

(18) Preventing Solidification Defects in Large Superalloy Castings Used in Advance Electric power Systems

This two-year effort will study macrosegregation in superalloy remelting processes. Weaknesses in existing models, particularly the inability to accurately predict partition coefficients of key elements under real operating conditions, will be addressed. Compositional effects of individual alloying elements in different alloys will be characterized so that a comprehensive database will be available in a useable format. A predictive methodology incorporating advanced computation technologies will be developed. Alloy index of freckle and center segregation formation can be determined for complex alloy compositions with efficient computational and laboratory analysis. The ultimate goal is to develop a predictive technology that can be applied commercially to prevent solidification defects for large superalloy castings used in advance electric power systems.

Total project cost: \$526,332

Funding request: \$375,473

Project Lead: West Virginia Research Corp. on behalf of West Virginia University

Project Participants: GE Energy; Special metals Corp.; Pennsylvania State University

Start Date: August 30, 2005

End Date: August 30, 2007

Presentations/Publications

None.

Patents

None.

Progress in Past Quarter and Current Status

Task 1: Solidification Modeling

Sub-task 1.1.1 Thermodynamic Modeling (Liu/PSU)

The goal for this subtask is to obtain the partition coefficients of the model systems Ni-Cr-Nb, Ni-Cr-Fe, Ni-Cr-Ti, Ni-Cr-Fe-Nb, and Ni-base superalloys IN 706 & IN 718, through first-principles calculation and thermodynamic/kinetic modeling. During the third quarter, the research efforts were focused on studying:

- (i) the available thermodynamic descriptions in the Ni-Cr-Fe-Nb system;
- (ii) the influences of different databases on the predicted partition coefficients;
- (iii) the partition coefficients of Cr and Nb in the Ni-Cr-Nb alloys.

(1) Review of thermodynamic descriptions in the Ni-Cr-Fe-Nb system

The valid thermodynamics of the Ni-Cr-Fe-Nb system is a fundament to predict the partition coefficients in the Ni-Fe base superalloy. Therefore it is worth to go in details to investigate the available commercial Ni-database and the recent progresses in this system. In the Ni-Cr-Fe-Nb system, four ternary systems are present, of which only the Cr-Nb-Ni and Cr-Fe-Ni systems have been modeled in the Ni-database. For the Cr-Nb-Ni system, the recent modeling work was done by Du et al [1]. For the Cr-Fe-Ni system, the recent modeling work was done by Tomiska [2]. However, for both the Fe-Nb-Ni and Cr-Fe-Nb systems, the ternary interactions are absent in the Ni-database and the literature. For the Fe-Nb-Ni system, the recent investigation [3] indicates that a compound with hexagonal structure was observed at composition around Ni-20Fe-22Nb (at.%), but the further information is scarce about this unknown phase, e.g., the detailed crystal structure, the melting point, and the formation enthalpy etc. The existence of this unknown phase

makes the modeling of Fe-Nb-Ni system difficult. Even for the binary Fe-Ni system, the current modeling do not describe well the γ'' phase (FeNi_3) due to the existence of magnetism [4]. For the Cr-Fe-Nb system, no ternary compounds were reported in the literature [5].

In summary, the Ni-database needs to be improved by the recently modeled Cr-Nb-Ni and Cr-Fe-Ni systems. The binary Fe-Ni and the ternary Fe-Nb-Ni and Cr-Fe-Nb systems need to be modeled in order to get a better thermodynamic description of the Cr-Fe-Nb-Ni system.

(2) The influences of different databases on the predicted properties

The available commercial Ni-database and Du et al's database [1] are used to probe the influences of different databases on the predicted properties including the Gibbs energies of solid and liquid phases, the solid/liquid (S/L) phase boundaries, and the partition coefficients of Cr and Nb, where the Ni-Cr-Nb alloy are selected as the model alloy.

Fig. 1 shows the calculated Gibbs energies of solid and liquid phases of Ni-15Cr-4.5Nb (wt.%) by using the Ni-database and Du et al's database [1]. For both solid and liquid phases, the calculated Gibbs energies by Du et al's database shift to the lower positions with respect to those obtained from Ni-database, indicating that the solid phase predicted by Du et al's database should be more stable than that predicted by Ni-database. As a consequence, the S/(S+L) and (S+L)/L phase boundaries calculated by Du et al's database should occur at higher temperatures. Fig. 2 illustrates the calculated S/(S+L) and (S+L)/L phase boundaries of Ni-15Cr-xNb and Ni-20Cr-xNb (wt.%) alloys by Ni-database and Du et al's database [1]. The differences of phase boundaries are clearly shown in Fig. 2.

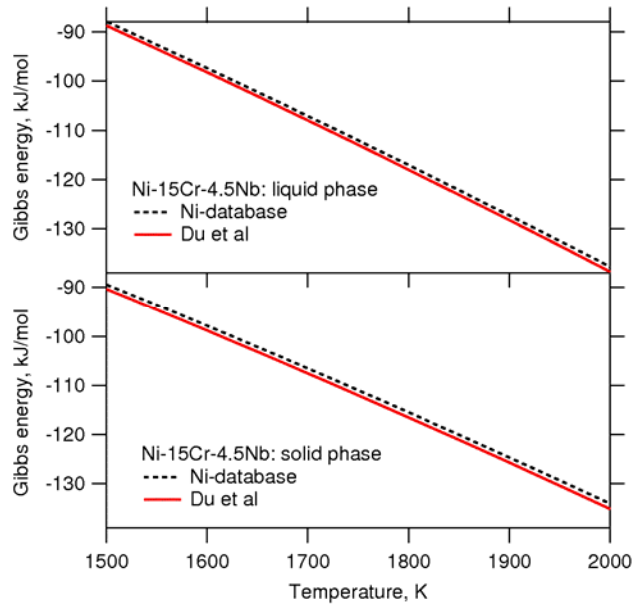


Fig. 1. Calculated Gibbs energies of solid and liquid phases of Ni-15Cr-4.5Nb (wt.%) by Ni-database and Du et al's database [1].

