



## THE INFLUENCE OF Nb AND C ON THE SOLIDIFICATION MICROSTRUCTURES OF Fe-Ni-Cr ALLOYS

J.N. DuPont<sup>1</sup> and C.V. Robino<sup>2</sup>

<sup>1</sup> Lehigh University, Bethlehem, PA

<sup>2</sup> Sandia National Laboratories, Albuquerque, NM

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### Introduction

There have been numerous experimental investigations into the solidification behavior of Nb strengthened superalloys [1–6]. This research has been motivated by the need to understand and control the microstructures of many commercially available Nb bearing alloys that are often fabricated by solidification processes such as casting and welding. It is now well established that these alloys generally solidify by a three step process [2,5,7] which includes 1) primary  $L \rightarrow \gamma$  solidification, followed by 2) a  $L \rightarrow (\gamma + \text{NbC})$  eutectic-type reaction which occurs over a broad temperature range, followed by 3) a terminal  $L \rightarrow (\gamma + \text{Laves})$  eutectic-type reaction which occurs over a smaller temperature interval. This solidification process is very similar to what is expected in the simple Ni-Nb-C system [5,7]. In view of this, it is not surprising to find [1,7] that minor additions of Nb and C have a strong influence on the transformation temperatures of the  $L \rightarrow (\gamma + \text{NbC})$  and  $L \rightarrow (\gamma + \text{Laves})$  eutectic-type reactions as well as the relative amounts of  $\gamma/\text{NbC}$  and  $\gamma/\text{Laves}$  constituents that form during solidification. Recently, a pseudo ternary  $\gamma$ -Nb-C solidification model has been developed to provide a quantitative description of the solidification behavior of austenitic alloys containing Nb and C [9]. The model is based on the Ni-Nb-C ternary system, where Nb and C are treated as the solutes and the (Fe,Ni,Cr) matrix elements are grouped together to form the  $\gamma$  “solvent” of the “ternary” system. Solute redistribution behavior is modeled for the realistic case of negligible solid state diffusion of Nb [2,8] and infinitely fast diffusion of C [8,10]. The model was validated by comparing calculated amounts of the  $\gamma/\text{NbC}$  and  $\gamma/\text{Laves}$  eutectic-type constituents with experimental measurements made on gas tungsten arc fusion welds in experimental Ni base (approximate proportions of 11Fe-Bal. Ni-20Cr) and Fe base (Bal. Fe-31Ni-20Cr) austenitic alloys, and good agreement was found [9]. The major application of such a verified model lies within its ability to interpolate solidification behavior over a broad range of composition. Thus, in this article, the model is used to explore the influence of nominal alloy composition on phase formation with the intent of providing guidance to alloy optimization efforts on materials of similar composition.

### Model Approach and Assumptions

The solidification model is explained in detail elsewhere [9]. Briefly, solute redistribution calculations are based on an approach developed by Mehrabian and Flemings [11] in which the classical single solute Scheil equation [12] was extended to ternary alloys by accounting for two solutes. The pertinent assumptions include: 1. negligible dendrite tip undercooling, 2. maintenance of thermodynamic equilibrium at the solid/liquid interface, 3. infinitely fast diffusion of each solute in the liquid, and 4. negligible diffusion of Nb in the solid. The only difference between the present approach and the M-F model is that the second solute, in this case C, is allowed to diffuse infinitely fast in the solid so that the lever rule is satisfied [8,10].  $\gamma$ -Nb-C pseudo ternary solidification surfaces, analogous to the liquidus projection in a true ternary system, were experimentally determined using electron probe microanalysis [8]. Experimental results showed that the nominal Fe content of the alloy had a significant effect on the segregation potential of Nb as well as the Nb content in the liquid needed to satisfy conditions for the  $L \rightarrow (\gamma + \text{Laves})$  reaction. Thus, two solidification surfaces were determined: one for Ni-base alloys (11Fe-Bal. Ni-20Cr) in which  $k_{\text{Nb}} = 0.45$  (where  $k$  is the equilibrium distribution coefficient) and the  $L \rightarrow (\gamma + \text{Laves})$  reaction occurs when the liquid reaches 23.1 wt% Nb, and a second for Fe-base alloys (Bal. Fe-31Ni-20Cr) in which  $k_{\text{Nb}} = 0.25$  and the  $L \rightarrow (\gamma + \text{Laves})$  reaction occurs when the liquid reaches 20.4 wt% Nb. Silicon will also decrease the amount of Nb needed in the liquid to satisfy conditions for the  $L \rightarrow (\gamma + \text{Laves})$  reaction [8], but the effect is not as great as Fe under the range of Si levels of interest (0.03 to 0.60 wt%). Thus, the solidification diagrams developed apply to alloys with Si additions within this range. All of the details on the model, along with sample calculations and comparison to experimental results, can be found in [9].

