

Center Segregation, Freckles and Development Directions
for Niobium-Containing Superalloys

P. Auburtin, S.L. Cockcroft, A. Mitchell, A.J. Schmalz

Department of Metals and Materials Engineering
University of British Columbia, Vancouver, Canada

Abstract

Macrosegregation defects, such as freckles and center-segregates, are currently one of the main problems encountered by attempts at scaling-up ingot diameters in order to supply industrial gas turbine manufacturers. Focusing on niobium-containing superalloys (IN718, IN706 and IN625), interdendritic liquid segregation and density profiles are presented, and the occurrence of fluid flow leading to macrosegregation is linked to the solidification sequence of these alloys. This paper also mentions the possible use of the Rayleigh number as a criterion to predict detrimental fluid flow patterns. Finally, it is suggested that slight modifications of alloy chemistry may be the only way to eliminate fluid flow related macrosegregation in conventional remelting processes.

Introduction

Niobium was originally added to superalloy formulations with the intention of adding a second precipitation hardening mechanism through the formation of delta phases. It was soon recognized that although this addition did indeed widen the window of forging parameters in respect of grain-size control, it also brought the significant disadvantages of primary carbide and Laves phase formation, and the introduction of another highly-segregating element. These latter disadvantages have provided the fundamental reasons why ingots of niobium-containing superalloys are difficult to manufacture in large section to high quality standards. Whether the ingots are made by VAR, ESR or alternative processes, we face the recurrent problems of freckles, center segregation, carbide size and the presence of Laves phases to some degree in all of these alloys.

Solidification Sequence

The solidification sequence of the alloys is typified by that of IN718, which has been reported in reference [1]. Although there is still disagreement in the literature as to the precise sequence of precipitation in the final eutectic reactions, there is general acceptance concerning the early stages of solidification which are the reactions principally influencing the segregation structure. The first phase to precipitate is a gamma solid solution, containing some of the alloy element content but rejecting a large fraction of the titanium and niobium present. The sequence of concentration variation in the interdendritic liquid remaining during solidification of IN718 has been measured by the authors in previous works [2,3] and is presented in Figure 1. The fraction liquid was also measured and is presented in the same Figure. Nominal compositions and melting range of IN718

and other alloys considered in this article are presented in Table I. Based on these results, initial partition coefficients k_o were estimated for each element using the well-known Scheil equation. The concentration profiles back-calculated by the Scheil equation are depicted as solid lines in Figure 1, and show very good agreement with the measured data. The values of k_o used in this study are presented in Table II and show relatively good agreement with literature data. Using these estimations of the elemental segregation coefficients, we may also compute the composition changes expected in other Nb-containing alloys with a chemistry similar to that of IN718, for example, IN706 and IN625, and these are shown in Figures 2 and 3. Titanium and niobium (as seen in Figures 1 to 3), as well as carbon, highly segregate into the interdendritic liquid up to levels yielding the precipitation of mixed primary carbides (Nb,Ti)C. This primary carbide precipitation occurs in all three alloys IN718, IN706 and IN625, although possibly at different stages during the solidification process. Previous work [4] has shown that the largest carbides are those which are precipitated at this point in the solidification sequence, their size distribution increasing with the local solidification time (LST) in the ingot or casting [5]. The remaining primary carbides (representing almost all of the alloy carbon content in the liquid at the eutectic reaction temperature) are formed in a narrow temperature range and have a size distribution with a smaller average dimension. Since the low cycle fatigue (LCF) properties of the alloys depend substantially on the size of the largest carbides, it follows that the LCF behavior of the product derived from a segregation-free ingot would be strongly influenced by the precipitation temperature and growth time of the first primary carbides to precipitate. Since an increase in ingot diameter can only be achieved with longer LST's, this latter feature presents an obvious upper limit to the ingot or casting section which can be produced by conventional remelting techniques. However, the most serious limitation lies in the non-equilibrium behavior of the interdendritic liquid, as detailed below.

Table I : Measured and nominal alloy compositions.