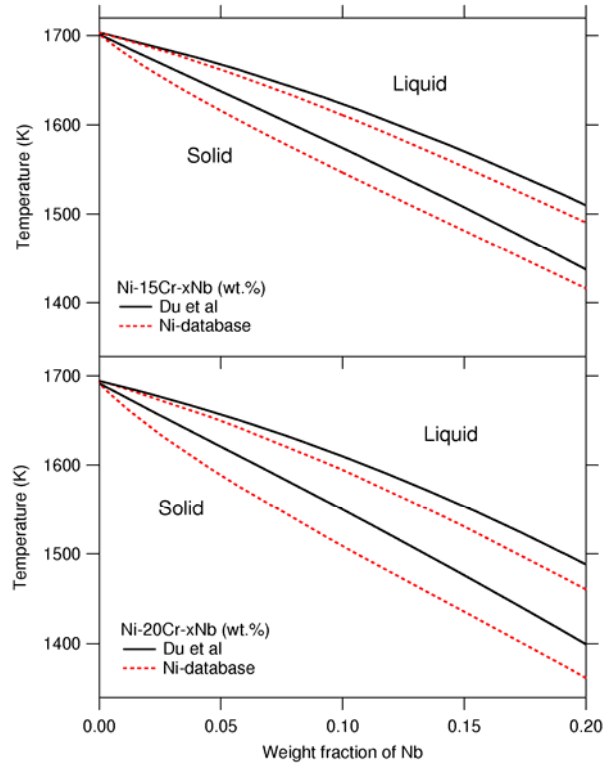


Fig. 2. Calculated solid/liquid phase boundaries of Ni-15Cr-xNb and Ni-20Cr-xNb (wt.%) by Ni-database and Du et al's database [1].

Fig. 3 gives the calculated phase transition temperatures and the partition coefficients of Cr and Nb as function of solid fraction for Ni-15Cr-4.5Nb (wt.%) alloy, wherein both the Ni-database and Du et al's database [1] are used, and three kinds of solidification models are employed as follows:

- 1) the equilibrium solidification, at each temperature both solid and liquid phases are in thermodynamic equilibria, where the diffusions of alloying elements in the liquid and solid phases are assumed to be infinitely fast;
- 2) the Scheil model, there are infinitely fast diffusions of all alloying elements in the liquid and no diffusions in the solid;
- 3) the Dictra method by considering of the kinetic influences, where the diffusions of alloying elements in both the solid phase (the so-called back diffusions) and the liquid phase are not infinitely fast. The cooling rate 10K/min is employed. The kinetic parameters of elements Ni, Fe, Nb are taken from the NIST Mobility Database.

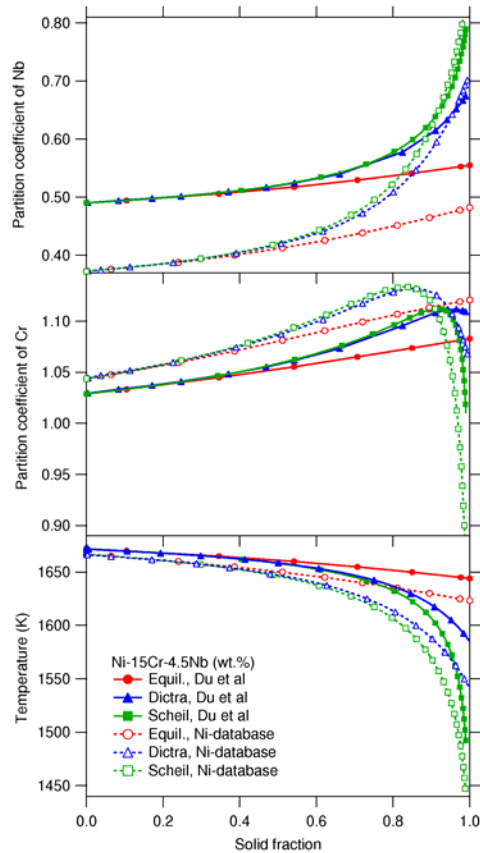


Fig. 3. Calculated phase transition temperatures and partition coefficients of Cr and Nb as function of solid fraction in Ni-15Cr-4.5Nb (wt.%).

Fig. 3 shows that the different databases (thermodynamic data) have large influences on the predicted phase transition temperatures and partition coefficients. Just as the phase boundaries shown in Fig. 2, the Ni-database predicts a lower phase transition temperatures with respect to those obtained by Du et al's database for all the three cases: equilibrium, Scheil and Dictra calculations. Regarding the predicted partition coefficients, the large differences present for the element Nb. The calculated partition coefficients of Nb by the Ni-database are lower than those obtained by Du et al's database (the difference is even larger than 0.1 at low solid fractions). Contrarily the predicted partition coefficients of Cr by Ni-database are higher than those obtained from Du et al's database.