### Results and Discussion

Figure 1a shows the variation in calculated combined total eutectic-type constituent ( $\gamma/\text{NbC} + \gamma/\text{Laves}$ ) as a function of nominal alloy composition for Ni base alloys ( $k_{\text{Nb}} = 0.45$ ) over the range of alloy compositions which are of typical interest [1–9]. The results are presented in weight percentages. However, previous work on Ni base alloys has shown the densities of each constituent are similar [2]. Thus, the values can also be used to represent the volume percentages. Similar calculated results are presented in Figure 1b for the Fe base alloys ( $k_{\text{Nb}} = 0.25$ ). (No data is available for the densities of constituents in Fe base alloys, but it is reasonable to assume their densities are also comparable.) The combined ( $\gamma/\text{NbC} + \gamma/\text{Laves}$ ) content increases with increasing amount of Nb and C in the alloy. The total eutectic-type constituent is simply equivalent to the amount of liquid which exists when the primary  $L \rightarrow \gamma$  solidification path intersects the line of two-fold saturation separating the  $\gamma$  and NbC phases (i.e., the “eutectic” composition). As the alloy is enriched in Nb and C, the nominal alloy composition moves closer to the eutectic composition and, as a result, less primary  $\gamma$  forms in the alloy. At any given nominal alloy composition, the Fe base alloys always form more total ( $\gamma/\text{NbC} + \gamma/\text{Laves}$ ) eutectic-type constituents. This occurs because Fe additions increase the segregation potential of Nb (i.e., lowers  $k_{\text{Nb}}$ ) and also lowers the liquid composition needed to satisfy conditions for the  $L \rightarrow (\gamma + \text{Laves})$  reaction (i.e., the lowers the eutectic composition). Each of these factors will increase the amount of eutectic-type constituent which forms during solidification.

Figures 2 and 3 show the individual amounts of  $\gamma/\text{NbC}$  and  $\gamma/\text{Laves}$  which form during solidification. Again, the Fe base alloys will always form more of each constituent for the reasons discussed above. In Figure 2, the kinks in the curves represent the locus of compositions at which the  $\gamma/\text{Laves}$  constituent begins to form. Alloy compositions to the left of these kinks do not form any  $\gamma/\text{Laves}$  and the amount of  $\gamma/\text{NbC}$  constituent is therefore equal to the total amount of eutectic constituent. Alloy

