Estimation of Liquidus Temperature of Duplex and Austenitic Stainless Steel

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ABSTRACT

Differential Thermal Analysis (DTA) and high frequency (HF) coil measurement were carried out in present work in order to measure the liquidus temperature of some austenitic and duplex stainless steel samples made by different steel companies in Sweden. A good agreement between the measured and thermal calculated values using Thermo-Calc software (Appendix 1) was found. The liquidus model used 1986 shows a lower value for most of these alloys. When the nitrogen gas used as an inert gas, the nitrogen content increased in the alloys because of the increasing of nitrogen solubility at high temperature. On the other hand, the nitrogen content decreased in the alloys when the argon used as an inert atmosphere because of the different partial pressure of nitrogen between the liquid alloy and the atmosphere. This changing has an effect on the microstructure and liquidus values especially in high nitrogen content alloys.

Keywords: Austenitic Stainless Steel, Duplex Stainless Steel, Differential Thermal Analysis and High Frequency Coil.

حساب درجة حرارة السيولة للفولاذ المزدوج والمقاوم للصدأ الاوستنايتي

الخلاصة

في هذا البحث تم استخدام التحليل التفاضلي الحراري **(DTA)** والفرن الحثي ذو التردد العالي **(HF)**لقياس درجة حرارة السيولة لبعض نماذج الفولاذ المقاوم للصـــدا الاوســـتنايتي والفـــولاذ المقاوم للصدا المزدوج **(duplex)** مصنعة من قبل شركات سويدية مختلفة مما لها تأثير مهم في عمليات تصنيع الفولاذ المقاوم للصدأ بطريقة السباكة المستمرة. حققت النتائج العملية توافقا جيـــدا مع القيم المحسوبة باستخدام برنامج الثرموكالك المبينة في الملحق (١). في حين اظهـــر موديـــل السيولة المستخدم عام ١٩٨٦قيم اقل لمعظم هذه السبائك.عند استخدام النتـــروجين كغـــاز خامـــل لحماية المنصهر من الاكسدة لوحظ ان نسبة النتروجين تزداد في السبيكة وذلك لزيـــادة ذوبانيـــة غاز النتروجين في الفولاذ عند ارتفاع درجات الحرارة. من ناحية اخرى لـــوحظ انخفـــاض فـــي نسبة النتروجين في السبائك الحاوية على نسبة عالية من النتروجين عند استخدام الاركون كغـــاز

خامل وذلك لاختلاف الضغط الجزيئي للنتروجين للسبيكة والمحيط.هذا التغييـــر اثـــر بصـــورة واضحة على التركيب المجهري وكذلك نتائج حساب درجة حرارة الانصـــهار للفـــولاذ المقـــاوم للصدا الحاوي على نسبة عالي نسبيا من النتروجين.

INTRODUCTION

Melting ranges are very important to the steelmakers as the success of the melting and casting operations depends on the correct selection of temperature. Once solidified and primary processed (rolling or forging) by the steelmaker, the melting temperature has little significance to designers, engineers and steel users. Although melting temperature does influence elevated temperature properties, such as creep strength, this is only of interest to researchers.[1]

An important task of the flow pattern is to deliver molten steel to the meniscus region that has enough superheat during the critical first stages of solidification. Superheat is the sensible eat contained in the liquid represented by the difference between the steel temperature entering the mold and the liquidus temperature.[2]

One of variables which affect the size of equiaxed and columnar zones during continuous casting of stainless steel is the casting temperature. An Increase of casting temperature produces an increase in columnar zone length, because at high casting temperature, crystals that form in the mould remelt. Few crystals then are available to form an equiaxed zone and the columnar dendrites can grow unimpeded to the strand centreline. The columnar zone length is important for two reasons:

- **It is more susceptible to cracking than the equiaxed zone, and**
- **A long columnar zone increases the severity of centreline segregation and porosity.**

Thus to minimize the columnar zone length, the casting temperature should be as low as possible. Too low a casting temperature, however, may result in nozzle freeze-off during long casts. Also low casting temperature do note promote the float-out of inclusions and may result in an increase in inclusion levels [3].

The aim of the present work is to estimate an accurate knowledge of liquidus temperature, which is necessary for the determination of process parameters such as casting temperature and casting speed relating to the given alloys.

MATERIALS

In the present work, fifteen austenite and duplex stainless steel samples were used to measure the liquidus temperature using DTA and HF coil techniques. Table 1 shows the chemical composition of the samples used in the present work.

Table (1). Chemical composition of materials.

Sample name	ASTM	Chemical composition wt%									
		C	N	Cr	Ni	Mo	Cu	Ti	Mn	Si	Co
Duplex 2101	S32101	0.023	0.225	21.36	1.56	0.29	0.31	-	4.91	0.66	0.029
Duplex 2304	S32304	0.02	0.115	23.3	4.8	0.45	0.3	-	-	-	-
Duplex 2205	S32205	0.02	0.17	22.41	5.68	3.15	0.156	0.004	1.5	0.4	-
Duplex 2404	S32404	0.025	0.245	23.98	3.65	1.63	0.36	-	2.96	0.28	-
Austenitic 304	304	0.021	0.065	18.2	8.10	-	-	-	1.7	0.35	-
Duplex 2507	S32750	0.02	0.27	25.07	6.91	3.82	0.22	-	0.83	0.23	-
Duplex 1601	S31601	0,044	0,198	16.20	1.46	0.07	2.85	-	6.47	0.71	-
Austenitic 6Mo	S31254	0.012	0.196	20.07	17.83	6.05	0.77	0.004	0.52	0.37	0.15
Austenitic 316	316	0.017	0.04	17.16	11.2	2.04	0.36	-	0.8	0.42	
Austenitic 2212	309S	0.056	0.081	22.1	12.19	0.32	0.33	-	1.38	0.40	0.15
Austenitic 2519	310S	0.048	0.034	25.35	19.19	0.17	0.1	-	0.68	0.62	0.052
Austenitic 1920	S33400	0.026	0.012	18.97	19.34	0.10	0.12	0.32	0.41	0.60	0.17
High-temp2417	S34565	0.023	0.48	24.5	17.7	4.5	-	-	5.6	0.25	-
High – temp 2111	S30815	0.084	0.171	20.78	11.01	0.16	0.16	0.003	0.59	1.62	0.07
Ferritic 1800	S43035	0.017	0.023	18.18	0.33	0.06	0.33	0.48	0.46	0.40	0.03

