**Solute redistribution and Rayleigh number in the mushy zone during directional solidification of Inconel 718**

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**Abstract:** The interdendritic segregation along the mushy zone of directionally solidified superalloy Inconel 718 has been measured by scanning electron microscope (SEM) and energy dispersion analysis spectrometry (EDAX) techniques and the corresponding liquid composition profile was presented. The liquid density and Rayleigh number (Ra) profiles along the mushy zone were calculated as well. It was found that the liquid density difference increased from top to bottom in the mushy zone and there was no density inversion due to the segregation of Nb and Mo. However carbide formation in the freezing range and the preferred angle of the orientated dendrite array could prompt the fluid flow in the mushy zone although there was no liquid density inversion. The largest relative Rayleigh number appeared at 1,326 ºC for Inconel 718 where the fluid flow most easily occurred.

**Key words:** superalloy; directional solidification; segregation; fluid flow

Inconel 718 is a Ni-Cr-Fe based superalloy containing a high content of alloying elements such as Mo, Nb, Ti, and Al. On the one hand, the addition of alloying elements makes Inconel 718 exhibit good performance at medium temperatures, and on the other hand, these added elements make Inconel 718 susceptible to heavy segregation and even macro-defects, such as freckles [1-8]. Freckles usually have diameters of more than 1 mm and are difficult to eliminate by pro-heat treatment and preprocessing. Therefore, ingots with freckles are scrapped, which limits the scale-up of the size and development of superalloy castings.

According to one of the traditional mechanisms, density inversion theory, freckles form by thermo-solutal convection driven by a density difference between the lighter liquid at the bottom of the dendrite and the heavier liquid at the dendrite tips. The Raleigh number is proportional to liquid density difference as given in literatures about freckles formation [1-4, 9-12] and its maximum value in the mushy zone can reasonably indicate the freckling tendency for an alloy. The larger the liquid density difference or density inversion, the bigger the absolute value of the Rayleigh number, and the higher the freckle formation tendency is. In this paper, the solute redistribution, liquid densities and the relative Rayleigh numbers at different locations in the mushy zone were calculated by the method provided in the references [9-12]. The purpose of the research is to analyze the density distribution in the mushy zone and the origination of the fluid flow for Inconel 718.

**1 Experimental procedures**

The chemical composition of Inconel 718 is listed in Table 1. The experimental materials were vacuum induction melted plus vacuum arc re-melted before the directional solidification experiment.

| Table 1: Chemical composition of Inconel 718 (wt %) |
|-----------------|---------------|--------|--------|--------|--------|      |
| C               | Nb            | Ti     | Al     | Mo     | Fe     | Cr    | Ni    |
| 0.021           | 5.36          | 0.97   | 0.56   | 2.98   | 19.93  | 17.72 | Bal.  |

The alloy under study was directionally solidified in a vacuum induction furnace and quenched in liquid metal of Ga-In-Sn. The cylindrical sample of 7 mm diameter (90–100) mm length was contained in an alumina tube which was withdrawn at rate of 20 µm/s, through a thermal gradient of 10 ºC/mm at the solidification front, leading to a dendrite network with a primary spacing of about 100 µm. Before complete solidification, the sample was quenched from the steady-state growth regime in order to reveal the solidifying structure without complications from diffusion during cooling.

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After the cylindrical sample was directionally solidified and quenched, the middle part cut from it, including the solid-liquid interface and the entire mushy zone (Fig. 1), was divided into two halves along its axis. One was used for longitudinal section microstructure observation and the other for the cross section microstructure observation in the mushy zone. For the latter, pieces of 0.5–4 mm thickness were sliced from it between the top and the bottom of the mushy zone. The observed longitudinal section and cross sections were finely polished and analyzed using SEM and EDAX techniques. The local temperatures \( T \), prior to quenching, were calculated for each cross section by using equation (1) (this temperature is easily calculated knowing the liquidus temperature \( T_{\text{liq}} \), the thermal gradient \( G \) and the distance \( h \) from the cross section to the tip of the dendrites).

\[
T = T_{\text{liq}} - h \cdot G
\]  

\( T \) is the temperature just before quenching, \( T_{\text{liq}} \) is the liquidus temperature, \( G \) is the thermal gradient, and \( h \) is the distance from the cross section to the tip of the dendrites.