(3) Predicted partition coefficients in the Ni-Cr-Nb alloy

Fig. 4 illustrates the calculated phase transition temperatures and the partition coefficients of Cr and Nb as function of solid fraction in the Ni-15Cr-xNb and Ni-20Cr-xNb (wt.%) alloys by Dictra simulation. The thermodynamic data are taken from Du et al's results [1], the cooling rate are set as 10K/min. With increasing of Nb and/or Cr content, Fig. 4 indicates that the phase transition temperatures decrease. The contents of elements Nb and Cr have opposite influence on the calculated partition coefficients of Cr and Nb. With increasing of Nb content, the partition coefficients of both Cr and Nb increase for each fixed solid fraction, while with increasing of Cr content the partition coefficients of Cr and Nb decrease. It should be remarked that the equilibrium calculation and the Scheil model will give the some trends as those obtained by Dictra calculation. The same trends still hold by using the Ni-database.

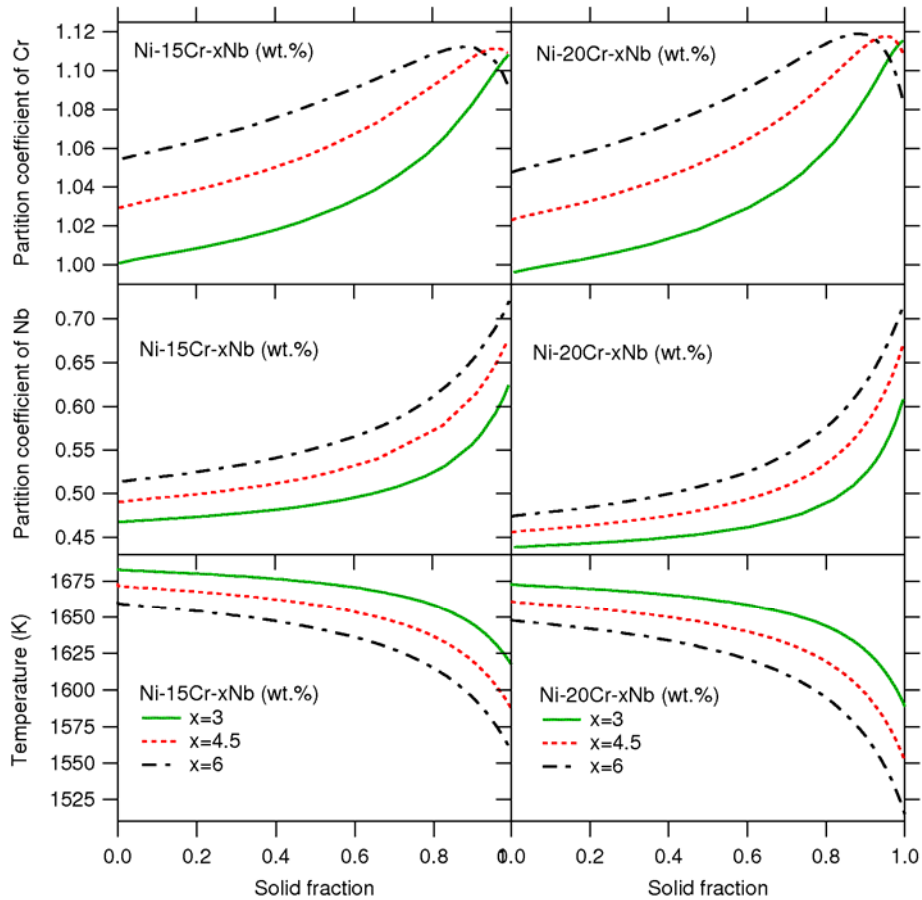


Fig. 4. Calculated phase transition temperatures and partition coefficients of Cr and Nb as function of solid fraction in Ni-15Cr-xNb and Ni-20Cr-xNb (wt.%) by Dictra simulation.

In summary of subtask 1.1.1, the thermodynamic description in the Ni-Cr-Fe-Nb system has been reviewed. It is found that the ternary interactions are absent in the Fe-Nb-Ni and Cr-Fe-Nb systems. The influences of different databases (the Ni-database and Du et al's database [1]) on the predicted properties have been investigated. This work shows that the large difference (> 0.1) presents for the predicted partition coefficient of Nb by different databases. The partition coefficients of Cr and Nb in the Ni-Cr-Nb alloy as functions of Cr and Nb contents have also been studied.

Sub-task 1.1.2 Experimental Investigation on Partition Coefficients (Liu/WVU)

Production of the Model Alloys

In the third quarter, the experimental investigation of the partition coefficients of the alloying elements continued, specifically the partition coefficient of Nb in the system Ni-Fe-Nb was studied.

Samples of all the model alloys for the Ni-Fe-Nb system were produced using the tri-arc bottom furnace and the chemical composition was determined by SEM/EDS. The chemical compositions are presented in table 1.

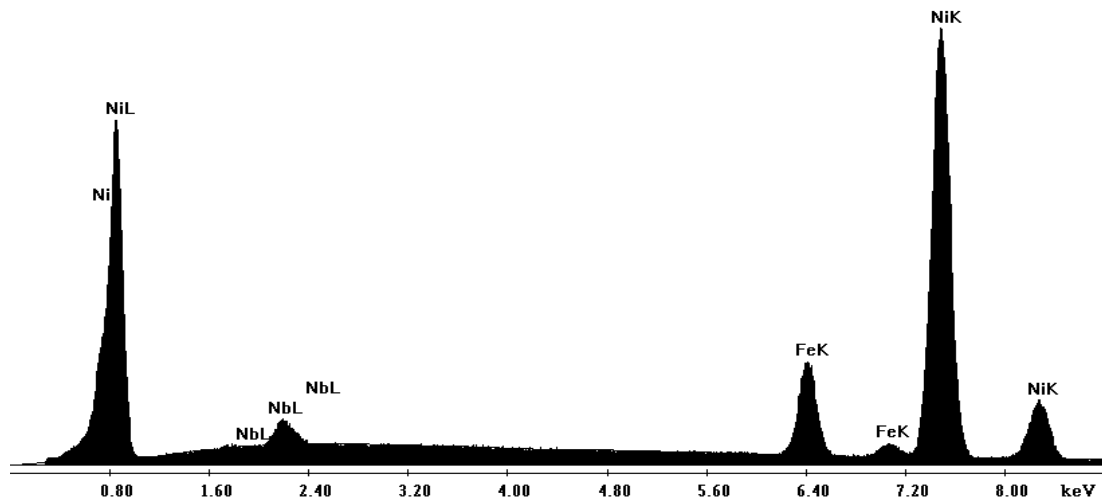
Table 1. Chemical Composition of Model Alloys Produced.