EXPERIMENTAL TECHNIQUES
DTA TECHNIQUE
BASIC PRINCIPLES OF (DTA)

Differential Thermal Analysis (DTA) is a thermal technique in which the temperature of a sample, compared with the temperature of a thermally inert material, is recorded as a function of time and temperature when the sample as well as the inert material are heated or cooled at a uniform rate. Temperature changes in the sample are due to endothermic or exothermic reactions during phase transition, fusion, crystalline structure inversion, boiling, sublimation and vaporization, dehydration reactions, dissociation or decomposition reaction, oxidation and reduction reaction, destruction of crystalline lattice structure, and other chemical reactions. Generally, fusion, phase transitions, dehydration and some decomposition reaction produce endothermic effects, whereas solidification, crystallization, oxidation and some decomposition reactions produce exothermic effects. The temperature ranges according during these chemical or physical changes are detected by a differential method as shown in Figure 1. If the sample and reference temperature are T_s and T_r, respectively, then the difference in temperature ($T_s - T_r$) as a function is recorded [4].

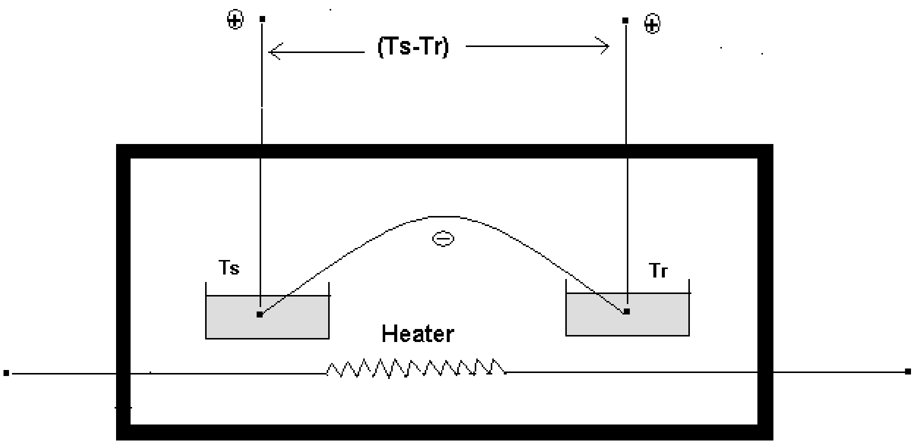
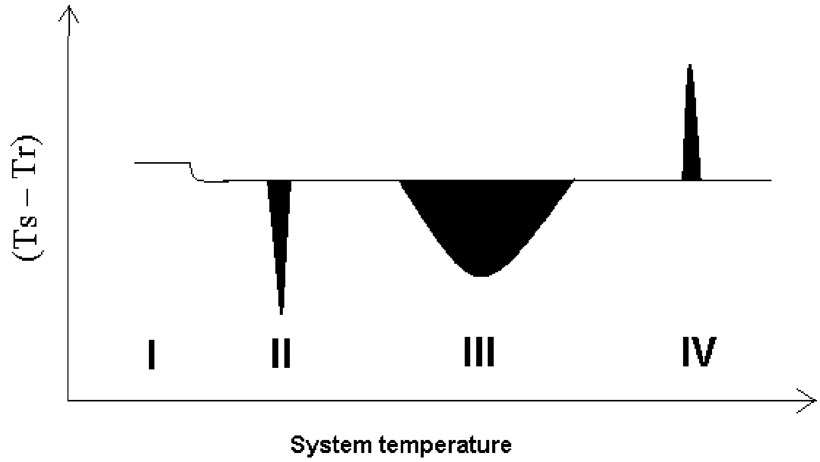


Figure (1). Basic DTA system.

A typical DTA curve is illustrated in Figure (2), where four types of transitions are illustrated:



Figure(2). Typical DTA curve.

I. **second order transition in which a change in the horizontal baseline is detected,**
II. **an endothermic peak caused by a fusion or melting transition,**
III. **endothermic peak due to decomposition or dissociation reaction, and**
IV. **an exothermic peak caused by a crystalline phase change.**

SETARAM TG 96 System shown in Figure 3 was used in present work which designed for high-temperature and thermogravimetric measurements, consist of:

- **A high temperature furnace house in a cabinet incorporating the electrical power supply as well as atmosphere control.**
- **A control assembly for the furnace and the acquisition of the experiment's parameters.**
- **A balance alone allows up to 100 g sample with suspension wires and crucible.**
- **The vacuum pump electrical supply is connected to one socket on the power module.**
- **Water connects to the cabinet base taking care to follow the inlet/outlet senses.**
- **Sweeping gas connect the bottle with a pressure relief valve, with a pressure of 3 bars, at the back of cabinet.**

- **Auxiliary gas.**

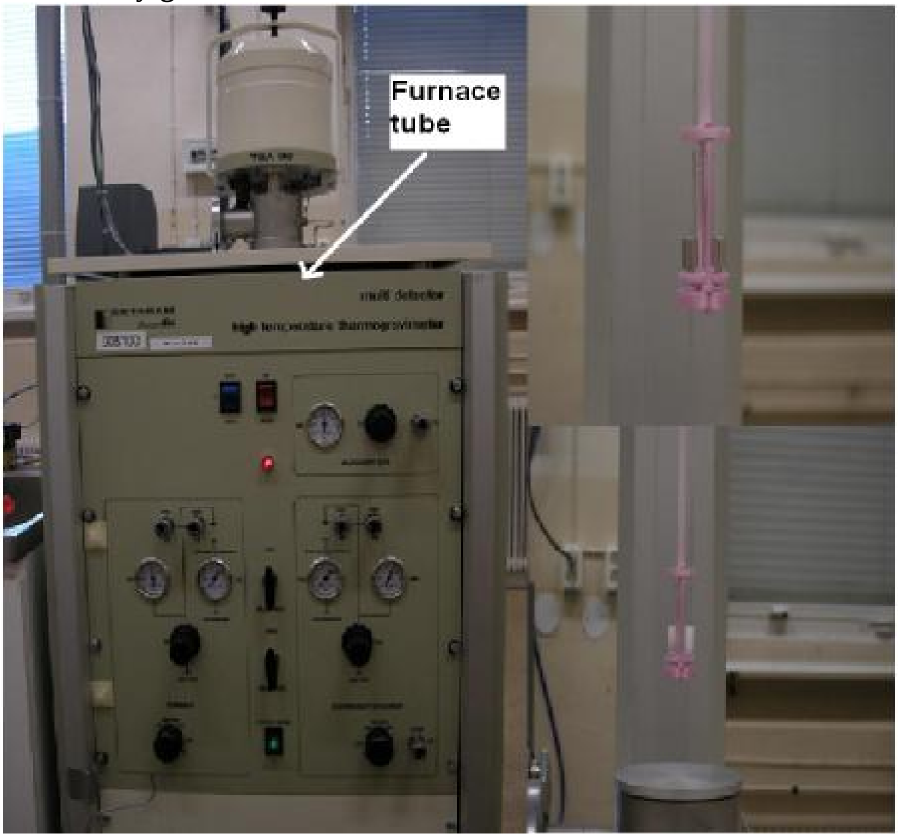


Figure (3): High temperature thermogravimeter.