	Al	Ti	Cr	Fe	Ni	Nb	Mo	Si	C	$T_{Sol} - T_{Liq}$
IN718*	0.6	1.0	15.0	17.7	54.9	6.1	3.7	-	-	1260-1336
IN718 ⁺	0.5	0.9	19.0	18.5	52.5	5.6	3.0	0.2	0.04	1260-1336
IN706 ⁺	0.2	1.8	16.0	39.0	40.0	2.9	0.0	0.2	0.03	1335-1370
IN625 ⁺	0.2	0.2	21.5	2.5	61.0	3.6	9.0	0.2	0.05	1290-1350

(* : Experimentally measured by microprobe ; ⁺ : Nominal)

Note 1 : The lower measured chromium level in IN718 indicates a noticeable loss during vacuum melting, but this does not invalidate the following discussions.

Note 2 : Due to the limitations of microprobe technology, silicon and carbon levels could not be measured in IN718. Subsequent calculations of density in IN718 do not take Si or C into account.

Table II : Initial partition coefficients k_o in IN718.

	Al	Ti	Cr	Fe	Ni	Nb	Mo	Si	C
k_o^*	1.20	0.55	1.12	1.16	1.02	0.35	0.90	-	-
k_o^+	-	0.63	1.02	1.06	1.05	0.48	0.87	0.48	0.3

(* : Present study ; ⁺ : Reference [6])

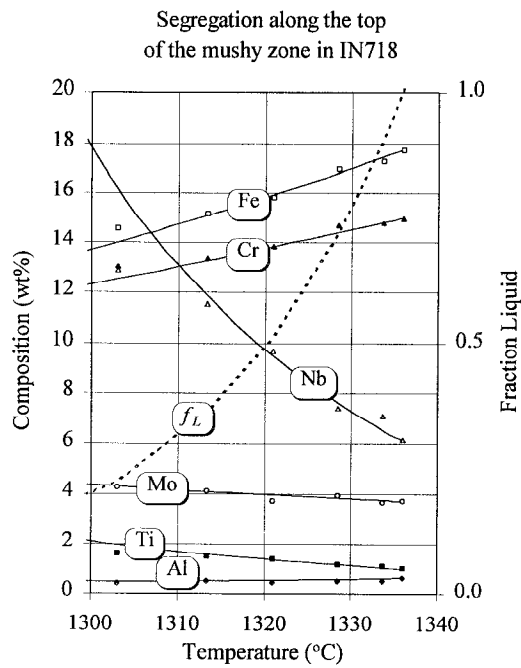


Figure 1 : Segregation profiles in IN718.

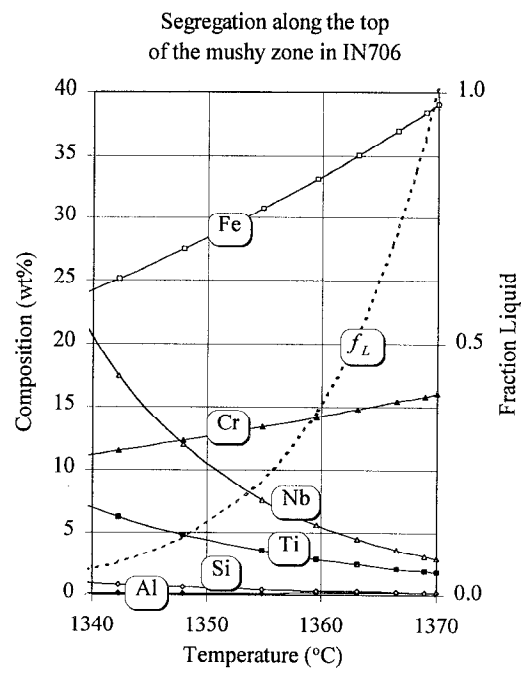


Figure 2 : Segregation profiles in IN706.

