fraction of the Laves phase, but at the same time they do not increase its solvus

temperature. This shows that only niobium additions have a significant impact on both the weight fraction and the solvus temperature of the Laves phase.

Figure 5.8 (b) shows the weight fraction of the (Ti,Nb)(C,N), which is estimated to be about 0.155 wt% maximum at about 800 °C. The solvus temperature of the TiNb (NC) is about 1500 °C.



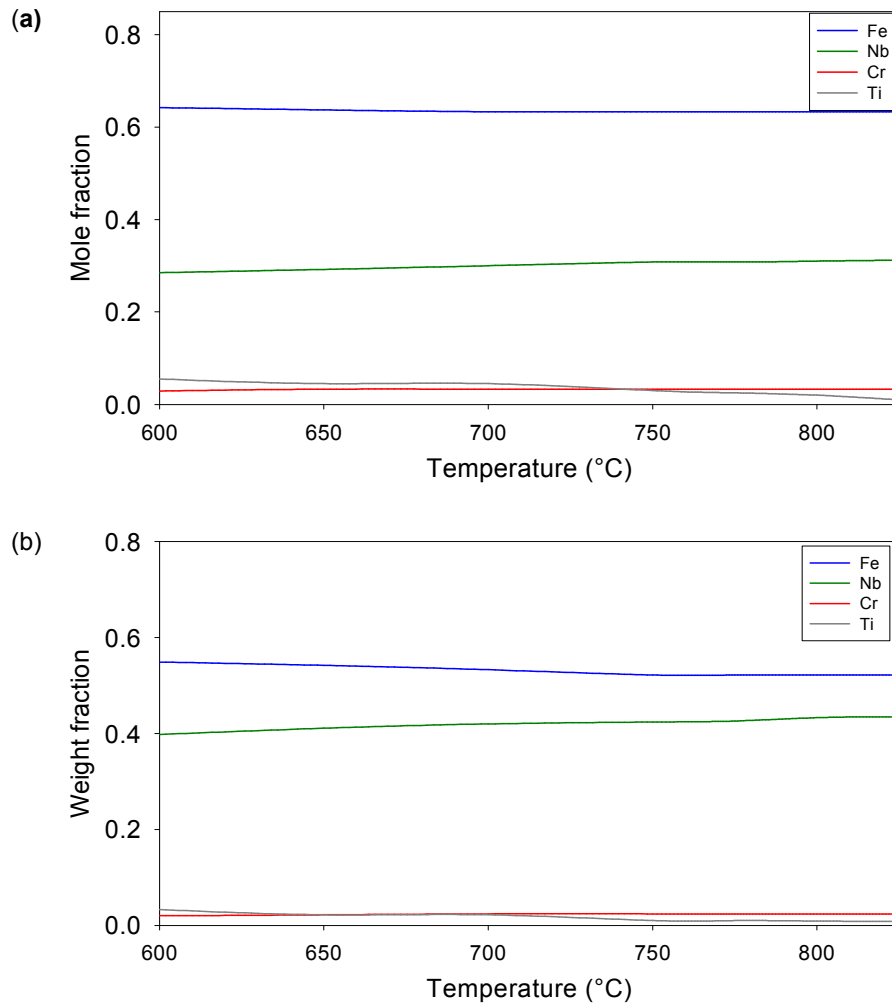
**Figure 5.8. Thermo-calc® plots of the weight fraction of the stable phases as a function of the temperature in the Steel E with composition 0.251Nb-0.106Ti-1.942Mo; (a) Laves phase and (b) (Ti,Nb)(C,N).**

## 5.8 EQUILIBRIUM CHEMICAL COMPOSITION OF THE LAVES PHASE

The chemical composition of a precipitate shifts towards the equilibrium composition during growth in which local equilibrium is maintained at the interface. Coarsening may then occur at a slower rate. The chemical compositions of the equilibrium Laves phase as a function of temperature are shown in Figure 5.9 – 5.13. The summary of the normalised weight fractions of the elements that form the Laves phase's composition at their respective temperatures, are shown in Table 5.6.