Figure 3.1: shows the example of DTA results using setaram 96.

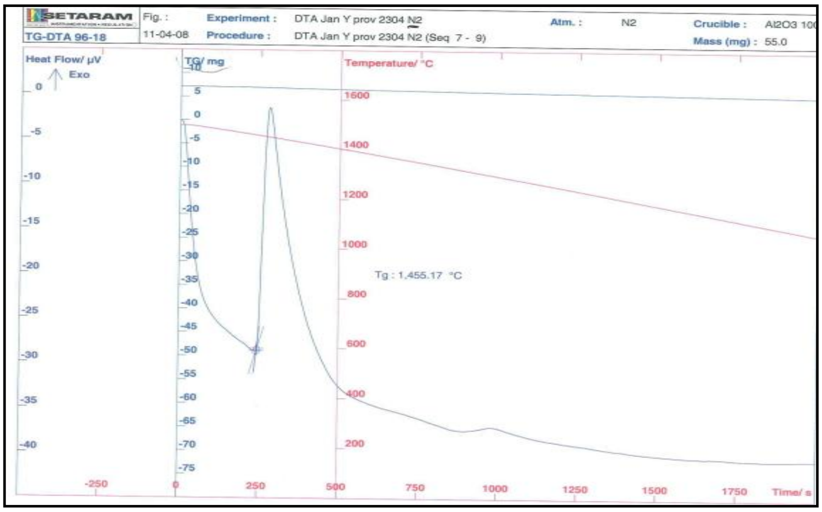


Figure 3.1:DAT curve of duplex 2404.

HF coil technique

In this technique, high frequency coil used to heat the sample to the liquid state and during the solidification, alumina protected thermocouple put in the liquid to measure time- temperature relation. At the liquidus temperature, no significant change of temperature with the time can be observed. It can be due to exothermic reactions, which supply some of heat to the surrounding.

Figure (4) shows the illustration of HF coil technique. The experiment was carried out under Argon gas atmosphere.

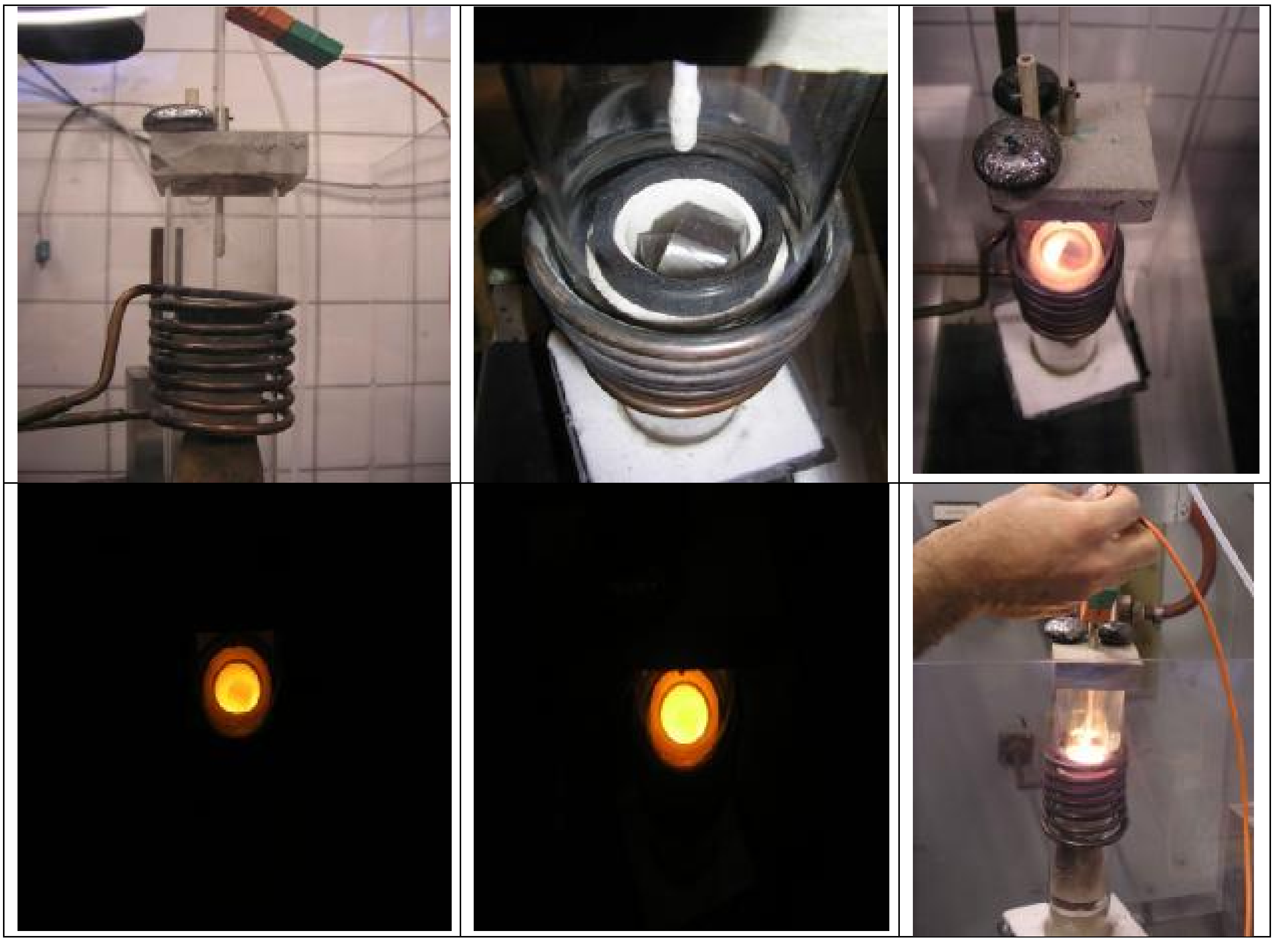


Figure (4): HF coil technique.