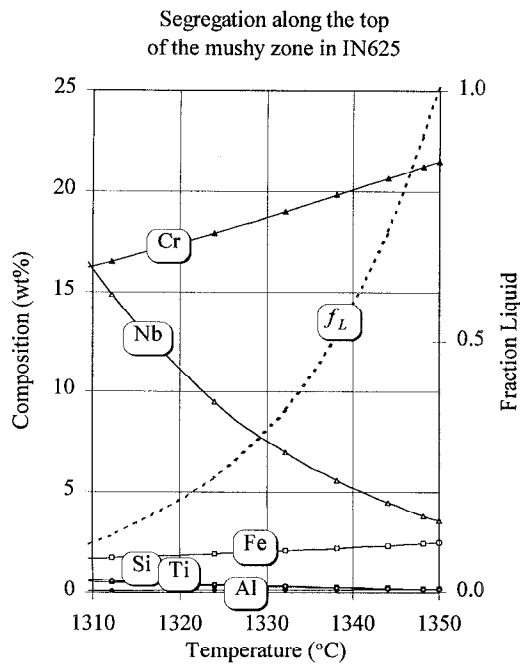


Figure 3 : Segregation profiles in IN625.

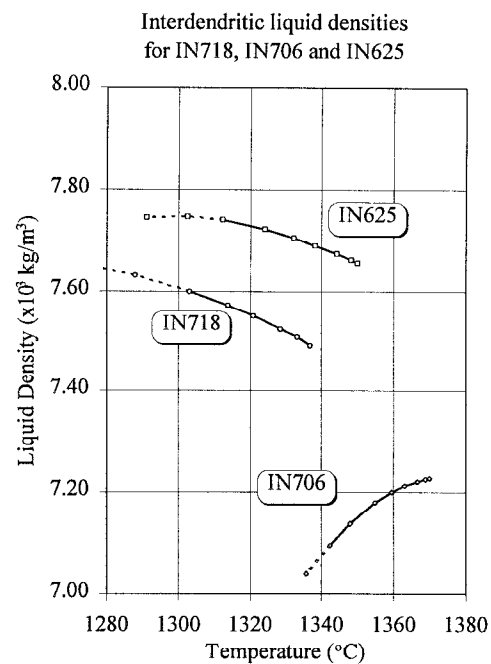


Figure 4 : Interdendritic liquid density profiles of IN718, IN706 and IN625.

Interdendritic Fluid Flow

The changes in the liquid density resulting from the segregation during freezing may be computed and are shown in Figure 4 for IN718, IN706 and IN625 (the details of the numerical model used to calculate the liquid density of an alloy of given temperature and composition have been described previously [2,3]). The effect of primary carbide precipitation on interdendritic liquid density in these alloys is very small since niobium has almost the same density as nickel and the amount of carbon removed from solution is relatively small. IN718 and IN625 exhibit a very similar behavior, in which the interdendritic liquid is held to continuously increase in density during the solidification process. In IN706 on the contrary, the interdendritic liquid becomes increasingly lighter as segregation progresses, yielding a significant density inversion. This inversion (as well as the overall lower density of IN706 compared to IN718 and IN625) can be linked to the relatively high content of both Si and Ti in IN706.

Liquid density inversions have been shown [7-9] to be responsible for the phenomenon known as “freckle” in many grades of superalloys and steels. The density inversion results in liquid instability which is converted into a rising plume of “light” liquid by either thermal or mechanical transients. The plume has a steady-state lifetime during which it collects interdendritic liquid by fluid movement in a direction approximately at right angles to the growth direction, and is established over one or more primary dendrite spacings [7-9]. The freckle channels eventually freeze, as the thermal profile passes through the region, and the solid structure shows the characteristic local high concentration of carbides and eutectic. Studies of freckle compositions have also shown [2,3] that the plume is drawing liquid from the region of approximately 50% solid fraction, i.e. about 10-20°C below the liquidus temperature in the case of the alloys in question. The niobium-containing superalloys are held to be “freckle-prone”, but in view of the fact that niobium segregation does not of itself create large changes in the density of interdendritic liquid, it is necessary to further clarify the situation leading to this type of segregation problem.