### ***AISI type 441: Steel A***

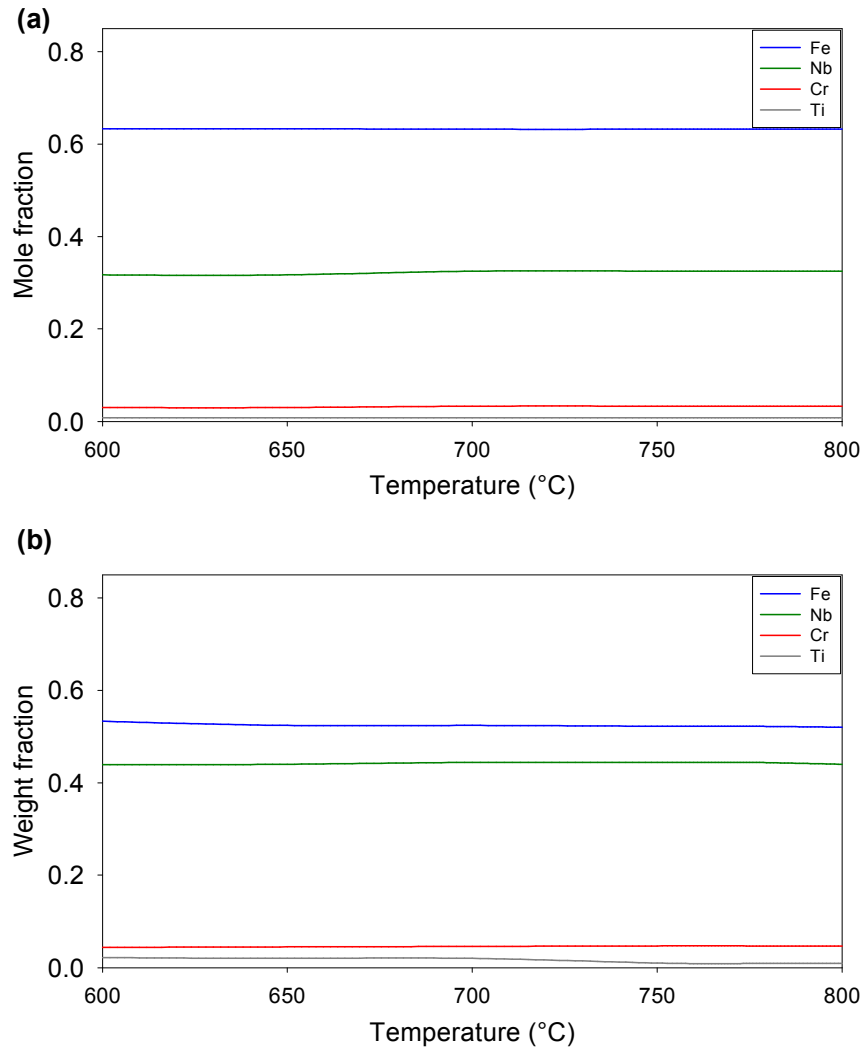
Figure 5.9 (a) shows the composition of the Laves phase (in mole fractions) which is mainly composed of Fe and Nb in the ratio of about 2:1, with less than 0.1% mole fraction of other alloying elements present within its composition, Ti being the major one at lower temperatures and Cr entering this phase at higher temperatures. Therefore, it can be concluded that the composition of the Laves phase is given by  $(\text{Fe,Cr})_2(\text{Nb,Ti})$ .



**Figure 5.9. The normalised chemical composition of the Laves phase in Steel A: (a) is the mole fraction and (b) is the weight fraction of a component in the phase.**