Figure (4.1) shows the example of the temperature- time curve of austenitic 2519 using HF coil technique.

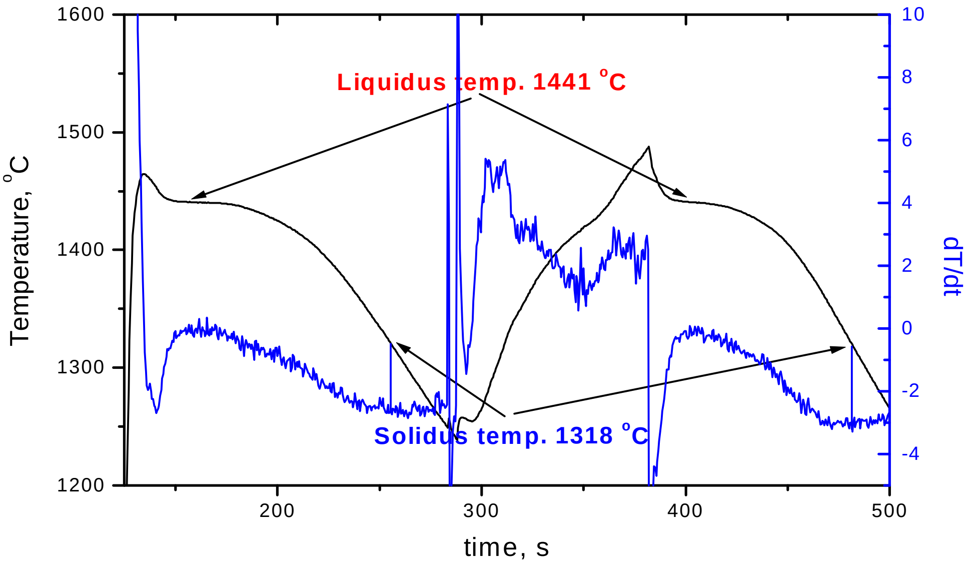


Figure (4.1): Temperature- time curve of austenitic 2519.

THERMO-CALC

Thermo-Calc is a software program for computational thermodynamics and has been used in this work to compare the calculated values with the measured values. Thermodynamic equilibrium has been considered during all calculations [5]. Figure (5) shows the thermo-calc curve of duplex 2507. Appendix 1 presents the Thermo-Calc results of the above mentioned alloys.

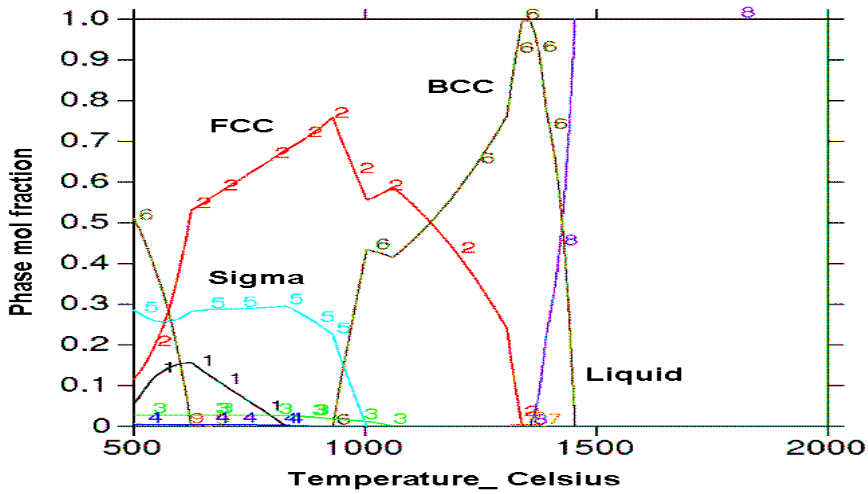


Figure (5): thermo-calc curve of duplex 2507.

RESULTS

Table (4) presented the DTA and HF coil techniques results in different atmosphere compared with the thermal calculated results using thermo-calc software.

The table also shows the calculated results using liqudus temperature model used of A. Löfgren 1986 [6].

$$T_{liqu} = 1532-148.42\ \%C - 3.68\ \%\ Si - 10.91\%Mn - 0.59\%Cr - 5.68\%Ni- 2.05\%Mo + 29.43\%Cu - 64.66\%N.$$

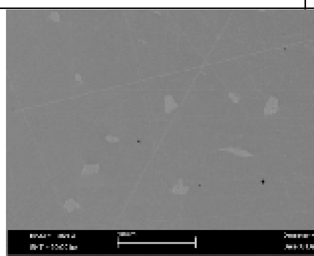
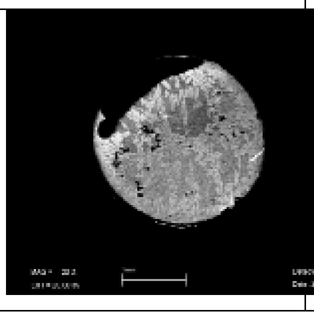
Table (2). DTA, HF coil and thermal calculated results.

