LIQUID DENSITY INVERSIONS DURING THE SOLIDIFICATION OF SUPERALLOYS AND
THEIR RELATIONSHIP TO FRECKLE FORMATION IN CASTINGS.

P. Auburtin, S. L. Cockcroft, and A. Mitchell

Department of Metals and Materials Engineering
University of British Columbia, Vancouver B.C. V6T 1Z4 Canada
Tel : (604) 822 3677 Fax : (604) 822 3619

Abstract

The interdendritic segregation along the mushy zone of five directionally solidified and quenched alloys (MAR-M002, MAR-M247, IN718, T1 and C-276) has been measured by SEM/EDAX techniques and the corresponding concentration profiles are presented. These profiles have also been translated into liquid density profiles by a numerical model. Chemical compositions and estimated liquid densities of freckles found in MAR-M002, IN718, T1 and C-276 are also reported. It was deduced from the observations in this study that freckles tend to initiate relatively close to the tip of the dendrites, about 15 to 20°C below the liquidus temperature of the alloy, where the fraction liquid is typically of the order of 0.4 to 0.6. The Rayleigh number as a criterion for freckling is described and it is shown that freckles could result from density inversion gradients of the order of 0.03(g/cm³)/°C, whereas 0.005(g/cm³)/°C is probably too low. The importance of incorporating minor alloying elements such as C, or Si when studying liquid buoyancy related to freckling has also been outlined. Finally, emphasis is put on the crucial role played by carbon in some freckle-prone alloys as a powerful trigger for freckling, both through segregation and through precipitation of heavy elements into carbides.

Introduction

Freckles, also known as channel segregates, are thin trails of equiaxed grains and/or eutectic enriched metal which induce highly undesirable inhomogeneities in the properties of the final casting. Although much research about freckles has been published in the past 25 years (an extensive literature review is available in (1)), freckles are still a recurring casting problem for many alloy systems. It is now widely accepted that freckles in the final casting are the result of specific fluid flow patterns, known as thermosolutal convection, in the liquid during casting. This flow was shown to be driven by a density inversion phenomenon (2-5). This freckling mechanism has been described in numerous studies on analog systems, especially Pb-Sn and NH₄Cl-H₂O (5-9), and in computer simulations (2,10). However, very little research has been published on freckling in actual industrial alloys. Thus, to date, knowledge on freckling in superalloys remains largely qualitative.

In an attempt to reduce the probability of freckle occurrence, a few criteria involving temperature gradient G and growth rate R have been developed for use in computer casting models. However, these criteria remain empirical and none of them is entirely satisfactory (11). So far, casters usually relied on high thermal gradients to avoid freckles. While this method is relatively efficient for small castings, high thermal gradients are not achievable in bigger castings such as large directionally solidified (DS) or single crystals (SX) blades for industrial gas turbines. It seems therefore necessary to develop a criterion based on the actual physical mechanisms involved in freckle formation. Among various published parameters used to characterize the probability of freckle occurrence (7,12-14), the Rayleigh number Ra , as described by Sarazin & Hellawell (14), appears to be the most closely related to the physical conditions in the casting. It can be expressed in the following dimensionless form:

$$Ra = g \cdot \frac{\rho \cdot D}{\eta \cdot h^4} \quad (1)$$

where g = gravitational constant
 ρ = density
 z = vertical coordinate
 η = dynamic viscosity
 D = thermal diffusivity
 h = characteristic linear dimension.

The numerator corresponds to the driving force in the liquid for fluid flow (to produce freckles) due to density inversion whereas the denominator represents the restriction to fluid flow (and freckles) due to viscosity, diffusivity and permeability in the liquid. The parameter h^4 has been linked to the dendritic array in the mushy zone with the following expressions: $h^4 = \lambda_1^4$ or $h^4 = K \cdot \lambda_1^2$ (where λ_1 is the primary dendrite arm spacing and K is the permeability). Ra greater than a critical value, Ra^* , can then be considered a physical criterion for freckle formation. However, the application of this criterion in numerical models requires the knowledge of its various parameters. η and D can usually be approximated with reasonably good precision. Numerical equations for the permeability of K are still a topic for research (especially in high or low fraction liquid) but various expressions are now available in the literature (15,16).