### ***AISI type 441: Steel B***

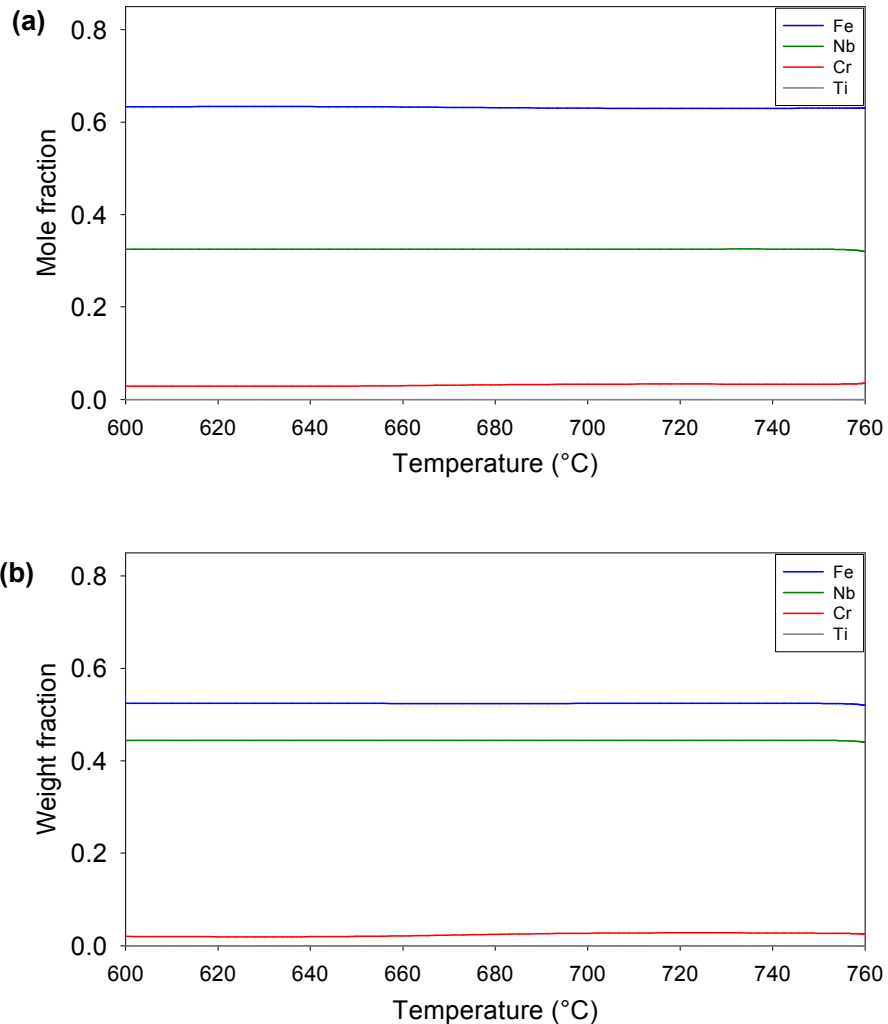
Figure 5.10 shows the composition of the Laves phase which consists mainly of Fe and Nb in the ratio of about 2:1, with less than 0.1% mole fraction of other alloying elements present within its composition, Cr being the major third element in this steel and with the Ti presence that is minimal in this steel as compared to Steel A. Therefore, it can be concluded that the composition of the Laves phase in this steel is also given by  $(\text{Fe,Cr})_2(\text{Nb,Ti})$ .



**Figure 5.10.** The normalised chemical composition of the Laves phase in Steel B: (a) is mole fraction and (b) is a weight fraction of a component in a phase.

