

## **(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.

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

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

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### Presentations/Publications

None.

### Patents

None.

### Progress in Past Quarter and Current Status

#### **Task 1: Solidification Modeling**

##### **Task 1.1 Thermodynamics Database and Partition Coefficients**

###### **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 fourth quarter of 2006, the research efforts were focused on studying:

- (i) the thermodynamic modeling of the Fe-Ni system;
- (ii) the ternary SQS's (special quasirandom structures) in order to estimate the ternary interactions in the Ni-Fe-Nb and Cr-Fe-Nb systems by first-principles calculations;
- (iii) the partition coefficients of Fe and Nb in the Ni-Fe-Nb alloys.

###### (1) Thermodynamic modeling of the Fe-Ni system

As mentioned in the third quarterly report, the thermodynamic modeling of the Fe-Ni system in the commercial Ni-database does not describe well the  $\gamma'$  (FeNi<sub>3</sub>) phase due to the existence of magnetism. We therefore re-modeled the ordered  $\gamma'$  phase using a three-sublattice model, (Fe, Ni)<sub>0.75</sub> : (Fe, Ni)<sub>0.25</sub> : (Va)<sub>1</sub> (1)

where Va represents the vacancy. The parameters in the Gibbs energy expression for the above three-sublattice model were estimated by the PARROT module in the Thermo-Calc code. The obtained Fe-Ni phase diagram is shown in Fig. 1, where the symbol  $\alpha$  represents the BCC disordered phase,  $\gamma$  the disordered FCC phase,  $\gamma'$  the ordered phase, i.e., FeNi<sub>3</sub>.  $\gamma_1$  and  $\gamma_2$  represent the non-magnetic and magnetic disordered FCC phases, respectively. Fig.1 shows that the presently calculated phase boundaries agree well with the measured ones. The modeled Fe-Ni system provided a starting point for the future investigation of the Ni-Fe-Nb

system.

(2) The generation of ternary SQS's (special quasirandom structures)

The thermodynamic description of the Ni-Fe-Nb system is an important basis to predict the partition coefficients in the Ni-Fe based superalloy. However, the absence of ternary interactions in this system makes the predictions worse, e.g., the phase transition temperatures (see the previously quarterly report). Therefore, the estimation of ternary interactions in the Ni-Fe-Nb system is crucial, especially for the FCC based  $\gamma$  phase with random mixing of elements Fe, Ni, and Nb. Due to the lack of experimental data in ternary Ni-Fe-Nb system, the first-principles calculations will be adopted to obtain the mixing of enthalpy for the random solution phase  $\gamma$  on the basis of the SQS's (special quasirandom structures).

SQS's are specially designed small unit-cell ordered structures with only a few (2–32) atoms per unit cell, which mimic the most relevant, near-neighbor pair and multisite correlation functions of random substitutional alloys. The essence of SQS is to find an **ordered** compound in order to mimic the properties of the corresponding **disordered** structure [1, 2]. Since a set of correlation functions (CFs) can be used to designate a structure [3, 4], the first step of SQS calculation is therefore to construct an ordered compound (the so called SQS) whose CFs are equal to (or close to) the corresponding CFs of the disordered structure. The second step is to perform the first principles calculation based on the constructed ordered compound, and then to investigate the properties of the corresponding disordered structure.

In the literature the available SQS's exist for binary FCC [1, 2], BCC [3] as well as HCP [4] structures. However, there are no available SQS's for ternary systems. We thus generated the SQS's for FCC based ABC alloy with 24 atoms per unit cell and A2BC alloy with 32 atoms per unit cell. Fig.2 illustrates both the SQS's for ABC and A2BC.

The details of the lattice vectors and the atomic positions for SQS-24 (ABC) and SQS-32 (A2BC) are given in Table 1. The analysis of their correlation functions with respect to the real random alloys is given in [5].

(3) Predicted partition coefficients in the Ni-Fe-Nb alloy by the commercial Ni-database

The commercial Ni-database is used to obtain the primary partition coefficients of Fe and Nb in the Ni-Fe-Nb alloys. The purpose of these predictions is to compare with the measurements by VWU. The final predictions will be performed when the ongoing modeling for the Ni-Fe-Nb system (see the above section) is done. In this section, the equilibrium calculation and the Scheil model are used in the calculations.

Fig. 3 illustrates the calculated phase transition temperatures and the partition coefficients of Nb and Fe as a function of solid fraction in the Ni-3Nb-xFe and Ni-5Nb-xFe (wt.%) alloys by equilibrium calculations. With increasing of Nb and/or Fe content, Fig. 3 shows that the phase transition temperatures decrease, while the partition coefficients of Nb and Fe decrease and increase respectively. When the composition of Fe is lower (e.g., < 18 wt.%), the partition coefficient of Fe shows the adjacent values. The same trends hold by using the Scheil model as shown in Fig. 4.

In summary of subtask 1.1.1, the thermodynamic description of the  $\gamma'$  (FeNi<sub>3</sub>) phase has been remodeled in the Fe-Ni system, the calculated phase boundaries agree well with the experiments. The ternary SQS's (special quasirandom structures) for the FCC based alloys ABC and A2BC have been constructed. The SQS's will be used to calculate the mixing of enthalpy of the disordered  $\gamma$  phase, and in turn the ternary phase diagrams of the Fe-Ni-Nb system etc. In this quarter, the primary partition coefficients of Fe and

Nb in the Ni-Fe-Nb alloys have also been calculated by a combination of the commercial Ni-database, the equilibrium calculation and Scheil model.