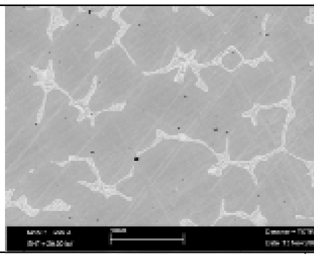
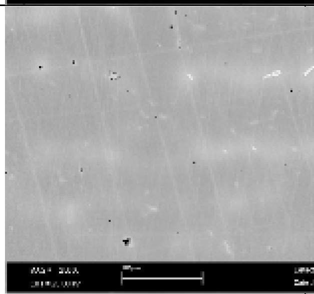
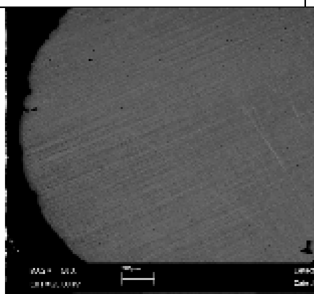
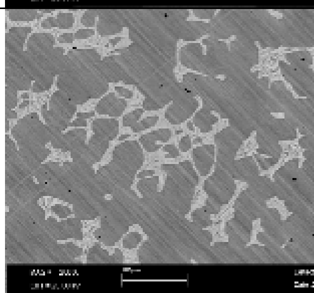
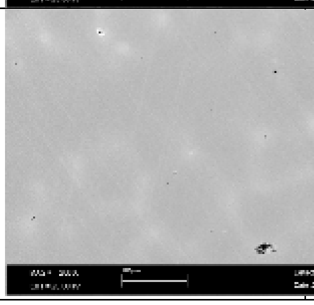
Steel grads	(DTA) T_{liqu},°C	(DTA) Atmosphere,	HF coil, Ar T_{liqu},°C	Thermo-calc °C	Liqudus temperature model °C
Duplex 2101	1461	N_2	1464	1473	1445
Duplex 2304	1483	Ar	1472	1473	1488
Duplex 2205	1463	Ar	1472	1469	1456
316	1449 1437	Ar N_2	1440	1460	1449
High-temp1705	1371 1382	Ar N_2	-	1360	1311
High –temp 2111	1416	Ar	-	1420	1426
Austinitic 6Mo	1403 1398	Ar N_2	-	1407	1407
Duplex 2404	1455	Ar	1462	1463	1452
304	-	Ar	1454	1459	1448
Duplex 2507	-	Ar	1446	1459	1447
Duplex 1601	1455	Ar	-	1463	1452
Ferritic 1800	-	Ar	1494	1426	-
Austenitic 2212	-	Ar	1435	1426	-
Austenitic 2519	-	Ar	1441	1431	-
Austenitic 2019	-	Ar	1419	1423	-

DISCUSSION

Table 2 shows that most of stainless steel samples used in present work have a good agreement with each other during DTA, HF coil measurements and thermal calculation except duplex 2304, which shows lower value in HF coil test. It can be concluded that the DTA and HF methods can be suitable methods to measure the liquidus temperature of alloys. Liquidus temperature model used 1986 shows a lower value of liquidus temperature of most of samples. Nitrogen analysed presented in Table 3 shows a higher content of nitrogen when nitrogen gas used as inert atmosphere due to increasing of nitrogen solubility at high temperature. On the other hand, the nitrogen content decreased in the alloys when the argon used as an inert atmosphere because of the difference in the partial pressure of nitrogen between the liquid alloy and the atmosphere. This changing has an effect on the microstructure since; the nitrogen is one of the austenite stabilizer elements and liquidus values especially in high nitrogen content alloys. It can be concluded that there is a reasonable agreement between the DTA and HF methods in most cases, and in most cases these values agree with the temperatures used for casting. The main problems associated with the two methods are nitrogen loss/gain and oxidation, respectively.

Table (3). SEM images and nitrogen analyses of duplex 2101, austenitic 6 Mo, high temp 2111 and duplex 2205 samples before and after DTA measurements.

Sample	Furnace atmosphere	SEM image after melting	N_2 % before melting	N_2 % after melting	Note
Duplex 2101	Argon		0.225	0.14	Not enough ferrite
Duplex 2101	Nitrogen		0.225	0.215	

austenitic 6 Mo	**Argon**		**0.196**	**0.14**	**Too much ferrite**
austenitic 6 Mo	**Nitrogen**		**0.196**	**0.36**	
Duplex 2205	**Argon**		**0.182**	**0.15**	**No austenite**
high temp 2111	**Argon**		**0.30**	**0.231**	
high temp 2111	**Nitrogen**		**0.30**	**0.468**	

Suggested further work

In future work the directional solidification of stainless steel will be studied using HF coil technique or vertical furnace if possible to study the solidification mode of the stainless steel presented above.

Also, the mixing of the inert gas in DTA measurements will be develop to keep the nitrogen content stable during melting process.

CONCLUSIONS

DTA and HF coil measurement was carried out in present work in order to measure the liquidus temperature of some austenitic and duplex stainless steel samples made by different stainless steel companies.

1. **A good agreement between the measured values and thermal calculated values was found.**
2. **The liquidus model used 1986 shows a lower value for most of these alloys.**
3. **The change of nitrogen content since argon or nitrogen gases used as an inert atmosphere has an effect on the microstructure and liquidus temperature only when the alloy has high nitrogen content.**

Figure (6) shows the summary of measured and calculated results.

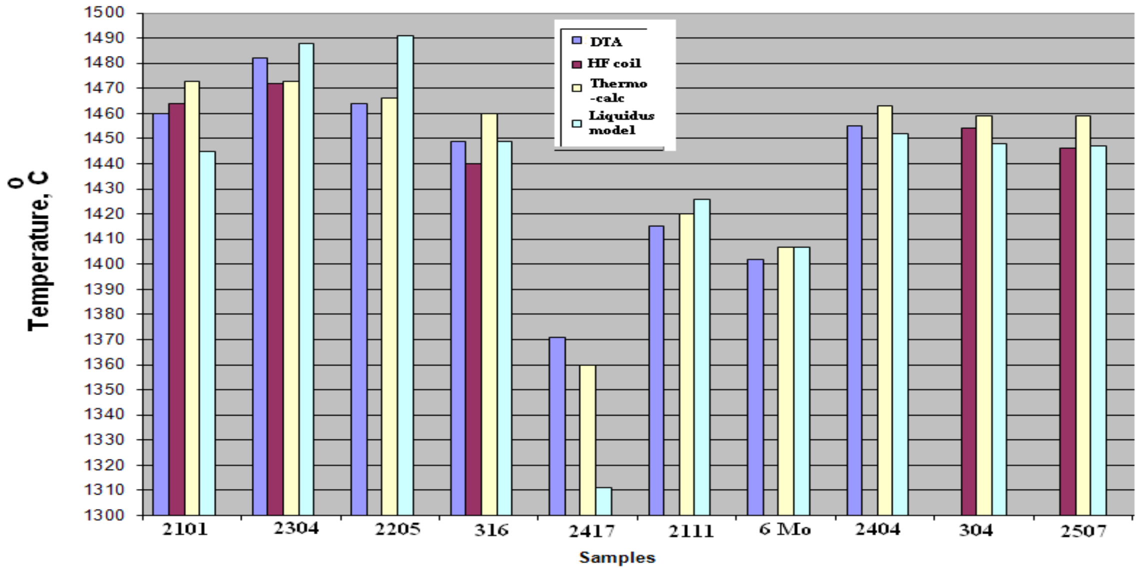


Figure (6). The entire results taken from DTA, HF, Thermo-calc and liquidus temp. model.