The main unknowns in the Rayleigh number criterion remain the density inversion factor (dp/dz) as well as the critical Ra^* for various industrial alloys. The aim of the present research is to evaluate the order of magnitude of the density inversion factor for various freckle-prone alloys.

Experimental procedure

Choice of alloys

In this study, four alloys exhibiting freckles were chosen : DS superalloy MAR-M002, IN718, tool steel T1 and corrosion resistance alloy C-276. A fifth alloy, DS superalloy MAR-M247, was also chosen for the fact that it is not prone to freckling despite a composition very similar to that of MAR-M002. The nominal composition and melting range of these alloys is presented in Table I.

Sample casting

The alloys under study were directionally solidified and quenched (DSQ) in a vacuum induction furnace. The samples (6mm diameter $\times$ 50-60mm length) were contained in an alumina tube which was withdrawn at a rate of 2.5×10^{-5} m/s through a thermal gradient of $10^\circ\text{C}/\text{mm}$ at the solidification front, leading to a dendrite network with a primary spacing of about 250-350 μm . Before complete solidification, the samples were quenched from the steady-state growth regime in order to reveal the solidifying structure, without complications from diffusion during cooling.

Sample analysis

For each DSQ sample, several cross-sections located between the top and the bottom of the mushy zone were finely polished and analyzed using scanning electron microscope and energy dispersion analysis spectrometry (SEM/EDAX) techniques. A temperature, prior to quenching, was calculated for each cross-section (this temperature is easily calculated knowing the liquidus temperature of the alloy T_{liq} , the thermal gradient G and the distance from the cross-section to the tip of the dendrites).

When the dendrite outlines could not be located directly under the SEM, the sample cross-sections were etched (with Kallings II or Marble's etch) and the dendrites were identified with micro-hardness diamond marks before repolishing the sample.

On each cross-section, at least four measurements of the quenched interdendritic liquid composition were made by EDAX. Other measurements, such as the composition at the dendrite centers and of carbides, were also carried out. SEM/EDAX measurements

were always performed on unetched finely polished surfaces for maximum precision and minimum contamination. For each alloy composition, all the major alloying elements (down to 0.5wt%, except for carbon in T1, due to EDAX limitations) were included in the analyses. All the chemical compositions presented in this article are averages over 4 or more direct EDAX measurements. It is to be noted that the standard deviation observed on these multiple measurements always lay well within the expected precision of EDAX, namely $\pm 5\%$ for major alloying elements (content greater than 5wt%) and up to $\pm 15\%$ for minor alloying elements (content lower than 5wt%).

Moreover, micrographs of etched cross-sections at various depths in the mushy zone of the samples were also recorded. A typical example of these micrographs is shown in Figure 1. The quenched interdendritic liquid (tertiary arms and dark eutectic precipitate) (areas of EDAX analysis) can be clearly distinguished from the dendrites (primary and secondary arms).

The dendritic array was manually outlined on several micrographs. Computer image analysis was then used to measure the area of the outlined dendrites relative to the total area of the micrograph. Thus the fraction liquid was estimated at various temperatures in the mushy zone for several alloys.

Density evaluation

In order to estimate the density variations in the interdendritic liquid, chemical compositions and temperature for a given cross-section were mathematically translated into density by "METALS", a model developed by National Physical Laboratories (NPL, UK). This model is based on a weighted average of the molar volumes of each pure element forming the alloy. This approximation is now a widely accepted approach (19-21). The basic equations for this model can be written as follows.