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

The objective for this subtask is to measure the partition coefficients of the model systems Ni-Cr-Nb, Ni-Cr-Fe, Ni-Cr-Ti, Ni-Cr-Al, Ni-Cr-Fe-Nb, Ni-Cr-Fe-Ti, Ni-Cr-Fe-Al, and Ni-base superalloys IN 706 & IN 718, through indirect calculation using regular DTA measurements, and by direct measurement using SEM/EDS microprobe over regular DTA solidified samples and quenched samples.

### **Production of the Model Alloys**

In this quarter, the purity of the protective argon atmosphere inside the arc bottom furnace was improved by installing a cold trap of liquid nitrogen between the vacuum pump and the chamber, preventing back streaming of the oil mist.

Considering the objective of preparing manuscripts based on the previously theoretical and experimental investigations about the partition coefficients of Cr and Nb in the Cr-Nb-Ni alloys, the samples of the first batch of model alloys were produced again in order to obtain more data about these alloys and increase its statistical significance.

Comparing to the results presented in the previous quarterly report, the chemical compositions obtained deviate from the target ones in different extend, indicating a degree of variability in the process of production of samples that is needed to address. Currently, support is being obtained by NETL-Albany in order to improve the production process of the model alloy samples.

Although the target compositions were not obtained, the samples produced on the repetitions could be used to develop DTA analysis and perform comparisons with theoretical simulations of the corresponding pseudo binary system (Ni, 21.2 %Cr) – xNb. In the past quarter, the model alloys for the Ni-Cr-Fe-Ti and Ni-Cr-Fe-Al systems were defined.

Table 3 shows the compositions selected for the model alloys.

The weighting of the raw materials was performed and the compressed disks to be melted were obtained for all the alloys in table 3. After melting two specimens for both alloys 19 and 20, the melting stage was postponed until new parameters for melting were defined and explored in order to obtain homogeneous composition samples.

### **DTA measurements**

Regular DTA experiments were performed for the repetition samples produced of the alloy system Ni-Cr-Nb. Three DTA runs were executed for each alloy at each heating/cooling rate.

The selected Heating/Cooling rates were 10 °C /min and 3 °C /min, and the measured values of transition temperatures on heating and cooling stages have been averaged to suppress the kinetics effects of superheating of the solid phase and undercooling of the liquid phase. The table 3 shows the averages obtained for each alloy.

The analysis of the DTA curves obtained with different rates of heating and cooling showed that the alloy system Ni-Cr-Nb is less sensitive to the kinetic effects with respect to the samples of the Ni-Fe-Nb system presented in the previous quarterly report. Figure 6 shows the DTA curves for the sample of alloy 2. On top, is presented the curve obtained when the heating and cooling rate were set at 10 °C /min. In the bottom graph, corresponding to the DTA experiment at 3°C /min, it is observed a feature at about 1325 °C which corresponds to an isothermal step on the

procedure. No considerable differences were observed in the solidus and liquidus points between the two graphs.

Complementary samples of the system Ni-Cr-Nb with weight percent of Niobium of about 10% were also produced in order to evaluate the behavior of the partition coefficients of Nb and Chrome at high content of Niobium, although no commercial superalloys include such high amounts. From the DTA curves obtained it was obvious the apparition of new features, corresponding to transformations of new phases, evidencing the high dominance that Niobium content has upon the solidification paths of the model alloys and on the Ni-based superalloys in general [7].

According to the solidification path proposed by Cieslak et al. [7], the transformation point about 1350 °C should correspond to the dissolution of the carbides (predominantly NbC), while the point at 1390.99 °C represents the matrix ( $\gamma$ ) solidus. The peak at 1407.02 °C corresponds to the liquidus point of the alloy.

## **Task 2 Directional Solidification Verification**

### **Task 2.1 Verification of Model Alloys (Liu/WVU)**

The thermocouple type B is expected to arrive at the beginning of the next quarter and the power supply installation process has already started. The directional solidification furnace is expected to be ready by March 2007. Once the furnace 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 thermodynamic modeling, experimental investigation of the partition coefficients and the evaluation of the kinetic effects. The experiments are expected to start in the next quarter of the project.

## **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 paper: partition coefficients of Cr and Nb in the Cr-Nb-Ni alloys;
- (ii) to perform the first-principles calculations using the ternary SQS's for Ni-Fe-Nb alloys.
- (iii) to model the ternary system Fe-Ni-Nb using calculated SQS results and the available measurements.

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

In the next quarter the experimental determination of the partition coefficients will be continued, and the following activities will be developed:

- (iv) Finishing the modified DTA experiments for the model alloys of the system Ni-Cr-Nb
- (v) Produce the model alloys of the Ni-Cr-Al and Ni-Cr-Fe-Al systems using the tri-arc furnace following the suggestions obtained from NETL-Albany advisors
- (vi) Explore the possibility of producing larger model alloys using the VAR furnace at NETLAlbany facilities.
- (vii) Complete the regular DTA experiments for the Ni-Fe-Nb samples prepared.

#### **Sub-task 1.1.3 Kinetic Effects**

The kinetics effects will be included by continuing with the experiments of regular DTA using two different heating/cooling rates selected to be 10 C/min and 3 C/min.

## **Task 2 Directional Solidification Verification**

### **Task 2.1 Verification of Model Alloys (Liu/WVU)**

**Task 2.2 Effect of Processing Parameters**

The most important task for the directional solidification experiments in the next quarter is to have the furnace ready after receiving the requested parts and the power supply is installed.

When the furnace is ready, the results obtained in subtasks 1.1 to 1.3 will be used to establish the experimental procedure for the directional solidification verification.