		Fe (Wt %)	Nb (Wt %)	Abs. Delta Fe	Abs. Delta Nb
Alloy 7	Target	5	3		
	Obtained	5.52	3.66	0.52	0.66
Alloy 8	Target	5	5		
	Obtained	4.68	4.68	0.32	0.32
Alloy 9	Target	10	3		
	Obtained	10.41	3.35	0.41	0.35
Alloy 10	Target	10	5		
	Obtained	10.0	6.0	0	1.0
Alloy 11	Target	18	3		
	Obtained	17.98	3.39	0.02	0.39
Alloy 12	Target	18	5		
	Obtained	18.75	4.83	0.75	0.17
Alloy 13	Target	36	3		
	Obtained	37.58	4.4	1.58	1.4
Alloy 14	Target	36	5		
	Obtained	35.75	5.97	0.25	0.97

From table 1 it can be seen that the process of producing the alloys using the tri-arc furnace has an average deviation of 0.48 from the correct amount of Fe, while the average deviation from the correct amount of Nb was of 0.61.

Fig. 5 shows the EDS spectra for alloys 9 and 13, as examples of the results obtained. Exceptional cases were encountered when the EDS analysis reported the presence of detectable amounts of Si and Al, which most probably come from the grinding and polishing materials used when preparing the samples, or when the EDS analysis showed the presence of W due to mass transfer from the stringer electrodes during melting of the raw materials. Special care was taken to avoid the typical contamination of hydrocarbons over the surfaces of samples using a cleaning procedure some minutes right before running the EDS experiments.

Label A: Alloy 9 08_21_2006



\\Edux\c\EDS\Liui, X\alloy 13 spot 08.spc

Label A: alloy 13 spot 08

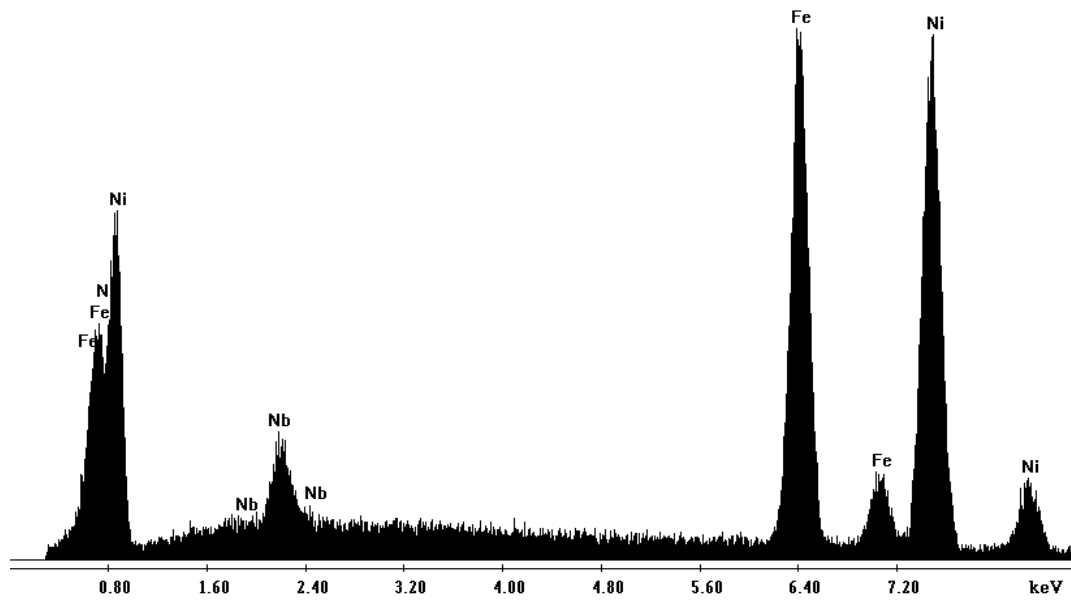


Figure 5. EDS spectra for Alloy 9 and Alloy 13

The samples of the system quaternary system Ni-Cr-Fe-Nb which complete the first batch of model alloys also were produced and currently are being under SEM/EDS analysis.

DTA experiments - Liquidus point and solidus point determination

The DTA experiments were conducted for all the model alloys of the system Ni-Fe-Nb. In all cases, the experiments were developed performing three repetitions for each of the samples.

Table 2 shows the experimental temperatures for the solidus and liquidus transformations obtained for the model alloys of the Ni-Fe-Nb system.

Table 2 Experimental Solidus and Liquidus temperatures for Model alloys of the Ni-Fe-Nb system.

Alloy Number	Solidus temperature (C)	Liquidus temperature (C)
7	1461.93	1488.61
8	1422.90	1460.22
9	1435.48	1465.4
10	1456.30	1459.14
11	1458.30	1461.38
12	1454.62	1462.42
13	1450.70	1481.00
14	1440.93	1453.43

Using the compositions obtained by SEM/EDS analysis for the model alloy samples, theoretical computation of the liquidus and solidus transformations were made using step module of ThermoCalc™ software (Commercial Database).