At the temperature T , the molar volume in the liquid phase MV_L^i of each pure element i (of melting point T_{mp}^i) is given by :

$$MV_L^i(T) = MV_L^i(T_{liq}) \times (1 + \alpha_L^i \times (T - T_{liq})) \quad (2)$$

$$\text{with } MV_L^i(T_{liq}) = MV_L^i(T_{mp}^i) \times (1 + \alpha_L^i \times (T_{liq} - T_{mp}^i)) \quad (3)$$

where α_L^i = expansion coefficient of pure element i in the liquid state.
 T_{liq} = liquidus temperature of the alloy.

Table I : Standard compositions (in wt%) and melting range of chosen alloys (17).
(T1 melting range estimated from reference (18))

Alloy	Nominal Composition (wt%)	$T_{sol}-T_{liq}$ ($^\circ\text{C}$)
MAR-M002	5.5Al, 0.15C, 10Co, 9.0Cr, 1.3Hf, 2.5Ta, 1.5Ti, 10W, Bal.Ni	1249-1365
MAR-M247	5.5Al, 0.15C, 10Co, 8.4Cr, 1.4Hf, 0.6Mo, 3Ta, 1Ti, 10W, Bal.Ni	1280-1360
IN718	0.5Al, 0.03C, 0.4Co, 19Cr, 3Mo, 5.5Nb, 52.5Ni, 1Ti, Bal.Fe	1260-1336
T1	0.75C, 4Cr, 0.3Mn, 1.1V, 18W, Bal.Fe	1320-1440
C-276	0.01C, 15.5Cr, 6Fe, 0.4Mn, 16Mo, 4W, Bal.Ni	1325-1370

For a given total weight W of an alloy of known composition, the number of mole a^i of each element is also known. Thus, the density of the liquid alloy, at any given temperature T , can be calculated as follows:

$$\rho_L(T) = W / (\sum (a^i \times MV_L^i(T))) \quad (4)$$

This model is held to be accurate to about 5%. It was tested in the present study and showed very good agreement with various liquid densities reported in the literature (19,21,22). All the liquid densities reported in this article were evaluated by this model.

Results

DSQ samples

DSQ samples were mono- or bicrystals with dendrites oriented at 10° or less to the longitudinal axis. The growth front was always flat across the samples. Average compositions measured by EDAX along the samples showed no noticeable differences from the nominal compositions before melting, indicating no "zone refining effect".

No freckle was observed in any of the DSQ samples.

The segregation profiles measured by EDAX in the interdendritic liquid along the mushy zone for MAR-M002, MAR-M247, IN718, Ti and C-276 are presented in Figures 2 to 6. Only the alloying elements are reported (the balance is Ni (or Fe for Ti)). These profiles are plotted against temperature in the melting range of each alloy.

The measured fraction liquid in the top part of the mushy zone is also reported on Figures 2 to 4 for alloys MAR-M002, MAR-M247 and IN718 (dashed lines). Fraction liquid measurements were not carried out for alloys Ti and C-276 due to difficulties in consistently outlining the dendrites throughout entire micrographs.

The density profiles in the interdendritic liquid for each alloy along their melting range were computed from the composition profiles shown in Figures 2 to 6. The results for all five alloys considered is presented in Figure 7.

The solid curves in Figures 2 to 7 are third degree polynomial regressions relative to the plotted data. The error bars in Figure 7 represent the worst possible effect of EDAX imprecision on the density calculations, when light and heavy alloying elements are shifted in opposite directions by their full expected imprecision.

Industrial castings exhibiting freckles

In order to develop a criterion for freckling, industrial castings with freckles were studied. Freckles could be easily observed by etching. They also showed specific characteristics: microporosity in MAR-M002, high concentration of niobium carbides in IN718, and larger concentration of carbides in Ti.

Freckle and matrix compositions and estimated liquid densities for industrial castings of MAR-M002, IN718, Ti and C-276 are presented in Table II.