The removal of Nb, Ti and C from the solution during the primary carbide precipitation cannot account for the required density inversion for freckle formation in IN718, since titanium and carbon are light elements. Moreover, the effects of small amounts of C and B on liquid alloy density are difficult to quantify by the numerical model because they are interstitial elements and do not follow the simple rule of mixtures. On the other hand, additions of silicon, aluminum or titanium decrease the density in the anticipated fashion although the quantitative effect is difficult to estimate with precision due to a lack of accurate thermochemical data on the solutions. It is seen from Figure 4 that a relatively small change in the segregation concentrations of Al, Ti and Si can produce a radically-different density gradient in the two alloys IN718 and IN706. It is probable that the alloy silicon content is responsible for the reported “freckles” observations. IN718 formulations of 10 or 20 years ago contained much more silicon than is normally present in today’s alloys. This higher level of silicon would have been sufficient to produce the necessary density inversion during solidification and hence to create a stable freckle plume. Over time, the silicon level has been lowered, ostensibly to reduce Laves phase formation, but at the same time the “freckle” morphology has changed into one in which the segregation channels are approximately parallel to the liquidus line rather than parallel to the growth direction. In these latter alloy ingots, the segregation liquid flow appears to have been one of heavy liquid seeping through the dendrite network towards the center of the ingot. Subsequent examination of heavily-forged billets has mis-identified the defect as classic freckle. The flow results from a density change, and also probably takes place at the same point in the solidification profile as does freckle flow, but the mechanism is substantially different. Microprobe analysis and density evaluation of freckles in recent VAR IN718 ingots also indicate that freckles are indeed heavier than the surrounding bulk metal, further confirming the above conclusion.

The development of fluid flow has been characterized by various mathematical expressions, but the characteristic dimensionless Rayleigh number presented below appears to best describe the components of the flow mechanism, as discussed by Auburtin [10].

$$Ra = \frac{g \cdot \frac{d\rho}{dz}}{\eta \cdot D_T / \lambda_1^4} \quad (1)$$

where : g = gravitational constant, η = dynamic viscosity,
 ρ = density, D_T = thermal diffusivity,
 z = vertical coordinate, λ_1 = primary dendrite arm spacing.

It is seen from the above that the most important parameters of the flow system are the density gradient and the interdendritic spacing. The former controls the driving force for the flow; the latter represents the resistance to flow. Based on numerical expressions of permeability in a dendritic network as reported by Poirier [11], the resistance to flow parallel to the growth direction is about twice that perpendicular to it, at an intermediate stage in the solidification process (around 50% fraction liquid)[10]. For alloys with a density inversion during solidification this feature accounts for the observation that freckle formation in castings is found invariably on the cast surface, whilst in remelt ingots of the same alloys the freckle incidence is usually greatest at the mid-radius [10]. The conventional technique for eliminating freckles in an ingot or cast structure is to reduce the dendrite spacing through reducing the local solidification time. In the remelting processes, this method has obvious limitations, arising in the Biot and Fourier criteria for heat flow in the system, and previous reports [12] have made it clear that for any given ingot diameter in either ESR or VAR there is an optimum condition of melting rate, which as the ingot diameter is progressively increased, may exceed the required local solidification time for the desired dendrite spacing. At this point, then it is not possible to make the required structure under any conditions of process parameter combination.

Although there have been several reports (referenced in [10]) of casting development using the Rayleigh number or similar criteria to establish appropriate freezing conditions, this method has not yet found general applicability to ingot structures. Based on the thermal profiles developed in a typical remelt ingot [5], it is possible to compute the local Rayleigh number, as shown in Figure 5. How this may be used to predict the presence or absence of segregation problems is, however, a more complex issue. Models of directional casting processes invariably assume that the growth direction is in the vertical sense. The Rayleigh criterion is hence computed on the basis of primary dendrite arm spacing with all forces having only vertical components and the subsequent freckle plume is assumed to move vertically. In a remelt ingot, this situation is not the case, as all isotherms have a definite curvature established by the process heat balance. Parameters such as “permeability” will therefore be directional and lead to a requirement for additional modifications to the formula given above. It is, however, probably correct to state that interdendritic fluid-flow of any kind is possible only when the local conditions conform to a particular maximum value of the Rayleigh number, calculated on the basis of a particular direction in the structure. Such a criterion would then indicate when segregation flow was possible, but would not predict that it would definitely take place.