### ***Nb – Ti alloy: Steel C***

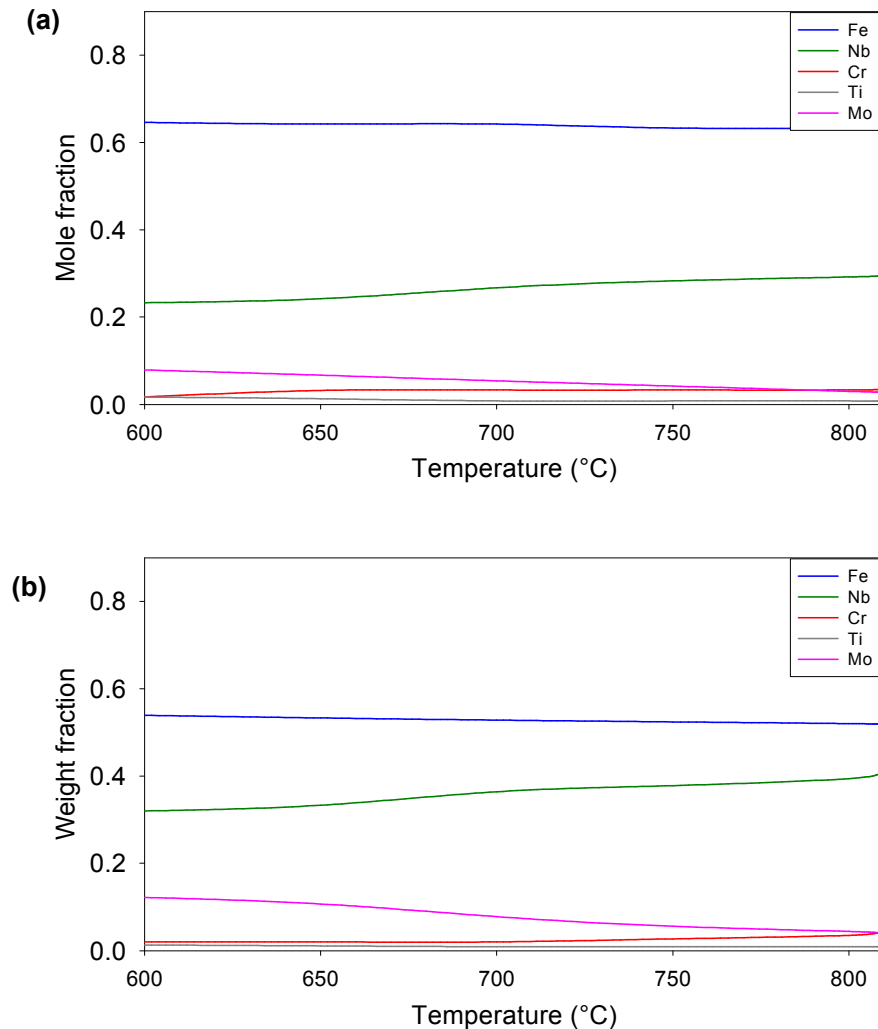
Figure 5.11 (a) shows the composition of the Laves phase in this steel, which mainly consists of Fe and Nb in the ratio of 2:1, with less than 0.05% mole fraction of other alloying elements present within its composition. Ti does not play a significant role in the composition of the Laves phase as was also the case in Steel A, but the Cr does play a significant role. Therefore, it can be concluded that the composition of the Laves phase is predicted to be  $(\text{Fe,Cr})_2\text{Nb}$  in this steel.