Density inversion provisions

Based on the Rayleigh number, it is possible to write :

$$\frac{dp}{dT} = \frac{dp}{dz} \times \frac{dz}{dT} = Ra \times \frac{\eta D}{g \lambda_1^4} \times \frac{1}{G} \quad (5)$$

Assuming a critical Rayleigh number $Ra^* = 1$ as reported in (14), and substituting numerical values (in SI units) provided by (14) and "METALS", and a thermal gradient $G = 10^\circ\text{C/mm}$ (i.e. 10^4K/m), yields :

In the case of Pb-10wt%Sn :

$$\frac{dp}{dT} = 1 \times \frac{2.5 \times 10^{-3} \cdot 1.1 \times 10^{-5}}{9.8 \cdot (3.0 \times 10^{-4})^4} \times \frac{1}{10^4} = 0.035 \text{ (g/cm}^3\text{) /}^\circ\text{C}$$

In the case of Pb-2wt%Sb :

$$\frac{dp}{dT} = 1 \times \frac{3.0 \times 10^{-3} \cdot 1.0 \times 10^{-5}}{9.8 \cdot (3.0 \times 10^{-4})^4} \times \frac{1}{10^4} = 0.038 \text{ (g/cm}^3\text{) /}^\circ\text{C}$$

In the case of Ni-based alloys (numerical data for pure liquid nickel at 1500°C) :

$$\frac{dp}{dT} = 1 \times \frac{4.4 \times 10^{-3} \cdot 1.0 \times 10^{-5}}{9.8 \cdot (3.5 \times 10^{-4})^4} \times \frac{1}{10^4} = 0.030 \text{ (g/cm}^3\text{) /}^\circ\text{C}$$

Thus, based on an estimation of the Rayleigh number criterion, freckles could result from density inversion gradients of the order of $0.03 \text{ (g/cm}^3\text{) /}^\circ\text{C}$.

Discussion

Measurement validation

The measured freckle composition for IN718 is in excellent agreement with that reported elsewhere (23). The proper calibration of the SEM/EDAX apparatus used in this study was confirmed by analyzing large sections of the samples. The global composition of these averaging sections corresponded very well to the nominal alloy composition. The nominal alloy composition (Table I) can also be found again in the interdendritic liquid at the top of the mushy zone (see right end of the curves in Figures 2 to 6).

Freckle initiation position

For any given alloying element in any given freckle-prone alloy considered in this study, it is possible to plot the freckle composition value (given in Table II) on the corresponding interdendritic segregation curve presented in one of Figures 2 to 6. When this is done for every element in a given alloy, all the plots exhibit very similar abscissa coordinates. This common abscissa value represents therefore the temperature (i.e. the depth in the mushy zone) at which interdendritic liquid is drawn to feed freckle plumes.

(a) $T = T_{Liq} = 1360^{\circ}\text{C}$

(b) $T = 1335^{\circ}\text{C}$

(c) $T = 1321^{\circ}\text{C}$

Figure 1 : Etched cross-sections at various depths along the mushy zone in DSQ MAR-M247, showing the dendritic array and the quenched interdendritic liquid.

Figure 2 : Interdendritic liquid segregation and fraction liquid profiles along the mushy zone in DSQ MAR-M002.

Figure 3 : Interdendritic liquid segregation and fraction liquid profiles along the mushy zone in DSQ MAR-M247.

Figure 4 : Interdendritic liquid segregation and fraction liquid profiles along the mushy zone in DSQ IN718.

Figure 6 : Interdendritic liquid segregation profiles along the mushy zone in DSQ C-276.

Figure 5 : Interdendritic liquid segregation profiles along the mushy zone in DSQ T1.

Figure 7 : Interdendritic liquid density profiles (estimated by numerical model) along the mushy zone in five DSQ alloys

Table II : Freckles and matrix compositions (measured by EDAX), and liquid state density range (estimated by numerical model) for various industrially cast alloys.