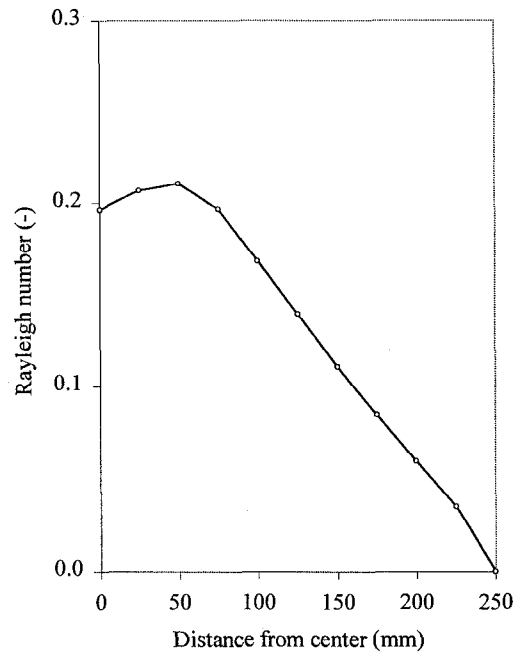


Figure 5 : Rayleigh number profile in a typical 500mm diameter VAR IN718 ingot.

The Manufacture of Heavy-Section Nb-containing Superalloys

The above discussion indicates the possibilities of predicting when segregation flow is likely to cause defects in an ingot or casting. The point at issue is, however, to extend this description towards an understanding of how to modify processes or alloys so as to minimize the problem. As we examine the components of the Rayleigh criterion, it is clear that most of them cannot be changed through process variables, since they are set by intrinsic properties or the Biot and Fourier function of the process. The most promising direction for development is that of modifying the alloy composition so as to minimize both the density gradients developed during solidification and the harmful effects of precipitation in the final eutectic regions.

The density gradients in this range of alloys are established principally by the segregation of Ti and Si. Although niobium segregates very strongly, the effect on liquid density is small. The principal elements of high density which segregate positively in these systems are Hf and Zr, both of which might potentially be substituted for a certain fraction of the Ti content. Since silicon is not a deliberate addition to the alloy, a reduction to the lowest practical value (as is frequently practiced at present) is indicated. If we assume that the silicon content has been reduced to less than 100ppm, the amount of Hf required to balance the density gradient in IN706, for example would be about 0.1wt%, as shown in Figure 6.

In an alloy with an elemental balance such that the interdendritic liquid has no, or very small, density gradient, the process limits would be set by the primary precipitation reactions, in particular the formation of the primary carbides. A small content of carbon is necessary in the alloy formulation so as to preserve the secondary solid-state precipitation of the carbides M_6C and $M_{23}C_6$ at heat-treatment temperatures, which will inevitably result in the precipitation of primary carbides during solidification. The carbon contents of the present commercial alloys have, however, not been optimized from the viewpoint, and probably contain a considerable excess of carbon over that required to provide secondary carbide precipitation.

In the example alloy IN718, the lowering of the carbon content to 80ppm completely removes primary NbC precipitation, with a concurrent substantial decrease in the average carbide size. It is likely that the same process applies to other alloys in this series, although since HfC is extremely stable, caution would have to be applied to the alloy balancing advocated above.

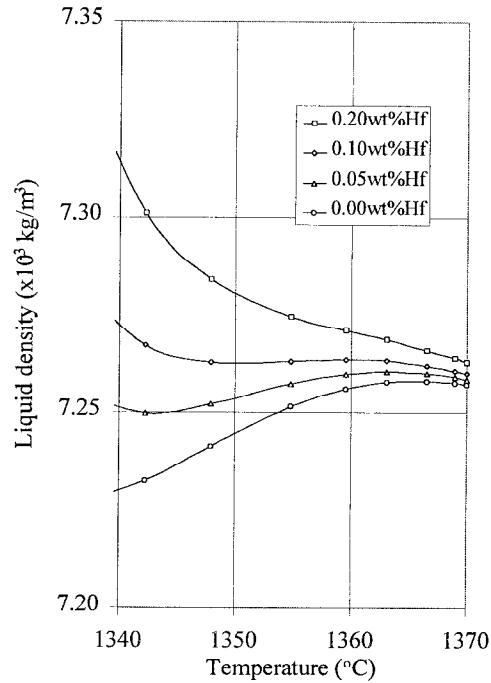


Figure 6 : Interdendritic liquid density along the mushy zone of IN706 for various hafnium contents.

