INVESTIGATION OF THE PARTITION COEFFICIENTS IN THE NI-FE-NB ALLOYS: A THERMODYNAMIC AND EXPERIMENTAL APPROACH

Jairo Valdes*, DongEung Kim+, Shun-Li Shang**, Xingbo Liu++, Paul King++, Zi-Kui Liu+

*West Virginia University WV, USA, Universidad del Valle, Cali-Coelmbia
+ Department of Material Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
** Department of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, WV 26506, USA
++ DOE-NTEL, Albany, OR 97321-2198, USA

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Introduction

Efficient and environmentally friendly energy production can be obtained by increasing the firing temperature and the size of the land based gas turbines. It is reported that every 50°F increase of the firing temperature results in a 1% improvement of combined-cycle efficiency. The large rotor discs required need to be made of Nb containing Ni based superalloys to avoid aging and withstand the higher operation temperatures. However, Nb containing alloys tend to present macrosegregation defects like freckles, caused by downward flow of segregated heavier interdendritic liquid, in the mushy zone of the u-shaped metal pool characteristic of the Vacuum Arc Remelting (VAR) ingots. In order to avoid freckles special melting techniques at increased cost have been developed to produce the large VAR ingots, which include multiple stages of remelting combined with liquid metal refining steps and rigorous computer control of the process. Production cost could be reduced by a better prediction of the freckle formation. The most accepted freckling criterion is the one based on the Rayleigh number, which requires accurate determination of the partition coefficients for the solute elements. In this work, the partition coefficients of Nb and Fe in the ternary system Ni-Fe-Nb were studied by experimental measurements and by thermodynamic calculations. Modified DTA experiments were performed for model alloys, and a thermodynamic database for the Ni-Fe-Nb ternary system was developed. Most of the calculated partition coefficients using the developed model agree well with the experimental data. One exception to this, as will be discussed later, is the partitioning coefficient of Fe for the alloy containing 36 wt. %Fe.

Abstract

The Nb containing Ni-based superalloys used for the production of large castings are highly sensible to the formation of macrosegregation defects like freckles and white spots. Production cost can be reduced by better prediction of the freckle formation. The most accepted freckling criterion is the one based on the Rayleigh number, which requires accurate determination of the partition coefficients for the solute elements. In this work, the partition coefficients of Nb and Fe on the ternary system Ni-Fe-Nb were studied by experimental measurements and by thermodynamic calculations. Modified DTA experiments were performed for model alloys, and a thermodynamic database for the Ni-Fe-Nb ternary system was developed. Most of the calculated partition coefficients using the developed model agree well with the experimental data. One exception to this, as will be discussed later, is the partitioning coefficient of Fe for the alloy containing 36 wt. %Fe.

Experimental Approach

The samples of the Ni-Nb-Fe system were prepared with two levels of variation on the contents of solutes. In the case of Nb the amounts were 3 and 5 (wt. %), while for Fe the contents were selected to be 5 and 36 (wt. %). A high purity Argon atmosphere was used and multiple steps of melting were performed to attain good composition homogeneity. Regular DTA experiments were carried out to define the temperature range of the mushy zone for the isothermal and subsequent quench steps during the quenching modified DTA experiments (MDTA). To perform the MDTA experiments, the thermocouple assembly of the standard differential calorimeter was modified to permit locating a quenching oil bath in the bottom of the alumina tube furnace as shown in the Fig. 1. On the top of the alumina rod which contains the sample and reference thermocouples, a solidified sample with good composition homogeneity. Regular DTA experiments were performed for model alloys, and a thermodynamic database for the Ni-Fe-Nb ternary system was developed. The samples of the Ni-Nb-Fe system were prepared with two levels of variation on the contents of solutes. In the case of Nb the amounts were 3 and 5 (wt. %), while for Fe the contents were selected to be 5 and 36 (wt. %). A high purity Argon atmosphere was used and multiple steps of melting were performed to attain good composition homogeneity. Regular DTA experiments were carried out to define the temperature range of the mushy zone for the isothermal and subsequent quench steps during the quenching modified DTA experiments (MDTA). To perform the MDTA experiments, the thermocouple assembly of the standard differential calorimeter was modified to permit locating a quenching oil bath in the bottom of the alumina tube furnace as shown in the Fig. 1. On the top of the alumina rod which contains the sample and reference thermocouples, a solidified sample with the typical semispherical shape can be observed. In all experiments, a 10 cm/min flow of high purity Argon was used. All samples were heated up to temperatures above the liquidus transformation at a 10 C/min rate and slowly cooled to the mushy zone temperature region (5 C/min). A short duration isothermal step preceded the quenching step which was executed by tapping off the sample from the rod to the quenching oil. In the preliminary regular DTA experiments it was observed that the solidus temperature was more sensitive to variations in the
thermal conditions that affect the experiments (wider variation range), than the liquidus, as expected by theoretical result shown in Fig. 2. It shows that the diffusion rates of alloying elements in the solid and liquid phases affect significantly the predicted solidus temperature.