Alloy	Freckle/Matrix Compositions (in wt%)	Liquid Density (in g/cm ³)	
		at T_{Liq}	at T_{Sol}
MAR-M002	Freckle: 7.5Al, 8.9Co, 8.0Cr, 4.6Hf, 60.7Ni, 2.7Ta, 1.8Ti, 5.8W	6.81	6.92
	Matrix : 6.8Al, 10.2Co, 9.2Cr, 1.8Hf, 58.0Ni, 2.6Ta, 1.3Ti, 10.1W	7.04	7.15
IN718	Freckle: 0.2Al, 16.9Cr, 0.5Cu, 16.8Fe, 4.1Mo, 10.1Nb, 50.2Ni, 1.2Ti	7.57	7.64
	Matrix : 0.3Al, 18.5Cr, 0.4Cu, 19.4Fe, 3.4Mo, 5.6Nb, 51.6Ni, 0.8Ti	7.49	7.57
T1	Freckle: 5.7Cr, 68.7Fe, 1.6V, 24.0W	8.29	8.41
	Matrix : 4.6Cr, 73.9Fe, 1.2V, 20.3W	8.09	8.20
C-276	Freckle: 16.7Cr, 6.5Fe, 19.8Mo, 53.3Ni, 3.7W	8.12	8.16
	Matrix : 16.1Cr, 6.6Fe, 17.3Mo, 55.5Ni, 4.5W	8.12	8.16

These positions correspond to temperatures about 1340°C, 1320°C, 1370°C and 1363°C for MAR-M002, IN718, T1 and C-276 respectively. It is interesting to note that in the case of MAR-M002, IN718 and C-276, freckles would thus initiate relatively close to the top of the mushy zone (about 15-20°C below T_{Liq}). Thus, freckles are only partially shifted toward the eutectic composition. This observation is further confirmed when considering data on binary analog systems. In Pb-2wt%Sb ($T_{Liq}=315^\circ\text{C}$), freckle composition averaged 4wt%Sb (corresponding to $T=300^\circ\text{C}$ according to the phase diagram, i.e. 15°C below the liquidus temperature of the alloy), whereas eutectic composition is 11.2wt%Sb (8). Similarly, in Pb-17wt%Sn ($T_{Liq}=290^\circ\text{C}$), freckle composition averaged 29wt%Sn (corresponding to $T=270^\circ\text{C}$ according to the phase diagram, i.e. 20°C below the liquidus temperature of the alloy), whereas eutectic composition is 61.9wt%Sn (8).

Moreover, freckle initiation position corresponds to a liquid fraction f_L of the order of 0.4-0.6 (as seen on Figures 2 to 4). This is consistent with the fact that fluid flow leading to freckles will develop more easily in regions of higher permeability.

Density inversion in MAR-M002 and MAR-M247

As shown on Figure 7, the curves representing the density of the interdendritic liquid along the mushy zone of MAR-M002 and MAR-M247 exhibit a noticeable minimum, slightly below T_{Liq} . In the case of MAR-M002, this minimum coincides exactly with the position of freckle initiation at $T=1340^\circ\text{C}$ as described above.

Moreover, as illustrated by the two tangents on Figure 7, it is possible to evaluate the density inversion gradient dp/dT for these two alloys : the density inversion gradient between the tip of the dendrites and the point of lowest density is of the order of 0.03(g/cm³)/°C for MAR-M002 and 0.005(g/cm³)/°C for MAR-M247. According to the provisions previously calculated with the Rayleigh number, 0.03(g/cm³)/°C could be enough to produce freckles whereas 0.005(g/cm³)/°C should be too low. This is consistent with the fact that MAR-M002 is usually prone to freckles and MAR-M247 is not.

It should be mentioned that the density inversion observed for MAR-M002 and MAR-M247 is directly linked to carbide precipitation during solidification. In these alloys, the carbides' average

metal composition was measured to be 55Ta+16W+16Hf+13Ti (wt%). Thus, carbide precipitation, by removing a significant amount of heavy elements from the interdendritic liquid (especially Ta), enhances its buoyancy since it is assumed that solid carbides do not participate in local liquid buoyancy. As Ta segregates preferentially toward the interdendritic liquid, thus making it heavier, it was suggested elsewhere (24) as a worthwhile addition to some alloy chemistries in order to eliminate freckles. This is probably valid for non-carbide forming alloys. However, in view of the present research in the case of carbide forming alloys, Ta may on the contrary favor and possibly trigger freckle formation. On the other hand, carbide precipitation in some alloys may also help prevent freckles by obstructing interdendritic channels, thus reducing the propensity to fluid flow and plume formation.