In all the alloys, the experimental values were above the theoretical ones calculated using the CalPhad methodology.

It was observed that with the increase of the weight percent of iron in the alloy the differences between the theoretical solidus values and the measured values increased, and those differences were even higher for the alloys with the higher amount of Niobium.

The figure 6 shows the solid fraction change with temperature for the set of model alloys of the Ni-XFe-3Nb type.

The theoretical curves obtained by CalPhad methodology present decreasing temperatures of solidus and liquidus reactions with the increase of the weight percent of iron, while the experimental results doesn't show this trend so clearly.

The increase of the amount of Niobium decreased the values of the solidus and liquidus for the theoretical results as well as for the experimental values measured for all the Iron contents. This result is shown from Figure 7 to Figure 10.

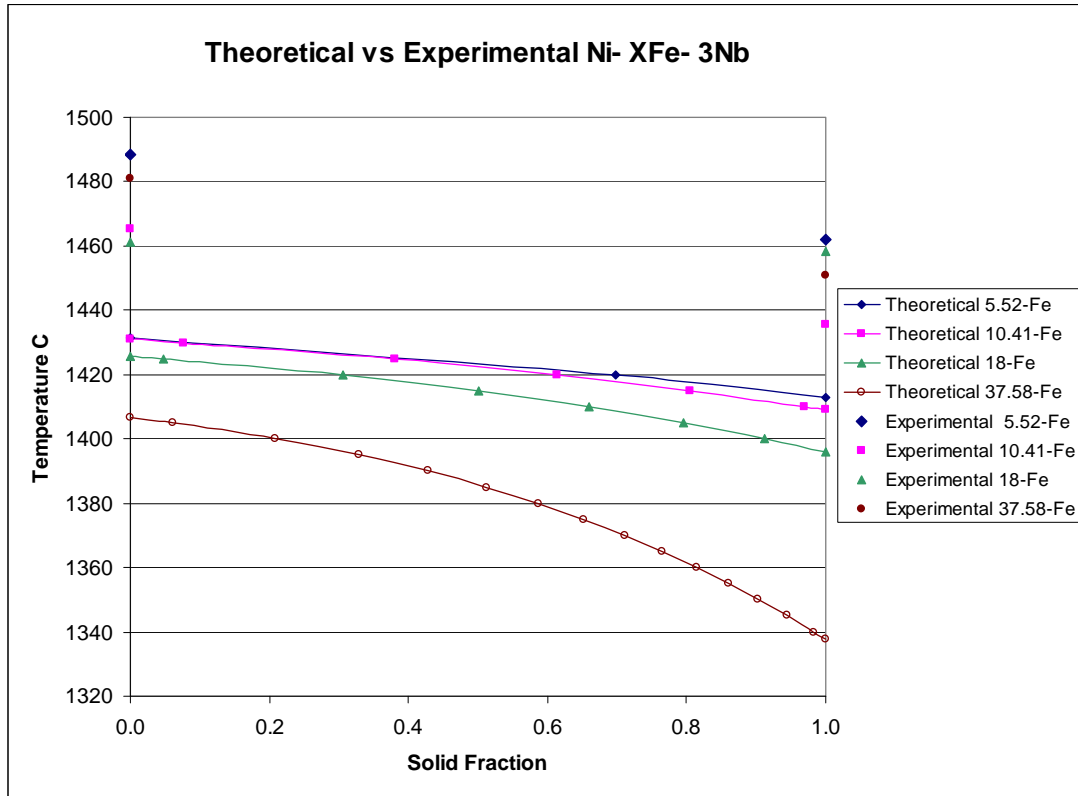


Figure 6. Solid Fraction for the Ni-XFe-3Nb alloys. Theoretical vs Experimental

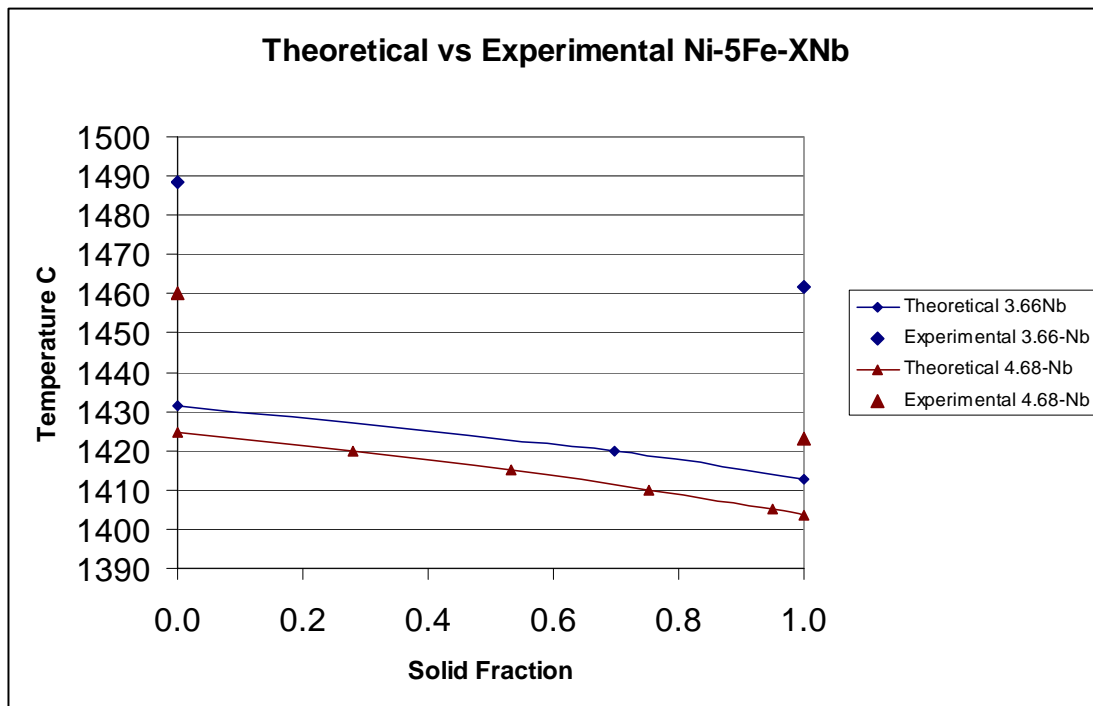


Figure 7. Solid Fraction for the Ni-5Fe-XNb alloys. Theoretical vs Experimental

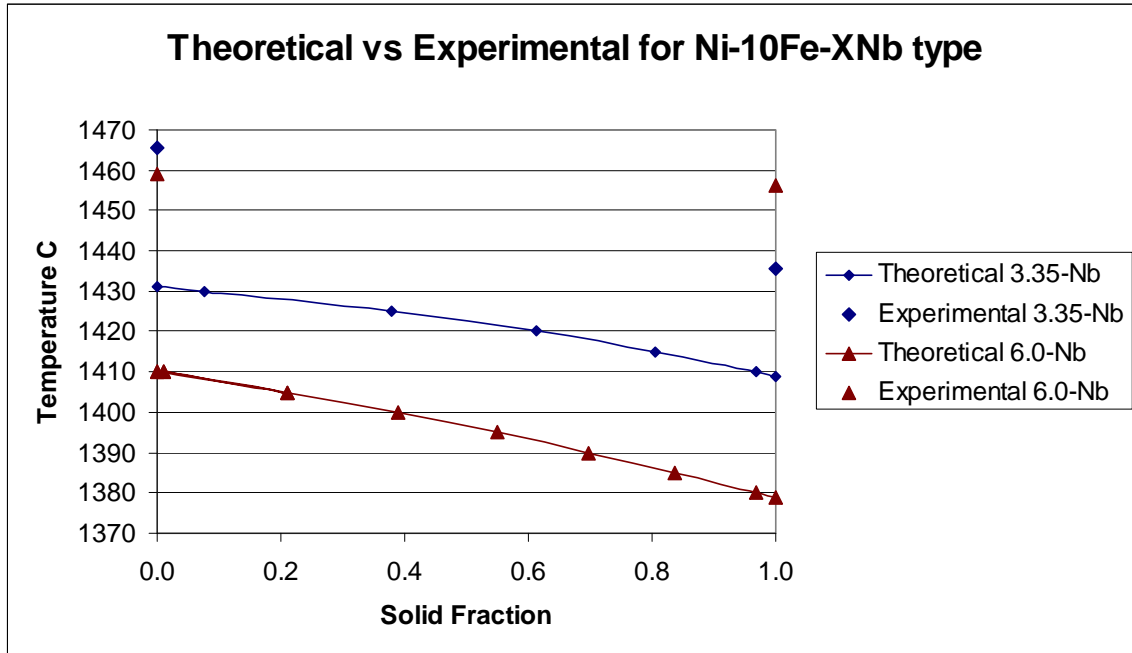