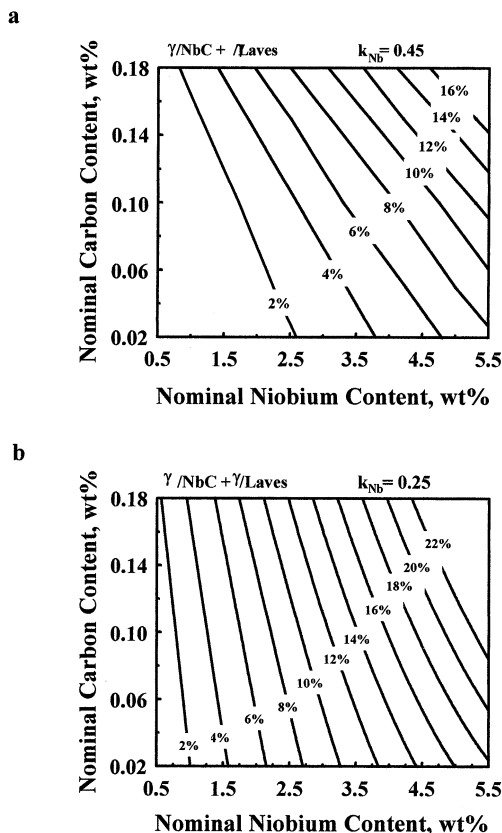


Figure 1. Calculated total eutectic constituent as a function of nominal alloy composition. a) Ni base alloys, b) Fe base alloys.

compositions to the right of the kinks will always form some  $\gamma$ /Laves. This transitional behavior is given by the 0% curve in Figure 3, which traces out the kinks in the curves presented in Figure 2. It is interesting to note that the iso-weight percentage curves for each constituent move in different directions; the  $\gamma$ /NbC constituent is favored by additions of both Nb and C while the  $\gamma$ /Laves constituent is promoted by alloys with low C and high Nb. Thus, although there is a wide range of alloy compositions which can lead to formation of identical amounts of the  $\gamma$ /NbC constituent, the amount of  $\gamma$ /Laves will be much different. This effect is linked to the influence of alloy composition on the primary solidification path. As the carbon content of the alloy increases, the primary solidification path extends farther into the C rich side of the solidification surface [9]. When the  $L \rightarrow (\gamma + \text{NbC})$  is initiated, the liquid composition must “travel” a long distance down the line of two-fold saturation separating the  $\gamma$  and NbC phase fields before the composition conditions for the  $L \rightarrow (\gamma + \text{Laves})$  reaction is satisfied in the liquid. Much of the liquid is consumed and converted to  $\gamma$ /NbC as the liquid composition “travels” down the two-fold saturation line, thus leading to high amounts of  $\gamma$ /NbC for alloys rich in C. In alloys which have a high C/Nb ratio, it is even possible for all the liquid to be consumed during the  $L \rightarrow (\gamma + \text{NbC})$  reaction so that none of the  $\gamma$ /Laves constituent forms [9]. In contrast, when the C content of the alloy is low, the primary solidification path travels very close to the  $\gamma$ -Nb “binary” edge of the solidification surface because the interdendritic liquid never becomes significantly enriched in C. Under this condition, very little liquid is consumed and converted to  $\gamma$ /NbC

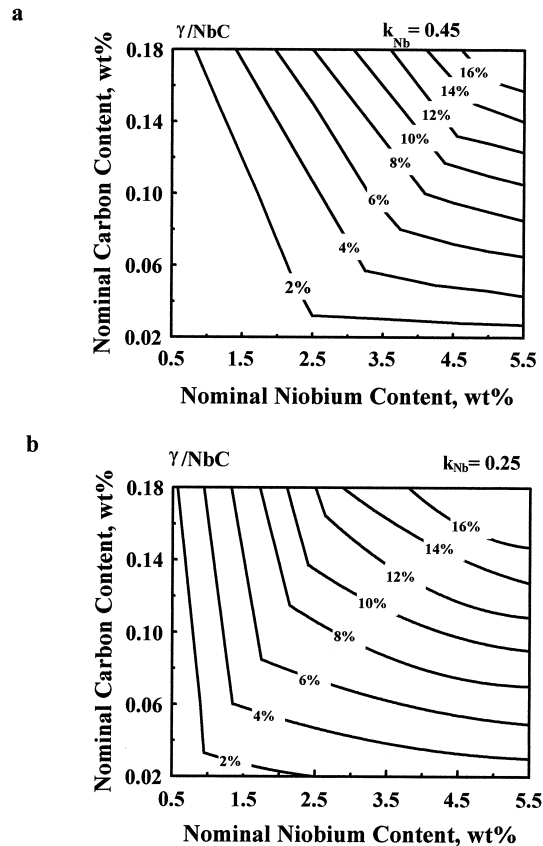


Figure 2. Calculated austenite/NbC constituent as a function of nominal alloy composition. a) Ni base alloys, b) Fe base alloys.

as the liquid travels only a short distance down the two-fold saturation line. Thus, there is still a relatively large amount of liquid left when the composition conditions required for the  $L \rightarrow (\gamma + \text{Laves})$  reaction are satisfied, and all this liquid is converted to  $\gamma/\text{Laves}$  as solidification goes to completion. These differences in solidification path account for the variations in  $\gamma/\text{NbC}$  and  $\gamma/\text{Laves}$  contents with nominal alloy composition.