Density profile in IN718

As seen in Figure 7, the calculated density of the interdendritic liquid is increasing down the mushy zone of IN718. Although in apparent contradiction with the freckling theory, this observation is consistent with the density calculations estimating freckles to be heavier than the surrounding matrix (see Table II). Assuming that the theory is true (i.e. freckles do arise from buoyant plumes), this observation yields four possible explanations:

(a) First, it is possible that the density model is not accurate enough. However, the weighted average theory is the only acceptable to date and further work would be required to estimate possible deviations from the ideal mixing behavior. In any case, although deviation correction may influence the average calculated density of liquid alloys, it should only have a small effect on the relative variations of liquid density along the mushy zone.

(b) Secondly, since freckles in IN718 exhibit a large concentration of niobium carbides, it is possible that solute carbon should be taken into account in the density calculations. Other minute alloying elements, such as Si, may also play a significant role. Although EDAX measurements are difficult or impossible for such elements, segregation concentrations can be estimated and densities can be recalculated by the model. Such an estimation is presented below for IN718 with a nominal content of 0.03wt%C and 0.3wt%Si with overall compositions as

reported in Figure 4 at the liquidus temperature (1336°C) and at the freckle initiation temperature (1321°C) :

Liquidus Compo. + 0.03C + 0.3Si : $\rho_L(1336^\circ\text{C}) = 7.44\text{g/cm}^3$
 1321°C Compo. + 0.03C + 0.3Si : $\rho_L(1321^\circ\text{C}) = 7.50\text{g/cm}^3$
 1321°C Compo. + 0.25C + 0.3Si : $\rho_L(1321^\circ\text{C}) = 7.46\text{g/cm}^3$
 1321°C Compo. + 0.25C + 1.0Si : $\rho_L(1321^\circ\text{C}) = 7.36\text{g/cm}^3$

It can be seen that segregation of carbon alone is insufficient to create density inversion. However, additional segregation of Si could result in a density inversion sufficient to form freckles. It is to be noted that NbC precipitation in IN718 would not favor density inversion like in MAR-M002, because removal of niobium from the interdendritic liquid has very little influence on alloy buoyancy due to very similar densities.

(c) A third possible explanation is that the macrosegregates observed in "freckled" IN718 are indeed heavier than the surrounding matrix. In this case, they would actually be center-segregates rather than freckles. After forging of an ingot, the pockets of center-segregates appear thin and elongated in the direction of the ingot, much like freckles.

(d) A fourth explanation is a combination of the preceding two. Historically, IN718 used to contain relatively high amounts of carbon and silicon. Freckles could then develop as shown by calculation. However, more recently, the silicon content was substantially reduced and it is possible that IN718 ingots are now subject to center-segregation rather than freckling.

In any event, more detailed analysis of the segregation of minor alloying elements such as C or Si is required for further investigation. Moreover, in order to eliminate it, it is necessary to unambiguously distinguish which macrosegregation mechanism is at work.

Density profile of tool steel T1

Similarly to IN718, the density profile of T1 in Figure 7 does not exhibit any density inversion. Also similarly to IN718, this is consistent with the estimated density of freckles in T1 being greater than that of the surrounding matrix (see Table II). Assuming that freckles in T1 are not actually center-segregation, the phenomenon at work in T1 is probably a combination of the mechanisms in IN718 and MAR-M002. Freckles in T1 most likely result from a relatively high carbon segregation and from the precipitation of tungsten carbides, strongly depleting the interdendritic liquid of heavy tungsten. It was estimated with the density model that segregation of carbon from a nominal 0.8wt% up to 3wt% or more is indeed sufficient to create a density inversion susceptible to form freckles. This higher carbon content as a mechanism is further confirmed by the fact that freckles in T1 exhibited noticeably bigger and more numerous carbides (about 3 times as much) than the surrounding matrix.