Figure 8. Solid Fraction for the Ni-10Fe-XNb alloys. Theoretical vs Experimental

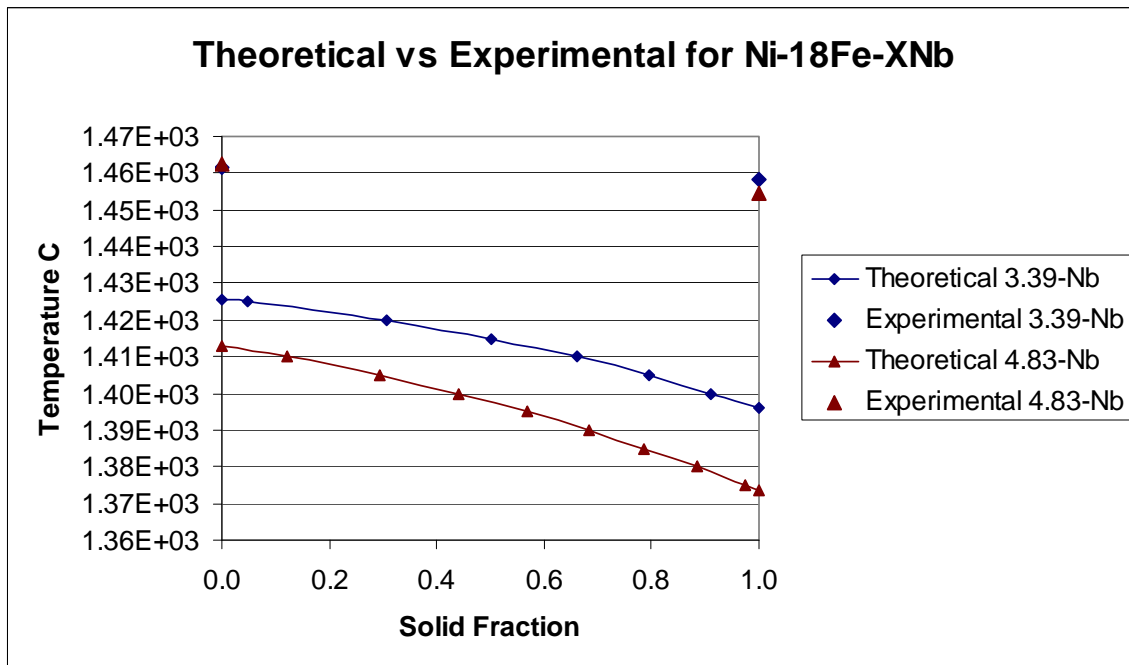


Figure 9. Solid Fraction for the Ni-18Fe-XNb alloys. Theoretical vs Experimental

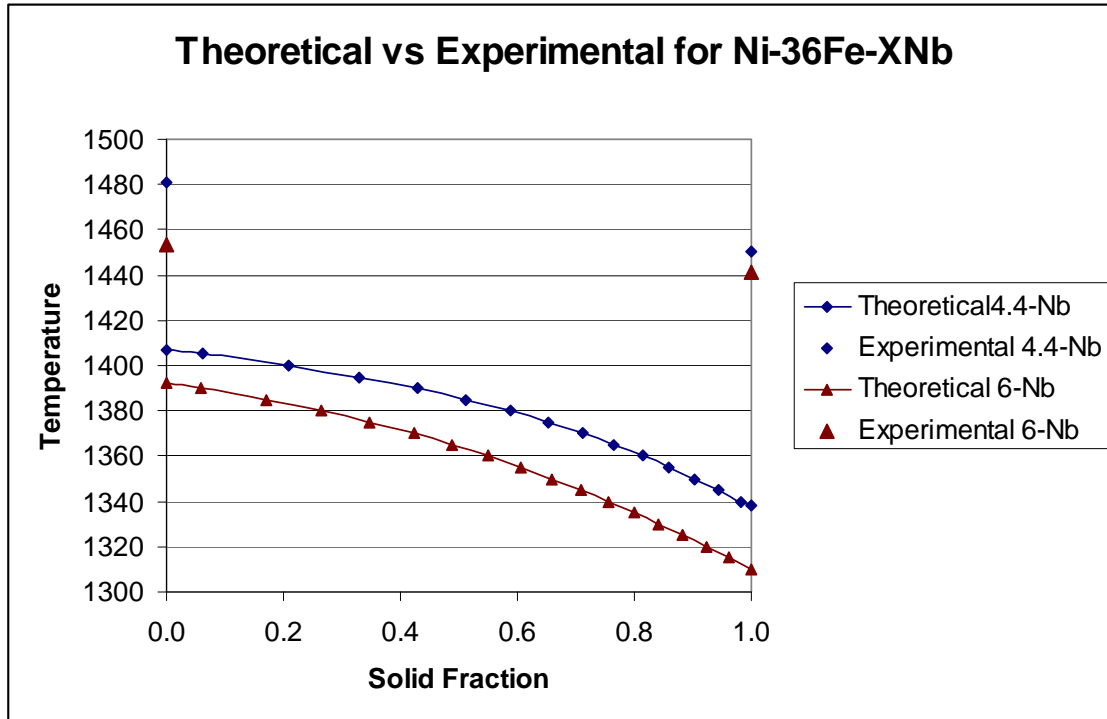
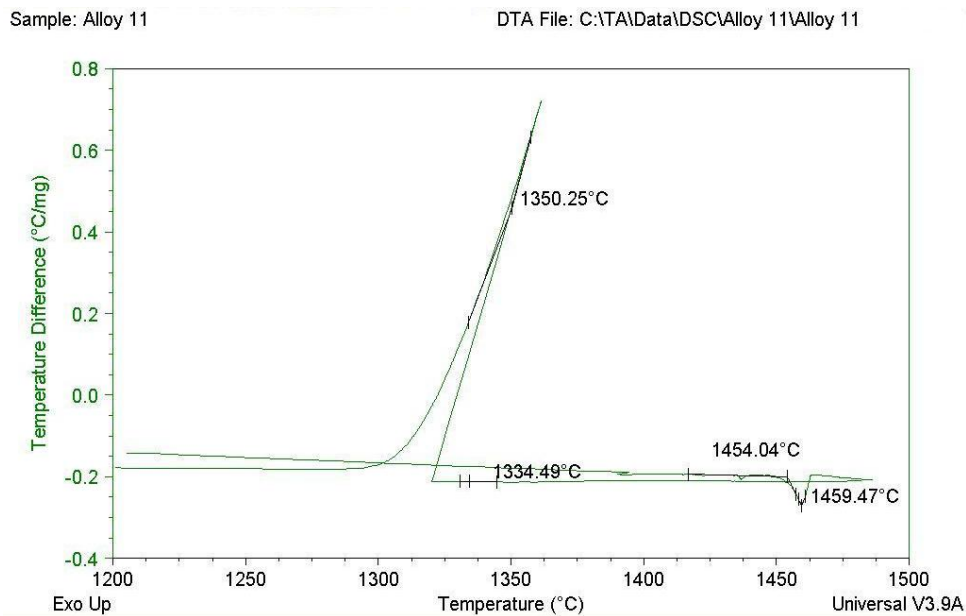


Figure 10. Solid Fraction for the Ni-36Fe-XNb alloys. Theoretical vs Experimental

Sub-task 1.1.3 Kinetic Effects

The partition coefficients and other solidification characteristics of the first batch (Ni-Cr-Fe-Nb) of alloys were investigated under various heating and cooling rates to study the kinetic effects on solidification behaviors of these alloys.