REFERENCES

[1].British Stainless Steel Association, (melting Temperature range of Stainless Steel). Copyright © 2007, Article 103.

[2].X. Huang, B.G. Thomas and F.M. Najjar. Modeling Superheat Removal during Continuous Casting of Steel Slabs. Metallurgical Transactions B, 23B: (6): 1992, pp 339-356.

[3].Continuous Casting, Vol 2, 1984, pp175.

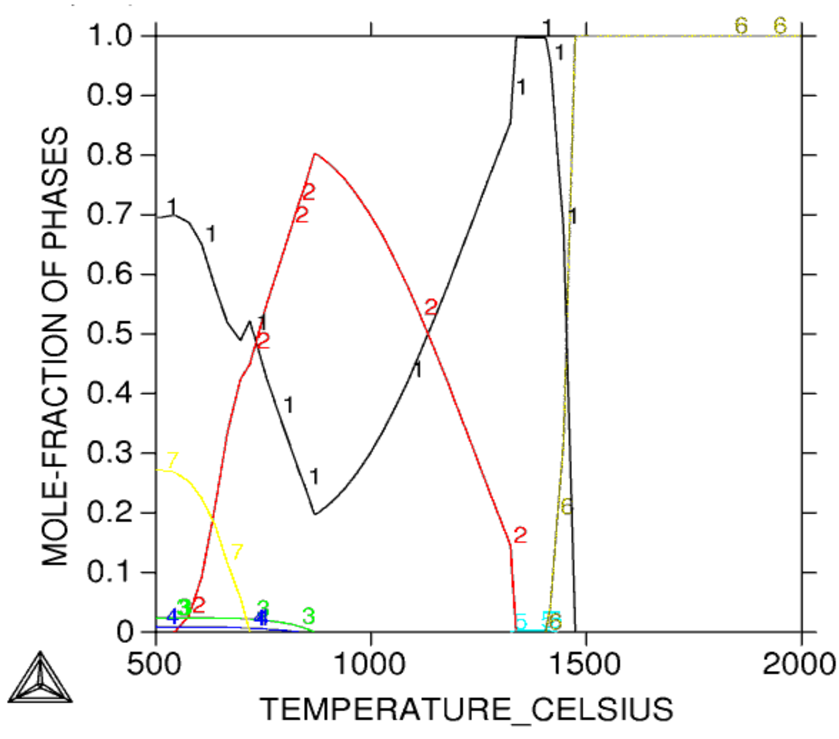
[4].F. Yosef: Solidification of Iron and Nickel Base Alloys and Its Relation to Hot Crack and Air Gap Formation. PhD thesis, Royal Institute of Technology, Stockholm, 2005.

[5]. J-O. Andersson, T. Helander, L. Höglund, P. Shi, B. Sundman: Elsevier Science LTD., Calphad, 26 (2002), 273.

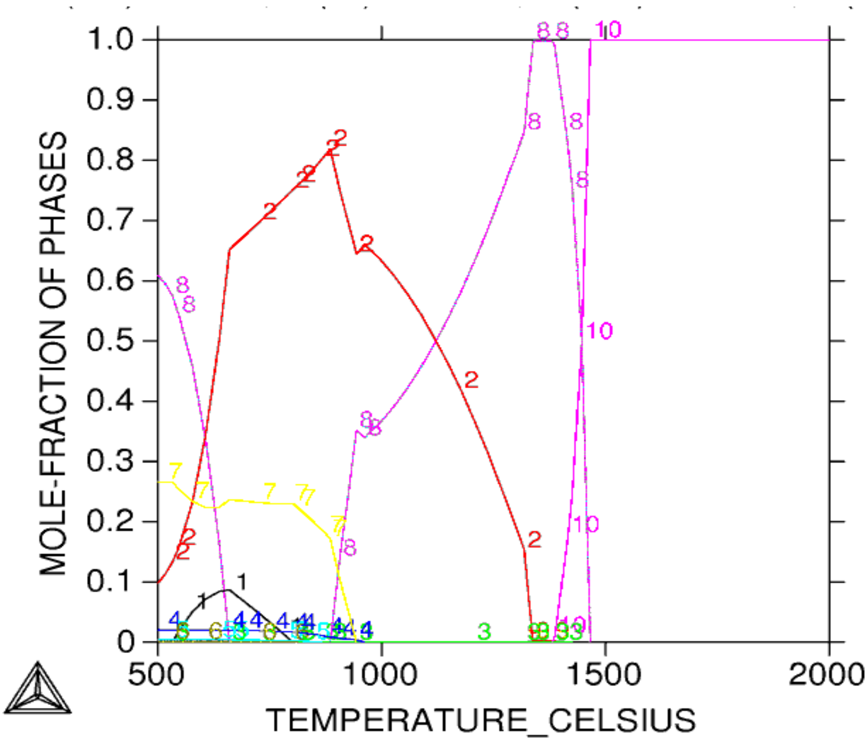
[6].A. Löfgren. Internal report, Avesta Research Centre, Sweden. 1986.