Other light elements such as Mn, P or Si may also play a significant role on freckle formation in tool steels. Moreover, unlike in MAR-M002 or MAR-M247 where carbides eventually became embedded in the dendrite cores and were therefore not interfering with measurements of the interdendritic liquid composition, carbides in T1 remained in the liquid. Due to the lack of data on the carbide precipitation temperatures in

T1, it was not possible to evaluate pro- and post-quench carbides. It is nevertheless interesting to note that the matrix surrounding interdendritic carbides contained only about 9wt%W, making it much lighter than any interdendritic liquid with an average tungsten content of 18wt% or higher. This confirms the definite effect of heavy element carbide precipitation on the potential for freckle formation. The estimated freckle initiation position is much further below T_{Liq} in T1 than in the other alloys in this study (70°C instead of 20°C). This could be due to a relatively low carbide precipitation temperature and identify carbon precipitation as a trigger for freckling.

Density profile in C-276

Figure 7 shows a slight increase in density of the interdendritic liquid down the mushy zone of C-276. Table II shows no density difference between freckle and matrix. Assuming freckling rather than center-segregation, and since C-276 does not normally form carbides, this confirms again the importance of measuring and taking into account the segregation patterns of seemingly minor light elements such as Al, B, C, Si or Zr.

Absence of freckles in the DSQ samples

Freckles did not appear in any of the DSQ samples. This is believed to be due to the relatively small cross-sectional area of the samples (of the order of 25mm²).

Indeed, it has been reported in the literature (5) that adjacent freckles are usually evenly spaced (about 5-10mm apart, yielding about 25-100mm² cross-sectional area per individual freckle). It is believed that 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 DSQ samples were evidently too thin to support such fluid flow cells, and freckles could not develop.

Summary and Conclusion

Freckle compositions in selected industrial alloys, as well as interdendritic segregation and fraction liquid profiles along the mushy zone of DSQ samples were measured by SEM/EDAX techniques. The corresponding liquid densities were estimated by a numerical model.

(a) It was found by comparing actual freckle compositions to the segregation, that freckles in the studied alloys would tend to initiate about 20°C below the liquidus temperature where the fraction liquid in the mushy zone typically is 0.4 to 0.6.

(b) Density inversions were observed for MAR-M002 and MAR-M247. These inversions were linked to the precipitation of heavy elements (Ta, W, Hf) into carbides, lightening the interdendritic liquid and acting as a trigger for freckle formation.

(c) A range for the minimum required density inversion to form freckles was also determined : MAR-M002 is known to exhibit freckles and shows a density inversion of 0.03(g/cm³)/°C, whereas MAR-M247 does not usually form freckles and shows a density inversion of 0.005(g/cm³)/°C. Therefore, freckling can be linked to density inversions of the order of 0.01(g/cm³)/°C or greater.

(d) In the case of IN718, C-276 and tool steel T1, all reportedly freckle-prone, no density inversion was observed. A first possibility is that the reported

freckles in these alloys are actually center-segregates, having the same appearance as freckles after ingot forging. A second possibility is that some alloying elements which were not included in the EDAX analysis (too small an atomic weight and/or too low a concentration) are indeed crucial to the determination of the liquid density.

(e) Estimates of the concentration of some of these minor elements in the mushy zone showed that segregation of carbon and silicon in IN718 (with high Si) could produce sufficient density inversion for freckling. In Ti, carbon segregation and tungsten carbides precipitation could also yield enough density inversion to form freckles.