**Figure 5.11. The normalised chemical composition of the Laves phase in Steel C: (a) is the mole fraction and (b) is the weight fraction of a component in the phase.**

### ***Nb – Ti – Mo alloy: Steel D***

Figure 5.12 shows the composition of the Laves phase in steel D which consists mainly of Fe, Mo and Nb. Note that Mo enters the Laves phase composition at lower temperatures, and its content within the Laves phase decreases gradually with increasing temperature whilst the Nb content, on the other hand, increases. This indicates that an addition of about 0.5wt.% Mo to an AISI type 441 stainless steel has a significant impact on both the composition and the volume fraction of the Laves phase. The composition of Laves phase changes from about 600 °C and higher as the Nb starts to replace the Mo to some degree. Also, Cr enters this phase at higher temperatures, therefore, it can be concluded that the composition of the Laves phase is predicted to be  $(\text{Fe,Cr})_2(\text{Nb,Mo,Ti})$  in this steel.



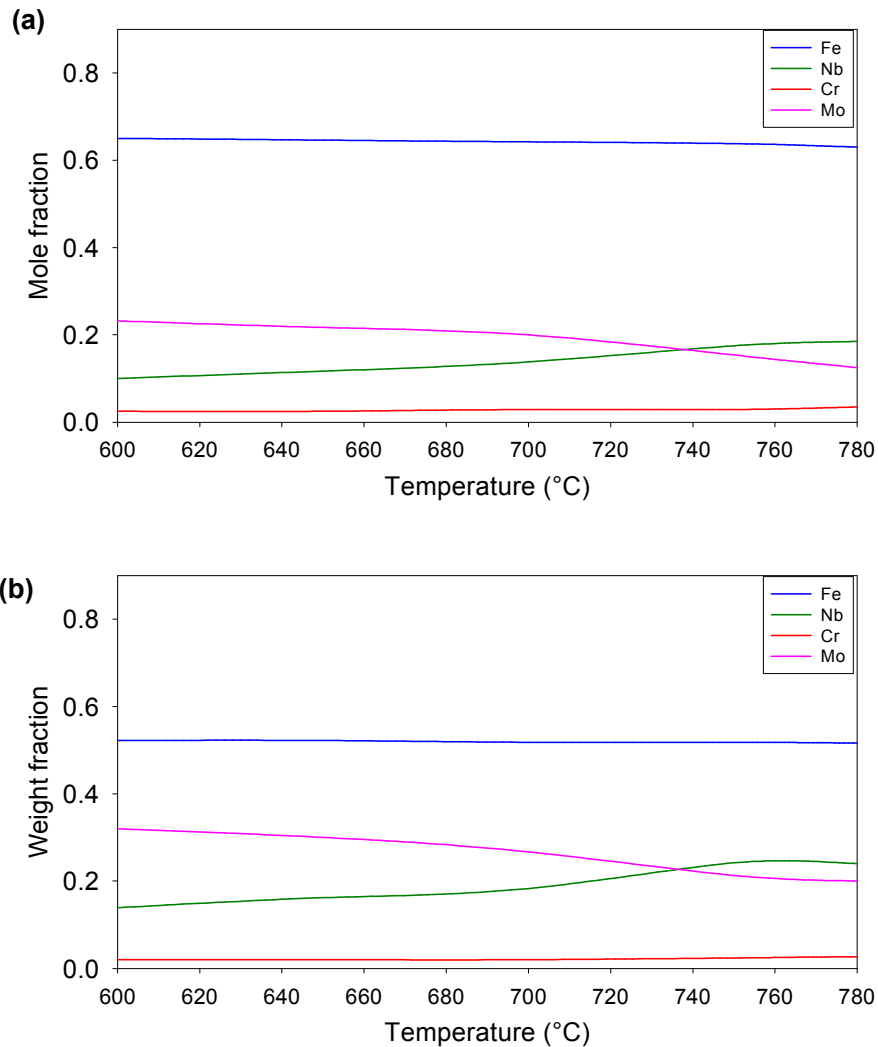
**Figure 5.12.** The normalised chemical composition of the Laves phase in Steel D: (a) is the mole fraction and (b) is the weight fraction of the component in the Laves phase.