Fig. 1: Schematics of the locations analyzed in the sample

On each cross section, at least five measurements of the quenched inter-dendritic liquid composition were made by EDAX. Other measurements, such as the composition at the dendrite centers and of some phases forming during solidification, were also carried out. All the major alloying elements (except for carbon) were included in the analysis. All the chemical compositions presented in this paper are averages of 5 or more direct EDAX measurements. The standard deviations are in the range of \( \pm 5\% \) for major alloying elements (content greater than 5\% by wt) and up to \( \pm 15\% \) for minor alloying elements (content less than 5\% by wt). Micrographs of the longitudinal section and cross sections at various depths in the mushy zone were also recorded.

The quenched inter-dendritic liquid (tertiary arms and dark eutectic precipitate) in the areas of EDAX analysis can be clearly distinguished from the dendrites (primary and secondary arms). The dendritic array was manually outlined on several micrographs. Image analysis software was then used to measure the area of the outlined dendrites relative to the total area of the micrograph. Thus the liquid fraction was estimated at various temperatures in the mushy zone. The standard deviation was less than \( \pm 5\% \) by wt.

Scheil simulation was employed to calculate the phases forming during non-equilibrium solidification and their mass fraction variation.

The freezing range of Inconel 718 is between 1,140–1,336 °C but there is still a little liquid (less than 5\%) below 1,140 °C and the composition and density of such liquid were analyzed as well.

2 Results and discussion

2.1 Solidification microstructures in the mushy zone

The directional solidification sample had typical dendritic microstructure as shown in Fig. 2. The solid-liquid interface was approximately plane and at right angles to the longitudinal axis with a maximum angle of tilt of less than 10 °, as shown in Fig. 2 (a). But the dendrites array orientation was not perpendicular to the solid-liquid interface (Fig. 2 (b)) and the angle was in the range of 30–50 ° under the experimental conditions. The prime dendrite arm spacing was about 100 µm.

The cross section microstructures located between the top and the bottom of the mushy zone are shown in Fig.3. It can be seen that more than 50 \% of the alloy had formed solid from liquid at 1,331 °C. As the temperature decreased, the residual liquid volume was reduced quickly to begin with but the transformation slowed down during later solidification. There was still about 10 \% of alloy as liquid in the microstructure at 1,316 °C and a small amount of residual liquid remained to a very low temperature.

Fig. 2: The longitudinal section microstructures of the directional solidification sample: the entire mushy zone (a); the dendrite array near the solid-liquid interface (b)
The transformation from liquid to solid was quick at the beginning of solidification but slowed finally. This was because, as the crystallization progressed, there were more and more low-melting point elements congregating in the residual liquid and the melt temperature of the residual liquid was lowered. There were no freckles observed in the directional solidification sample. This was mainly due to the relatively small cross section area of the sample (about 38 mm$^2$). It has been reported in the literature\cite{1, 10} that adjacent freckles are usually evenly spaced (about 5–10 mm apart, yielding about 25–100 mm$^2$ cross sectional area per individual freckle). This represents a minimum required area in order to support the fluid flow patterns associated with freckle formation (upward freckle plume and slow downward feed flow). In the present case, the directional solidification sample was too narrow to support such fluid flow cell and freckles could not develop.

2.2 Segregation and liquid fraction variation in the mushy zone

The inter-dendritic liquid segregation profile along the mushy zone for Inconel 718 measured by EDAX is presented in Fig. 4 (a). The profile is plotted against temperature in the melting range of Inconel 718. The dash dot line shows the variation in liquid fraction in the mushy zone. It can be seen that the content of Nb increased sharply and greatly during the beginning solidification. There was about 20 % by wt. Nb in the final liquid although there was only 5.36 % by wt. Nb in the nominal composition. The increase of the Nb content is concentrated at temperatures above 1,300 °C, by when the liquid fraction has dropped to less than 20 % of the original volume. The content of Mo was also significantly raised. However the content of Ti in the liquid fraction had only a slight increase during solidification. The concentrations of Fe and Cr were significantly reduced in the residual liquid with the decrease of temperature. The liquid fraction variation was consistent with that shown in Fig. 3.

In order to accurately investigate the segregation behavior during solidification of Inconel 718, the partition coefficients of the alloy elements between solid and liquid were calculated as well and the results are shown in Fig. 4 (b). For alloy elements of positive segregation, such as Nb and Mo, the ratios were less than 1 and the lower the partition coefficients, the higher the contents of them in the inter-dendritic liquid and the greater the segregation. It can be seen that the segregation of Nb and Mo was very great during solidification of Inconel 718 as their partition coefficients were much less than 1. But for elements Fe and Cr, the higher the partition coefficients, which are more than 1, the lower the concentration of them in the liquid was.