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References

1. P. Auburtin, "Determination of the influence of interdendritic segregation during the solidification of freckle-prone alloys", (M.A.Sc. thesis, Univ. Of British Columbia, 1995), 3-41.
2. J.C. Heinrich, S. Felicelli, and D.R. Poirier, "Vertical solidification of dendritic binary alloys", Computer Methods in Applied Mech. and Eng., 89(1991), 435-461.
3. D.G. Neilson and F.P. Incropera, "Effect of rotation on fluid motion and channel formation during unidirectional solidification of a binary alloy", Int. J. Heat Mass Transfer, 36(2) (1993), 489-505.
4. G.B. McFadden et al., "Thermosolutal convection during directional solidification", Met. Trans. A, 15A(12) (1984), 2125-2137.
5. J.R. Sarazin, A. Hellawell, and R.S. Steube, "Channel convection in partly solidified systems", Phil. Trans. R. Soc. Lond. A, 345(1993), 507-544.
6. R.J. McDonald and J.D. Hunt, "Fluid motion through the partially solid regions of a casting and its importance in understanding A type segregation", Trans. Metall. Soc. AIME, 245(09) (1969), 1993-1997.
7. S.M. Copley et al., "The origin of freckles in unidirectionally solidified castings", Met. Trans., 1(08) (1970), 2193-2204.
8. L. Wang, V. Laxmanan, and J.F. Wallace, "Gravitational macrosegregation in unidirectionally solidified lead-tin alloy", Met. Trans. A, 19A(11) (1988), 2687-2694.
9. M.H. McCay and T.D. McCay, "Experimental measurement of solutal layers in unidirectional solidification", J. Thermophysics, 2(3) (1988), 197-202.
10. W.D. Bennon and F.P. Incropera, "The evolution of macrosegregation in statically cast binary ingots", Met. Trans. B, 18B(09) (1987), 611-616.

11. A.L. Purvis, C.R. Hanslits and R.S. Diehm, "Modeling characteristics for solidification in single-crystal, investment cast superalloys", JOM, 01(1994), 38-41.
12. T.M. Pollock and W.H. Murphy, "The breakdown of single crystal solidification in high refractory nickel-base alloys", To be published.
13. M.C. Flemings and G.E. Nereo, "Macrosegregation : Part I", Trans. Metall. Soc. AIME, 239(09) (1967), 1449-1460.
14. J.R. Sarazin and A. Hellawell, "Channel flow in partly solidified alloy systems", Advances in Phase Transition, 10(1987), 101-115.
15. D.R. Poirier, "Permeability for flow of interdendritic liquid in columnar-dendritic alloys", Met. Trans. B, 18B(03) (1987), 245-255.
16. M.S. Bhat, D.R. Poirier, and J.C. Heinrich, "Permeability for cross-flow through columnar dendritic alloys", Met. Trans. B, 26B(10) (1995), 1049-1056.
17. "Properties and selection : irons, steels and high performance alloys", ASM International Metals Handbook 10th edition, ed. J.R. Davis et al., ASM International, 1(1990), 950-1006.
18. A. Grellier, private communication, Aubert & Duval, 28 July 95.
19. A.F. Crawley, "Densities of liquid metals and alloys", Int. Metallurgical Reviews, 19(1974), 32-47.
20. K.C. Mills and P.N. Quested, "Measurements of the physical properties of liquid metals", Liquid Metal Processing and Casting Conf. Proc., Am. Vacuum Soc., ed. A. Mitchell et al., Sept. 1994, 226-240.
21. T. Iida and R.I.L. Guthrie, The physical properties of liquid metals, (Clarendon Press, 1988)
22. A. Sharan, T. Nagasaka and A.W. Cramb, "Densities in liquid Fe-Ni and Fe-Cr alloys", Met. Trans. B, 25B(12) (1994), 939-942.
23. K.O. Yu et al., "Macrosegregation in ESR and VAR processes", Journal of Metals, 01(1986), 46-50.
24. T.M. Pollock et al., "Grain defect formation during directional solidification of nickel base single crystals", Superalloys 1992, TMS, ed. S.D. Antolovitch et al., (1992), 125-134.