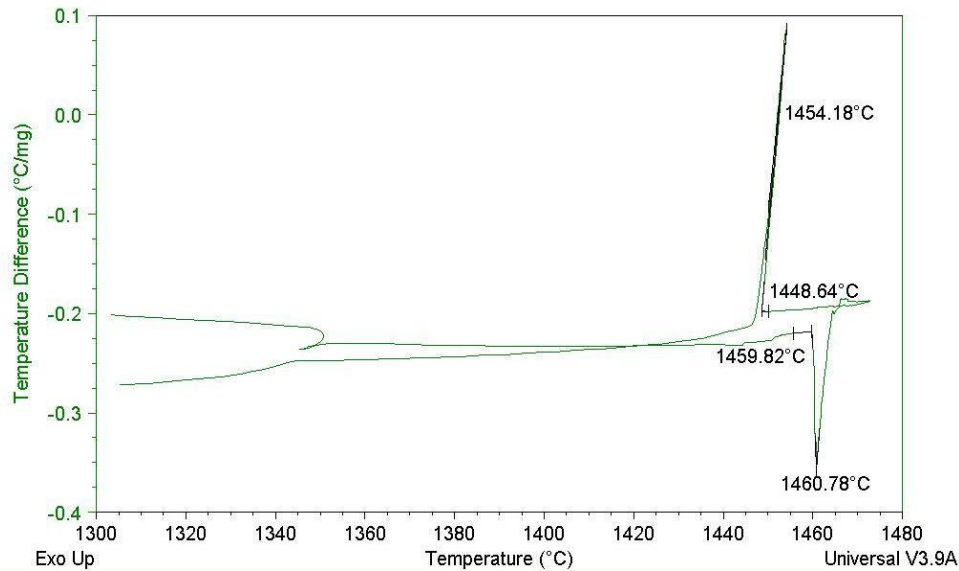


Figure 11. DTA curves for alloy 11 at 10 C/min (top) and 5 C/min (bottom)

As an example, Figure 11 shows the difference between the curve obtained for alloy 11 at heating/cooling rates of 10 C/min (top curve), with respect to the curve obtained at heating/cooling rates of 5 C/min (bottom). It can be seen that the effect of kinetics is more pronounced at cooling stage, in accordance to the undercooling effects on DTA experiments reported by Feng et al [6].

In order to accurately find the solidus and liquidus points, additional experiments were performed at heating/cooling rates of 3 C/min when the effects of kinetics were still noticed at 5 C/min rates.

Task 2 Directional Solidification Verification

Task 2.1 Verification of Model Alloys (Liu/WVU)

The research effort during this quarter has been focusing on experimental setup for the directional solidification furnace. Up to now, the new Type B thermocouple has been ordered and the research team is working with WVU physical plant to connect the power for the furnace.

Plan for Next Quarter

Task 1: Solidification Modeling

Task 1.1 Thermodynamics Database and Partition Coefficients

Sub-task 1.1.1 Thermodynamic Modeling (Liu/PSU)

In the next quarter, the following tasks will be performed:

- (i) to prepare a manuscript based on the previously theoretical (PSU) and experimental (WVU) investigations: partition coefficients of Cr and Nb in the Cr-Nb-Ni alloys;
- (ii) to investigate the γ'' phase in the Fe-Ni system and the ternary interactions in the Fe-Nb-Ni system, and to obtain a valid thermodynamic database of Fe-Nb-Ni system;
- (iii) to investigate the partition coefficients of Fe and Nb in the Fe-Nb-Ni alloys by considering both the thermodynamic and kinetic influences.

The research effort of the next quarter will focus on bring to operational state the DS furnace and run the first experiments, using the batch of alloys defined in table I, under different rates of cooling.

Sub-task 1.1.2 Experimental Investigation on Partition Coefficients (Liu/WVU)

Production of the Model Alloys

During the next quarter, the Ni-Cr-Ti, and Ni-Cr-Al alloys will be produced by tri-arc button furnace.

DTA measurement

The research for next quarter will focus on the following:

- a. Determining the liquidus and solidus transitions for all the model samples prepared for the Ni-Cr-Ti and Ni-Cr-Al ternary systems.
- b. Run exploration experiments to test the modification of the DTA machine for quenching.
- c. Perform Modified DTA calibration and run experiments to calculate partition coefficients from direct measurements of core dendrite and liquid composition
- d. Defining the next batch of experimental alloys

Task 2 Directional Solidification Verification

Task 2.1 Verification of Model Alloys (Liu/WVU)

Once the thermocouple type B is obtained and the power supply is ready, the directional solidification experiments for the model alloys of the system Ni-Cr-Nb and Ni-Fe-Nb will start.

Task 2.2 Effect of Processing Parameters (Liu/WVU)

The research team will decide the experimental plan on the investigation of processing parameter effect, based on results of tasks 1.1.1 through 1.1.3. The experiments are expected to start from the third quarter of the project.

References

1. Y. Du, S. H. Liu, Y. A. Chang and Y. Yang, *Calphad*, **29** (2005) 140-148.
2. J. Tomiska, *Journal of Alloys and Compounds*, **379** (2004) 176-187.
3. V. Raghavan, *Journal of Phase Equilibria and Diffusion*, **25** (2004) 552-552.
4. G. Cacciamani, J. De Keyzer, R. Ferro, U. E. Klotz, J. Lacaze and P. Wollants, *Intermetallics*, **14** (2006) 1312-1325.
5. V. Raghavan, *Journal of Phase Equilibria and Diffusion*, **25** (2004) 554-555.
6. Q. Feng, L.J. Carrol, and T.M. Pollock, *Metallurgical and Materials Transactions*, **37A** (2006) 1949-1962