During the freezing of Inconel 718, the alloying elements will be redistributed between solid and liquid. The elements of positive segregation, such as Nb, Mo and Ti, will tend to remain in the liquid. So the concentration of them in the liquid will increase quickly as the liquid fraction decreases. On the other hand, the negative segregation elements, such as Fe and Cr, will concentrate in the solid. Because of the large atom size and low diffusion coefficient, Nb segregation is the most noticeable and the concentration of Nb reached as much as 20 % by wt. in...
Mo segregation was great as well and the content of it in the final solidified liquid exceeded about 9% by wt.

2.3 The liquid density variation along the mushy zone

The density profile in the inter-dendritic liquid of Inconel 718 along the melting range was computed from the composition profile shown in Fig. 4. In the calculation of the density variation in the inter-dendritic liquid, the chemical composition and temperature for a given cross section were mathematically translated into density by the method provided in the literatures [9, 10]. This calculation model is based on a weighted average of the molar volumes of each pure element forming the alloy and the “mixing molar volume”. This approximation is now confirmed to be more accurate than that without considering the “mixing molar volume”. The basic equations for this model can be written as follows:

\[
\rho = \frac{\sum X_i A_i}{V_i + \Delta V^M}
\]

\[
V_i = \frac{A_i}{\rho_i} \left[1 + 0.01 \times f(T)\right] \frac{\Delta V_M}{T_0}
\]

\[
f(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3
\]

\[
\Delta V_M = d_0 + d_1 X_1 + d_2 X_2 + d_3 X_3
\]

Where \(\rho\) is the liquid density; \(X_i\) the molar fraction of element \(i\); \(A_i\) is the atomic weight of element \(i\); \(V_i\) is the molar volume of the pure element \(i\); \(\Delta V^M\) is the mixing volume; \(\rho_i\) is the density of each element at 20 °C; \(a_0, a_1, a_2, a_3\) and \(d_i\) are thermal expansion coefficients for the elements of the superalloy; \(T\) is the local temperature; \(d_0, d_1, d_2\) and \(d_3\) are constants which are given in the literature [9]; \(X_i\) is the atom fraction of \(Al\); \(X_1\) is the atom fraction of \(Cr\) and \(Ti\); \(X_2\) is the atom fraction of \(Mo, W, Ta, Nb, Re\) and \(Hf\).

The calculated results for the liquid density are shown in Fig. 5. It was increasing from the top to the bottom of the mushy zone but had slight fluctuations at about 1,300 °C and 1,220 °C. There was no notable density inversion through the whole mushy zone. Although it was in contradiction to the density inversion theory, this observation was consistent with the result of density calculation of freckles to be heavier than that of the surrounding matrix [1]. Assuming that theory is true, the observations generated these explanations for the freckling fluid flow in the ingots of Inconel 718.

Firstly, there were phases forming during solidification which changed the real concentration and density distribution in the mushy zone. In the literature [1], freckles in Inconel 718 exhibit a large concentration of niobium carbides, and it is obvious that the effects of carbide formation on the freckling convection should be taken into account. The result of Scheil simulation of Inconel 718 is shown in Fig. 6. The calculated liquidus is slightly higher than that in the experiment. The phases forming in the freezing range mainly are MC and Laves in sequence. The temperatures at which MC and Laves begin to form are 1,246 °C and 1,140 °C, respectively in the simulation result. In fact, the precipitation temperatures of MC and Laves are often higher than that in the calculated results due to the heavy segregation of Nb. Large blocks of carbides are frequently observed in the inter-dendritic area in industrial ingots as shown in Fig. 7. Because precipitation of both MC and Laves consumes Nb and Mo from the liquid surrounding them, there will be a Nb/Mo-depleted region near them in the
liquid and a low density region can be generated. The resulting local liquid density inversion changes the mono increasing distribution of liquid density from top to bottom in the mushy zone of Inconel 718 which should be taken into account when considering the triggering of liquid flow related to liquid density inversion.

Secondly, the inter-dendritic liquid of Nb-bearing superalloys flows approximately perpendicularly to the primary dendrite in the mushy zone according to the literatures [13, 14] and the flow driven force is the combined result of the liquid density difference and thermal gradient. Thus the distribution of the dendrite array is critical to the permeability. In Fig. 2 (b), although the solid-liquid interface was perpendicular to the longitudinal axis, the dendrite arms were neither perpendicular nor parallel to the thermal gradient direction under the experimental conditions and an angle of about 40° existed between the orientation of the dendrite arm and the longitudinal axis. In fact, inter-dendritic fluid flow much more easily occurs under such a condition than under the condition where the orientation of the dendrite array is parallel to the longitudinal axis. The “tilted” orientation of the dendrite array can play the role as a tilted solidification front which can dramatically decrease the critical Rayleigh number for freckle convection [12, 14].