Conclusions

- The segregation profiles, as well as density profiles, in the interdendritic liquid of IN718, IN706 and IN625 have been presented.
- The influence on interdendritic liquid density of the segregation and/or precipitation of various alloying elements was discussed.
- It was concluded that freckles in these alloys probably arose from the high silicon content present 20 years ago. On the other hand, today's much lower silicon levels may now account for pockets of center segregation, mis-identified as "freckles" for historical reasons.
- The onset of interdendritic fluid flow, whether leading to freckles or center-segregates, is probably best described by the Rayleigh number, although in its current form, this latter may be more suitable for vertical directional solidification than ingot remelting geometry.
- Since process parameters may be difficult or impossible to adjust to avoid fluid flow related macrosegregation in conventional remelting processes, it is suggested that alloy chemistry be slightly altered in order to eliminate any density gradients during solidification.

Acknowledgments

The authors would like to acknowledge the support from the Nickel Development Institute. They would also like to thank National Physical Laboratories for providing the much needed "METALS" model. Finally, the assistance from the following companies was also most appreciated : Asea Brown Boveri, Aubert & Duval, Inco Alloys International, Rolls-Royce, Sandia, Special Melted Products, Special Metals Corporation, Teledyne/Allvac Vasco and Pratt & Whitney Aircraft Engines.

References

1. B. Radhakrishnan, R.G. Thompson, Met. Trans. A, 20A (1989), 2866-2868.
2. P. Auburtin, "Determination of the influence of interdendritic segregation during the solidification of freckle-prone alloys", M.A.Sc. Thesis, University of British Columbia, Canada (1995).
3. P. Auburtin, S.L. Cockcroft, and A. Mitchell, "Liquid density inversions during the solidification of superalloys and their relationship to freckle formation in castings", Superalloys 1996, ed. R.D. Kissinger et al., Min. Met. & Mat. Soc., Seven-Springs (Sept. 1996), 443-450.
4. A. Mitchell et al., High Temp. Mat. and Proc., Vol. 15, No 1-2 (1996), 27-40.
5. A.S. Ballantyne, A. Mitchell, and J.F. Wadier, "The prediction of ingot structure in VAR/ESR Inconel 718", Proc. of 6th Int. Vac. Met. Conf., ed. G.K. Bhat and R. Schlatter, San Diego (Apr. 1979), 599-623.
6. G.A. Knorovsky et al., "Inconel 718 : a solidification diagram", Met. Trans. A, Vol. 20A (1989), 2149-2158.
7. A.F. Giamei, B.H. Kear, "On the nature of freckles in nickel base superalloys", Met. Trans., Vol. 1 (August 1970), 2185-2192.
8. S.M. Copley et al., "The origin of freckles in unidirectionally solidified castings", Met. Trans., Vol. 1 (August 1970), 2193-2204.
9. J.R. Sarazin, A. Hellawell, and R.S. Steube, "Channel convection in partly solidified systems", Phil. Trans. R. Soc. Lond., A (1993) 345, 507-544.
10. P. Auburtin, A. Mitchell, "Elements of determination of a freckling criterion", Proc. Vac. Met. Conf., ed. A. Mitchell and P. Auburtin, Santa Fe (Feb. 1997), 18-34.
11. D.R. Poirier, "Permeability for flow of interdendritic liquid in columnar-dendritic alloys", Met. Trans. B, Vol. 18B (1987), 245-255.
12. A.S. Ballantyne, A. Mitchell, Proc. of 6th Int. Vac. Met. Conf., ed. G.K. Bhat and R. Schlatter, San Diego (Apr. 1979), 581-598.