Appendix 1

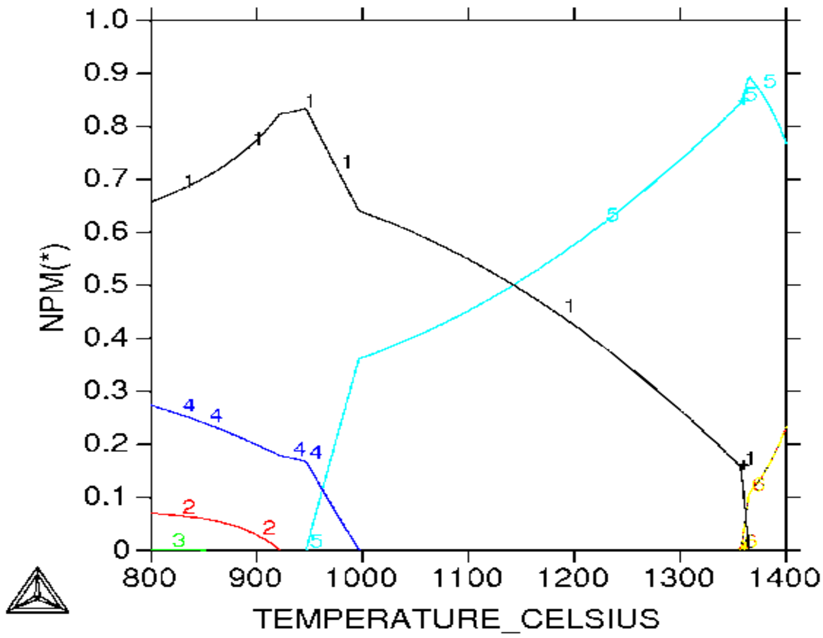
Thermo-Calc results



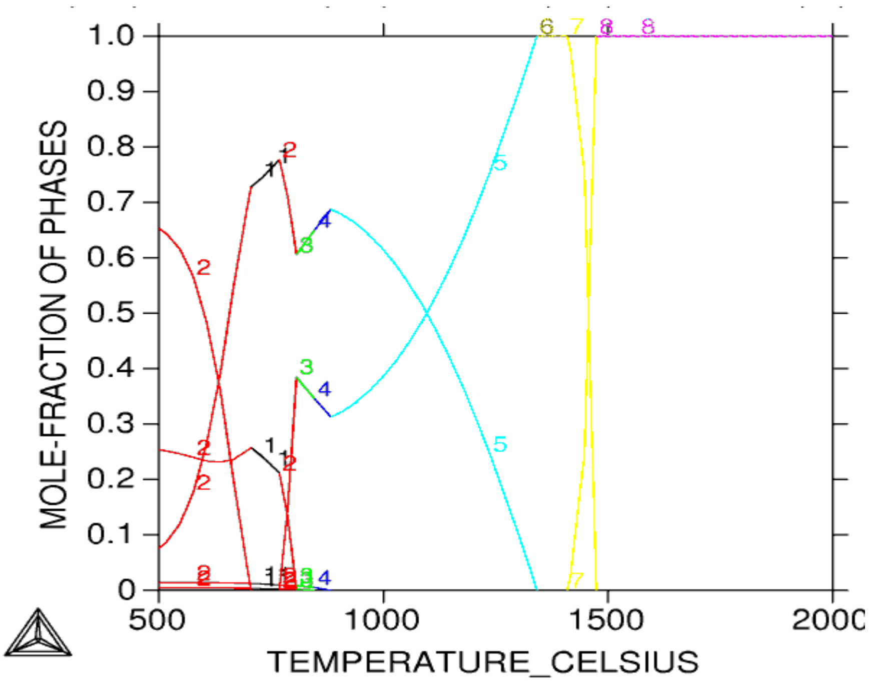
1. **Duplex 2101**



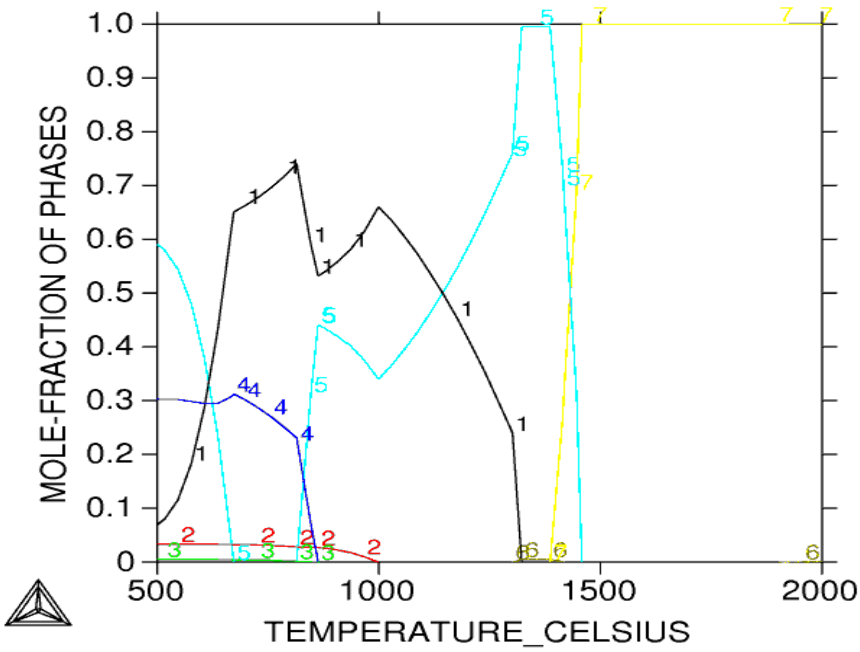
2. Duplex 2205



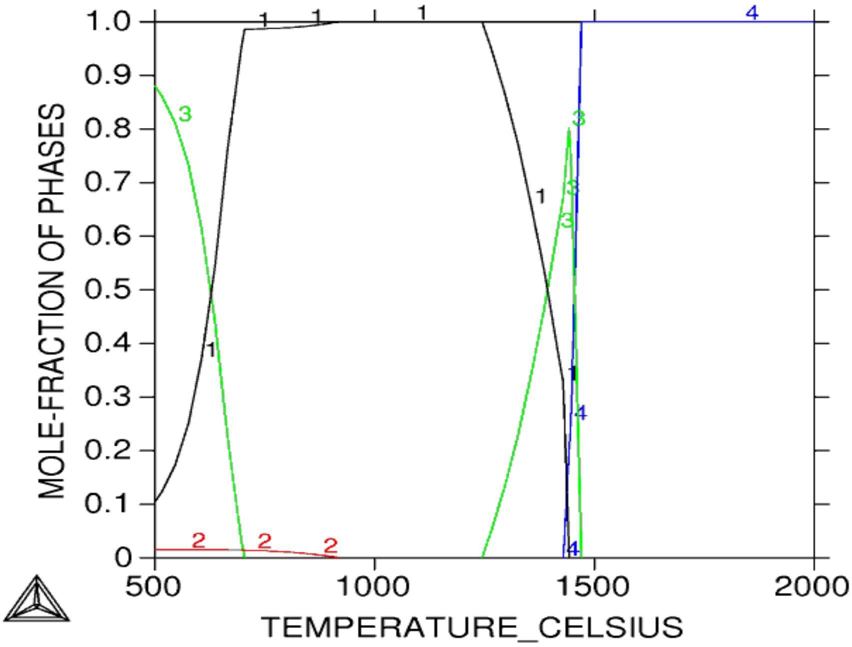
3. Duplex 2507



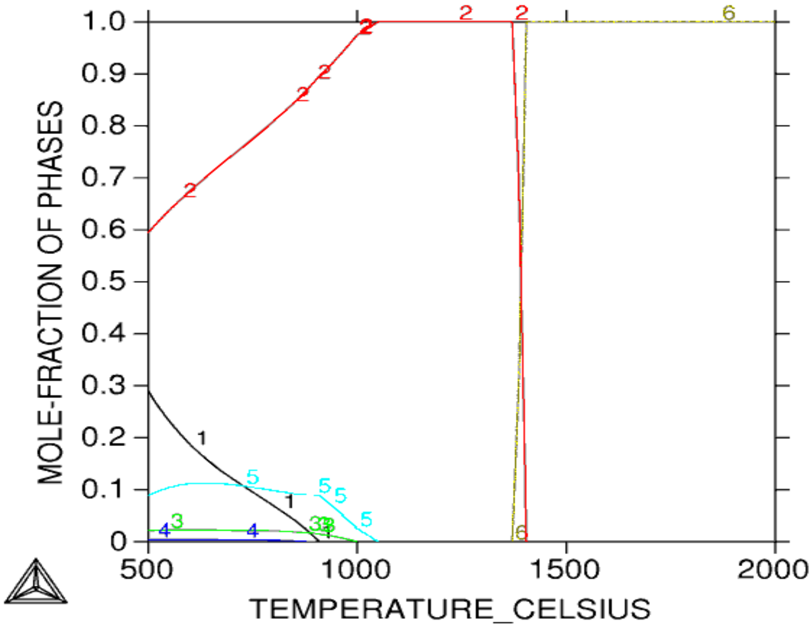