### ***AISI type 444: Steel E***

Figure 5.13 shows that the composition of the Laves phase in Steel E consists mainly of Fe and Mo, with Nb entering this phase at higher temperatures. Cr forms a minor content of this phase. Therefore, it can be concluded that the composition of the Laves phase in this steel is predicted to be  $(\text{Fe,Cr})_2(\text{Nb,Mo})$  with Nb and Fe being the major elements up to about 700°C and Fe and Mo the major elements above that temperature. Also, from this steel it is observed that although a Mo addition increases the Laves phase's content it also lowers its solvus temperature. Fujita et al. [99] have observed this enhancement of the Laves phase precipitation by a Mo addition, and they have



suggested that a Mo addition can slow the precipitation rate of the Laves phase by lowering the diffusivity of Nb.



**Figure 5.13.** The normalised chemical composition of the Laves phase in Steel E: (a) is the mole fraction and (b) is the weight fraction of a component in the Laves phase.

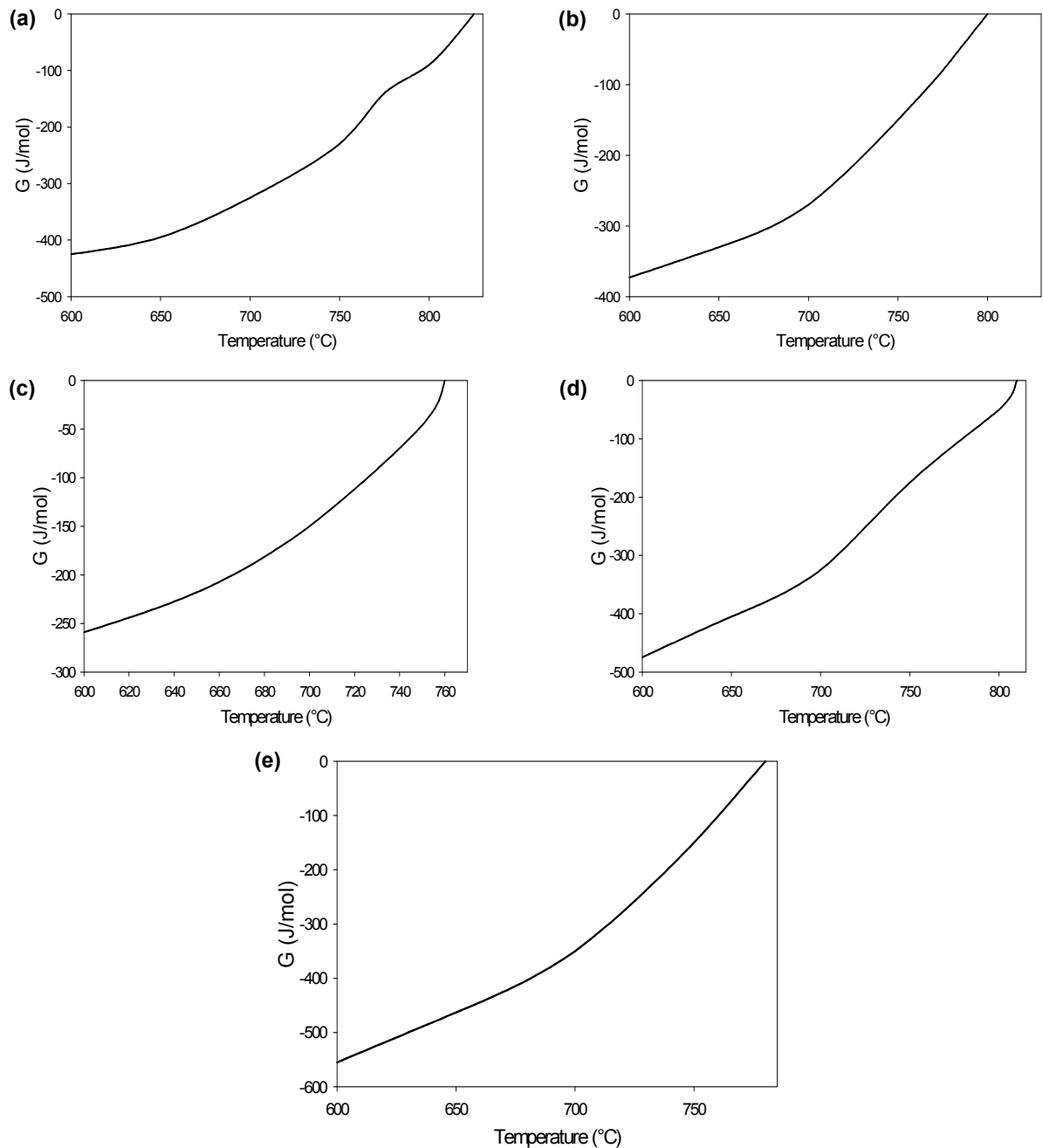
## 5.9 DRIVING FORCE FOR NUCLEATION

The Gibbs free energy changes for the Laves phase formation in the five steels were also calculated using Thermo-Calc®. Figure 5.14 shows the relationship of the free energy change for the Laves phase reaction in these steels as a function of temperature and for equilibrium states. The free energy change increases (becomes less negative) as the temperature increases from 600°C towards the solvus temperature, and its values are dependent on the composition of the specific alloys.

The calculated values are not the driving force for nucleation  $\Delta G_V$  but rather the overall Gibbs free energy change  $\Delta G$  for the reaction. With these results, the driving force for nucleation  $\Delta G_V$  can be obtained from:

$$\Delta G_V = \frac{\Delta G}{\nu V} \quad \text{Equation 5.1}$$

where  $V$  is the equilibrium volume fraction of the Laves phase and  $\nu$  is the molar volume of the Laves phase.



**Figure 5.14.** The free energy change  $\Delta G$  for the precipitation reaction of Laves phase in ferrite with temperature for : (a) Steel A; (b) Steel B; (c) Steel C; (d) Steel D and (e) Steel E, calculated using Thermo-Calc®, ( $G = \text{J/mol}$ ).

## 5.10 SUMMARY

The thermodynamic equilibrium data have been generated for AISI type 441 ferritic stainless through Thermo – Calc® software, see Table 5.5 for a summary table and Table 5.6 for a detailed comparison. These data will be used to determine the



nucleation kinetics in the alloys. The results obtained from this model will be compared directly to the experimental results. Hopefully, a better understanding of the Laves phase precipitation will be possible, and the effects of composition on its kinetics will be predicted.