Lastly, although the averaged liquid composition can give its general variation tendency in the mushy zone, the distribution of alloy concentration and density in the residual liquid at different locations in a cross section at the same temperature cannot be indicated in detail due to the complex solidification action. The liquid composition at the inter-dendritic center was notably different from that at the edge area close to the dendrite. The residual liquid was also far from uniform. There were fluctuations in the concentration and density of the liquid at different locations in the inter-dendritic area which could affect the origination of the freckling flow.

2.4 Variation of Rayleigh number in the mushy zone

Based on density inversion theory and Flemings’ macro-segregation theory, Yang W. and his co-workers summarized the Rayleigh criteria. The Rayleigh number (Ra), derived by Flemings and his co-workers, as given in equation (6), was found to predict the freckle formation satisfactorily [12]. The equation is:

$$Ra = \frac{\Delta \rho \cdot g \cdot \Pi}{\nu \cdot f_L} \cdot \frac{1}{R}$$

(6)

Where

- $\Delta \rho$ — the liquid density difference;
- $g$ — the gravity;
- $\Pi$ — the permeability;
- $\nu$ — the liquid viscosity;
- $f_L$ — the liquid fraction, and
- $R$ — the crystal growth speed.

In this paper, only the compositional effect on freckle formation was discussed. The viscosity change during solidification was not considered because the viscosity did not vary significantly in the mushy zone temperature range for superalloys [13, 15, 16]. Therefore, a simplified equation (7) was used to calculate the relative $Ra$:

$$Ra_r = \frac{\Delta \rho \cdot \Pi}{f_L}$$

(7)

At the temperature $T$, the local density difference $\Delta \rho$ is given by:

$$\Delta \rho = \frac{\rho_0 - \rho(h)}{\rho_0} \times 100\%$$

(8)

Where $\rho_0$ is the liquid density at the tip of the dendrites or cells, or the density of the bulk alloy at the liquid temperature; $\rho(h)$ is the liquid density at a location at a given distance $h$ below the dendrite tip, evaluated for the local temperature $T$ and segregated liquid concentration. Obviously, the values of $\Delta \rho$ for Inconel 718 increased down the mushy zone like the liquid density did.

The method used to calculate the permeability was initially proposed by Poirier and modified by Yang et al [12]. According to the literatures [13, 15], the permeability can be calculated using equation (9) if the liquid flow is perpendicular to the primary dendrite arm:

$$\Pi = \frac{\Delta T}{\int_\infty^0 f_L^{-3.34} \, dT}$$

(9)
Figure 8 gives the calculated relative $Ra$ number during solidification of Inconel 718. The calculated result showed that Inconel 718 had the largest relative $Ra$ number at about 1,325 °C where the liquid fraction was about 60 % as shown in Fig. 4 (a). This agreed with the idea that the liquid fraction was in the range of 40%–60 % as freckling convection formation reported in the literature [11]. As the temperature decreased, the liquid density difference increased, but the permeability decreased due to the reduction of the liquid fraction. As a result, the maximum relative $Ra$ number appears at a liquid fraction of about 40%–60 % where the liquid density difference was great and the permeability was not very low.

![Fig.8: The variation of the relative Rayleigh number in the mushy zone](image)

The tendency to form freckling convection in an alloy can be indicated by the maximum $Ra$ number in the mushy zone $^{[13,17]}$. The bigger the value of $Ra$ number, the higher the freckle flow tendency. During solidification of Inconel 718, considerable Nb and Mo segregation results and a large liquid density difference is generated. Meanwhile, the liquid fraction and the permeability decrease down the mushy zone. Thus the resultant $Ra$ reaches the biggest value at the temperature 10–20 °C below the temperature where the fluid flow most easily occurs $^{[11]}$. The maximum value of $Ra$, number here was possible not the critical $Ra$, number for freckle formation in Inconel 718 but it indicated when and where the freckling convection tendency was the largest in the mushy zone.

### 3 Conclusions

During solidification of Inconel 718, there is serious segregation of Nb and Mo into the liquid which makes the liquid density increase from top to bottom in the mushy zone and there is no density inversion. Carbide formation in the freezing range and the favorable angle of the orientation of the dendrite array can prompt the freckle flow in the mushy zone of an alloy which has no liquid density inversion. For Inconel 718, the largest relative Rayleigh number ($Ra_l$) occurs at 1,326 °C where the freckling fluid flow most easily occurs.

### References