The results presented here provide useful guidance into optimization of solidification microstructures for various purposes. For example, it has been shown that the solidification cracking susceptibility of (Fe-Ni-Cr-Nb-C) experimental alloys [13] and commercial alloys of similar composition [2–4] is controlled by the alloy composition and its resultant influence on the solidification path and amount of each eutectic-type constituent. Alloys that are relatively high in C and form less than two percent of the  $\gamma/\text{Laves}$  constituent exhibit excellent resistance to solidification cracking. The results presented here are useful for identifying the range of alloy compositions which display such behavior. However, it should also be noted that effects from additional solutes such as Mo and Si can change these results in a way which is not captured quantitatively here. For example, Mo and Si are each Laves stabilizers and behave in a manner similar to Fe in that they lower the amount of Nb required in the liquid to initiate the  $L \rightarrow (\gamma + \text{Laves})$  reaction [2,8]. As noted earlier, the solidification surfaces were developed from alloys with approximately 0.03 to 0.60 wt% Si (but no Mo additions). As a result, alloys with higher Si contents

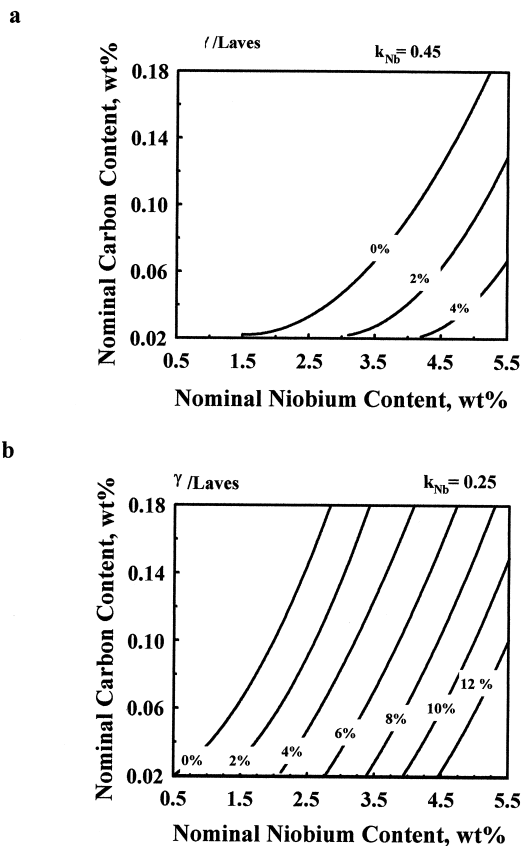


Figure 3. Calculated austenite/Laves constituent as a function of nominal alloy composition. a) Ni base alloys, b) Fe base alloys.

and/or Mo additions will generally form more eutectic type constituents. Also, alloys with intermediate Fe contents will lead to results which lie between the two cases presented here. A recent correlation between nominal Fe content and  $k_{Nb}$  has been presented which can be used to account for this behavior [8]. Such effects need to be considered when applying these results to alloys with significant differences in composition.

### Summary

A parametric analysis is presented which summarizes the amount of total ( $\gamma/NbC + \gamma/Laves$ ) and individual  $\gamma/NbC$  and  $\gamma/Laves$  constituents which form during solidification of  $\gamma_{(Fe,Ni,Cr)}$  alloys with variations in nominal Nb and C contents. Calculated results are presented for Fe base alloys and Ni base alloys. The results provide a quantitative rationale for understanding the relation between alloy composition and solidification microstructures and should provide useful insight into commercial alloys of similar composition.

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