**Table 5.5. A summarised results from the Thermo-Calc® predictions.**

Steel	Main secondary alloying elements	Composition differences with reference to steel A	Laves phase			(Ti,Nb)(C,N)		Conclusions
			%Wt frac. at 600 °C	Solvus temp °C	Molar composition	%Wt frac at 600 °C	Solvus temp °C	
A	0.012C-0.0085N-0.444Nb-0.153Ti-~0 Mo	Main reference steel	0.920	825	(Fe,Cr) <sub>2</sub> (Nb,Ti)	0.108	1480	
B	0.015C-0.021N-0.445Nb-0.149Ti-0.008Mo	Increased N content but C, Nb and Ti relatively unchanged	0.840	800	(Fe,Cr) <sub>2</sub> (Nb,Ti)	0.173	1550	Increased weight fraction of (Ti,Nb)(C,N) from increased N content
C	0.023C-0.024N-0.36Nb-0.171Ti-<0.01Mo	Increased (C+N), lower Nb and higher Ti content	0.573	764	(Fe,Cr) <sub>2</sub> (Nb)	0.225	1525	Laves phase solvus decreases with lower Nb content
D	0.012C-0.026N-0.39Nb-0.171Ti-0.54Mo	Lower C and Nb content, N and Ti relatively unchanged, and Mo addition	1.111	815	(Fe,Cr) <sub>2</sub> (Nb,Mo,Ti)	0.176	1520	Laves phase content increased with the addition of Mo. (Ti,Nb)(C,N) content and solvus temp increased from increased N content
E	0.014C-0.016N-0.251Nb-0.106Ti-1.942Mo	C relatively unchanged, N increased, lower Nb + Ti contents, high Mo content addition	1.542	780	(Fe,Cr) <sub>2</sub> (Nb,Mo)	0.150	1500	Laves phase content increases with the Mo addition. Its solvus temp decreased with lower Nb content



**Table 5.6. Detailed results of thermodynamic calculations (Thermo-Calc®). The normalised weight and mole fractions of the Laves phase composition components are shown.**

Steel	Solvus temp (°C)	Temp (°C)	$\Delta G$ J/mol	Wt frac. (%)	Concentration in Laves phase ppt (wt)					Concentration in Laves phase ppt (mole)				
					Fe	Nb	Cr	Ti	Mo	Fe	Nb	Cr	Ti	Mo
A	825	600	-425	0.920	0.549	0.398	0.020	0.033		0.642	0.285	0.029	0.050	
		650	-395	0.817	0.542	0.411	0.022	0.022		0.637	0.292	0.033	0.055	
		700	-325	0.617	0.533	0.420	0.024	0.022		0.633	0.300	0.033	0.055	
		750	-230	0.413	0.522	0.424	0.024	0.010		0.633	0.308	0.033	0.055	
		775	-125	0.283	0.522	0.426	0.024	0.010		0.633	0.308	0.033	0.055	
		800	-90	0.142	0.522	0.433	0.024	0.009		0.633	0.310	0.033	0.055	
B	800	600	-373	0.840	0.533	0.439	0.044	0.022		0.633	0.317	0.030	0.008	
		650	-330	0.607	0.524	0.440	0.044	0.044		0.633	0.317	0.030	0.008	
		700	-270	0.520	0.524	0.444	0.044	0.044		0.632	0.325	0.033	0.008	
		750	-150	0.273	0.522	0.444	0.044	0.044		0.632	0.325	0.033	0.008	
		775	-80	0.160	0.522	0.444	0.044	0.044		0.632	0.325	0.033	0.008	
C	760	600	-259	0.573	0.524	0.444	0.020			0.633	0.325	0.029		
		650	-218	0.464	0.524	0.444	0.020			0.633	0.325	0.029		
		700	-150	0.300	0.524	0.444	0.027			0.630	0.325	0.033		
		750	-46	0.100	0.524	0.444	0.027			0.630	0.325	0.033		
D	810	600	-475	1.111	0.539	0.320	0.020	0.013	0.122	0.646	0.233	0.017	0.017	0.079
		650	-405	0.861	0.533	0.333	0.020	0.011	0.107	0.642	0.242	0.032	0.013	0.067
		700	-325	0.639	0.528	0.364	0.020	0.009	0.078	0.642	0.267	0.033	0.008	0.054
		750	-175	0.333	0.524	0.378	0.020	0.009	0.056	0.633	0.283	0.033	0.008	0.042
		800	-50	0.056	0.520	0.394	0.020	0.009	0.044	0.633	0.292	0.033	0.008	0.030
D	780	600	-555	1.542	0.522	0.139			0.320	0.650	0.100	0.025		0.232
		650	-463	1.231	0.522	0.162			0.300	0.646	0.117	0.025		0.217
		700	-350	0.807	0.518	0.183			0.267	0.642	0.138	0.029		0.200
		750	-150	0.292	0.518	0.242			0.213	0.638	0.175	0.029		0.154