**Measurement of the Partition Coefficients**

The SEM/EDS analysis of the quenched samples suggested that the 5 Cº/min cooling rate before quenching was slow enough to maintain local equilibrium in the primary solid–liquid interface with no solute entrapment and negligible back diffusion, indicating the Scheil model was still applicable. For quenched high Nb content samples, the chemical composition was measured by SEM/EDS micro probe analysis along arbitrary oriented scan lines over primary gamma dendrites. Point measurements over interdendritic areas were discarded for the segregation profile fitting as suggested by Gungor. The data was ranked and assigned an apparent solid fraction according to the segregation tendency following the methodology proposed by Flemings et al. The solid volume fraction at the temperature of quenching was determined by areal measurement using Hillard’s quantitative metallography analysis.

Fig. 3 shows a backscattered electrons SEM image on which can be identified the dendritic structure along with the interdendritic eutectic, composed of Nb$_7$Ni$_6$ ($\mu$) lamellar phase and eutectic gamma.

A higher magnification backscattered electrons image is presented in Fig. 4, where a composition scan was taken covering secondary arm dendrites and the interdendritic eutectic between them.

Fig. 3. Backscattered electrons SEM image showing the microstructure found on the quenched Ni-5Fe-3Nb model alloy.

The solute profiles were then fitted to the Scheil equation and the partition coefficients were determined by minimizing the squared error. Fig. 5 gives an example showing the fitting error of segregation profile to the Scheil model for Ni-5Fe-5Nb sample alloy. The obtained partition coefficients of Nb and Fe by Scheil fitting method are presented in table 1. In general, the cumulative curves of solid fraction vs. solute composition fit well with the Scheil model description in accordance to the results obtained by Lacaze et al. for the quenched samples with 0.7 solid volume fraction.

Fig. 4. Backscattered electrons SEM image showing the lamellar eutectic ($\mu$ phase + gamma) between secondary arm dendrites.

Determination of the initial partition coefficients was performed for the low Nb content samples using area scanning measurements representing the average chemical composition of the primary dendrites and the overall composition of the eutectic constituent.
The obtained results are included in Table 1. For this experimental methodology, it was assumed that the overall composition measured on the eutectic constituent area represent the liquid composition at the temperature of quenching.

**Ni-Fe-Nb system**

**Binary Systems**

Recently, the Fe-Ni system was remodeled to consider the ordering in the $\gamma$-FeNi$_3$ phase. The Fe-Nb and Ni-Nb binary systems were also remodeled by Toffolon and Chen, respectively. These three binary systems are in better agreements with the experimental data than the TTNi6 Ni-database, especially Laves (Fe,Nb) phase in the Fe-Nb system and $\mu$ (Nb,Ni) phase in the Ni-Nb system.

The $\mu$ phase is one of the stable phases in the Fe-Nb and Nb-Ni binary systems, but different sublattice models were introduced, i.e., $(\text{Fe},\text{Nb})_4(\text{Fe},\text{Nb})_4(\text{Fe})_6$ used in the Fe-Nb system, whereas $(\text{Nb},\text{Ni})_4(\text{Nb},\text{Ni})_4(\text{Nb},\text{Ni})_6$ employed in the Nb-Ni system. The sublattice model of the same phase in the binary systems needs to be consistent in order to model the ternary system.