4. Duplex 2304



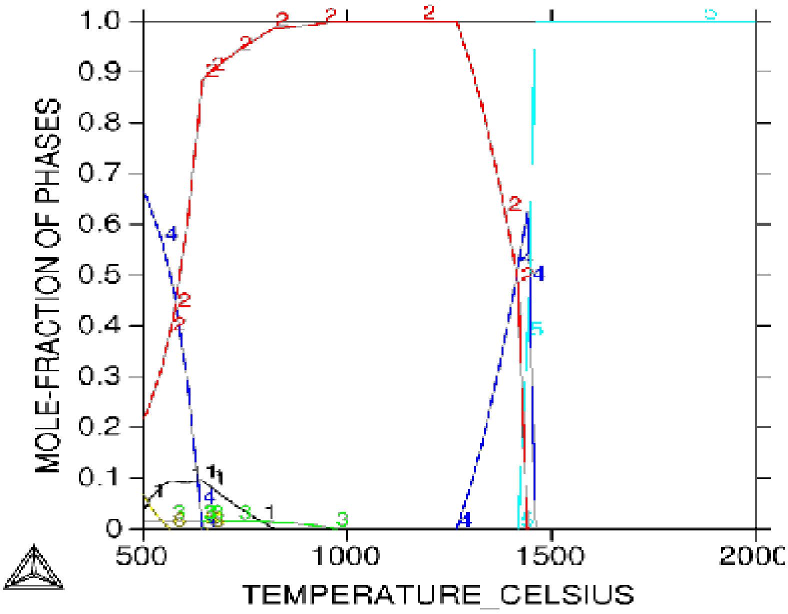
5. Duplex 2404



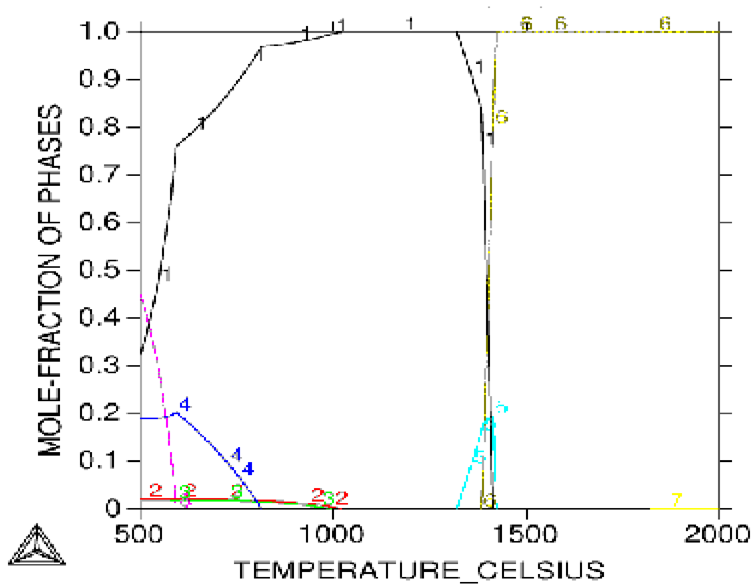
6. Austenitic 304



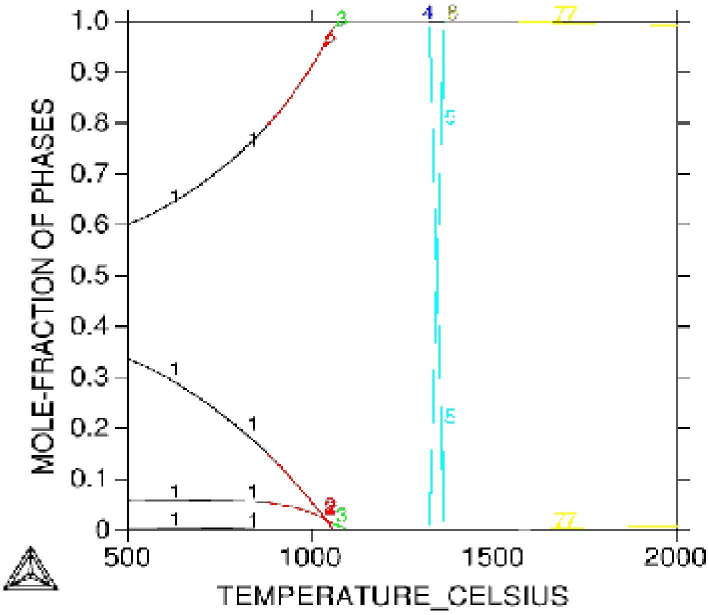
7. Austenitic 6Mo



8. Austenitic 316



9. High- temp 2111



10. High- temp 2417