**Development of the Ternary System**

Based on the three binary systems, the Ni-Fe-Nb ternary system has been modeled herein. The compositions of ternary alloys measured at 1473K by Takeyama et al. were employed to model the ternary interaction parameters of the liquid phase. In the present work, ternary intermetallic compounds were ignored, though one compound with hexagonal structure was reported at composition around Ni-22Nb-20Fe (at.%), but the detailed information is still not available for this compound such as the melting point and enthalpy of formation, etc.

<table>
<thead>
<tr>
<th>MDTA Experiment sample</th>
<th>Assumptions</th>
<th>Mean partition coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-5Fe-3Nb</td>
<td>Overall composition.</td>
<td>$K_{\text{Nb}}$ $K_{\text{Fe}}$</td>
</tr>
<tr>
<td>Ni-36Fe-3Nb</td>
<td>of eutectic constituent equal to $C_1$</td>
<td>0.52 1.03</td>
</tr>
<tr>
<td>Ni-5Fe-5Nb</td>
<td>Scheil fitting</td>
<td>0.63 1.05</td>
</tr>
<tr>
<td>Ni-36Fe-5Nb</td>
<td></td>
<td>0.29 1.05</td>
</tr>
</tbody>
</table>

**Prediction of Partition Coefficient for the Ni-Fe-Nb Alloys**

The partition coefficients of Fe and Nb in the Ni-Fe-Nb alloys were calculated based on the current model and the TTNi6 Ni-database. Fig. 8 illustrates the calculated partition coefficients of
 Nb and Fe as a function of solid fraction in the Ni-5Fe-3Nb and Ni-36Fe-5Nb (wt. %) alloys by equilibrium calculations. Experimental results for the initial partition coefficients are included. In Fig. 9, the results using the Scheil model are presented including the experimental results obtained by Scheil equation fitting. Fig. 8 shows that the partition coefficient of Fe increases as increasing the content of Fe in the alloy while, in case of Nb, the partition coefficient decreases for both the current model and the TTNi6 Ni-database. The same tendencies were observed for equilibrium and Scheil calculations (cf. Fig. 9).

Comparing with Theoretical Values

The experimental analysis of MDTA samples of the Ni-Fe-Nb system by the methodology of fitting to Scheil equation showed that the partition coefficient of Nb decreased with the increase of Fe content (higher segregation tendency), in agreement with the thermodynamic modeling of the ternary Ni-Fe-Nb system performed using both the database developed in the present work and the TTNi6 Ni-database. This result is in accordance to the experimentally determined trend reported by Yang et al. for commercial superalloys with different amounts of Fe, and with the redistribution modeling results reported by DuPont et al. This result supports the explanation that associates the negative curvature with noise of the X-ray measurements.

Fig. 8 shows that most of measurements have good agreement with the equilibrium predicted values; however there is a relatively large difference for the partition coefficient of Fe of Ni-36Fe-5Nb. The same trend was observed in Fig. 9 when the Scheil model was used. The difference, which remains to be resolved, could be associated to the fact that the solidification on the experiments occurred in global conditions that depart from equilibrium, but it seemed to be more likely related to difficulties in the measurement, because the predicted values from both the current model and the TTNi6 Ni-database are similar.

Summary

Experimental measurements of the partition coefficients of Nb and Fe were obtained for different compositions of the Ni-Fe-Nb ternary system. Computational thermodynamic modeling of the
Ni-Fe-Nb ternary system is performed based on three binary systems and the available experimental data. The sublattice model for the μ phase in the Fe-Nb binary system was also updated to keep consistency with the Nb-Ni binary system. The partition coefficients of the current model and the TTNi6 Ni-database are calculated and they agree with experimental data but it is shown that the measured partition coefficients of Fe for the alloy containing Fe of 36 wt. % have relatively large differences with the calculated results. The discrepancies remain to be resolved.

REFERENCES


