Solidification and Precipitation in IN718

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Abstract

The superalloy IN718 has been extensively studied and as a result its solidification and physical properties are well-understood, in contrast to many other industrially-useful similar alloys. In this work we present the results of several studies in which we have used IN718 as a "model" superalloy. The investigations cover the columnar/equiaxial transition in grain growth; the nature of second-phase precipitation; and the formation of solidification defects related to segregation. We find that the results of the investigations provide valuable information on the supercooling effects found in superalloy casting in both ingot and directional processes. They also indicate alloy development directions in relation to the problems of manufacturing large section ingots by remelting, or in manufacturing large single-crystal castings.

Introduction

Alloy IN718 has a long history of industrial use and it is not surprising that there exists a wealth of information on the alloy's solidification and precipitation characteristics (1,2,3). It is almost certainly the best-understood of the superalloys in terms of these aspects of its behaviour. For this reason, in the present study we have used the alloy as a "prototype" superalloy in order to better understand aspects of the equivalent properties in more complex alloys, particularly those used in cast applications as single crystals.

The study was undertaken in order to understand the effects of several processes on the as-cast metallurgical structure. These are;

- crystallisation morphology
- interdendritic segregation and fluid-flow
- second-phase precipitation in the liquidus-solidus interval

Crystallisation Morphology

The definitive studies of crystallisation in the superalloys are collated and reported by McLean (4) and his summary of structures is shown in Fig 1. It will be noted from this figure that the boundary separating columnar dendritic structure from equiaxial crystallisation contains no experimental points in the region of interest to ingot solidification in conventional remelting processes, and none also in the regions critical to large single crystal castings. The columnar/equiaxial transition (CET) has been studied extensively in low-temperature analog systems and theories concerning the onset of the transition with decreasing temperature gradient and solidification rate have been developed from these results, for example in the works of Hunt (5), or the "KGT" theory (6). There is, however, little experimental evidence as to the numerical values of the parameters governing the transition in superalloys. This lack of data is a significant barrier to the computation of predicted structures in both ingots and castings, even when the corresponding heat flows etc are known with considerable accuracy. Experimental work on the CET in superalloys, including IN718, (7) indicates that in alloys with a conventional content of non-metallic inclusions, the nucleation process which creates the equiaxed grains requires an undercooling of approximately 3.7°C at the liquidus surface. A typical transition is shown in Fig (2). Using the approach of either Hunt or the KGT formulation, such a value corresponds to one nucleation site/s.cm^3. This density of nucleation sites is compatible with the nucleation frequency of grains observed in a typical ingot structure where the columnar dendritic morphology breaks down into the equiaxed grain region. The solidification conditions of these experiments show that the CET occurs in the region where the solidification rate, R, is approximately 3×10^{-4} m.s^{-1} and the temperature gradient, G, is approximately 1.5×10^{2} C.m^{-1}. The results presented on Fig 1, extrapolated into this region in a linear fashion indicate a CET at conditions very significantly different from this result, at a much larger value of G and a much smaller value of R i.e. requiring a larger undercooling for nucleation. Since the results reported experimentally showed little variation with composition across a range of superalloys, it seems likely that the CET is not a simple function of G and R as shown in Fig 1, at least in the region of interest to remelt ingot structures and also to large directional castings.

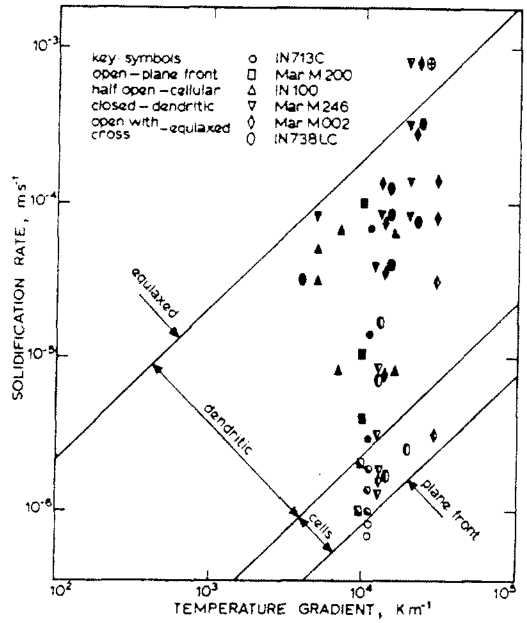

Figure 1: Morphologies of directionally solidified nickel based superalloys mapped on a plot of log R and log G. (4)

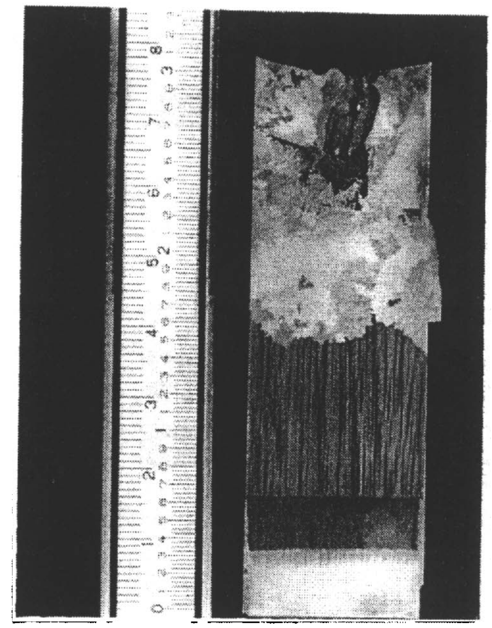

Figure 2: A typical CET transition with alloy AM1.

A second feature of the CET as illustrated by the above experiments relates to the modeling of solidification conditions in superalloy ingots or castings. As shown in Fig 3 the enthalpy release at the liquidus in columnar dendritic solidification is quite different to that experienced in the equiaxed region, due to the recalescence effect. Typically, in solidification modeling, heat release in the liquid + solid zone is held to follow either a simple linear partition, or to follow the amount of solid precipitated according to the phase diagram. Effects due to non-equilibrium solidification, undercooling etc are generally not included, although they have a considerable influence on the computed position of the solidus and on the temperature gradients computed for the solid + liquid region. Since the investigations on IN718 and related alloys showed little influence on composition from the viewpoint of heat release due to undercooling it would be reasonable to introduce the above values in such computational structures.

The nucleation problem has occupied a considerable amount of attention in the field of superalloy casting, particularly in relation to the defect known as "random grain" in single crystal casting. This defect occurs when the intentional single crystal columnar dendritic solidification is interrupted by the formation of a new grain of a differing principal crystallographic orientation, as shown in Fig 4. The reasons for grain nucleation are complex, but fundamentally centre around the presence of a volume of suitably-supercooled liquid and the presence of suitable nucleating agents such as irregular mold surfaces, non-metallic inclusions or dendrite fragments which have circulated out of the solidifying interface by a fluid-flow mechanism. Experimental work has been carried out on IN718 in order to investigate the role of these effects, using the alloy as a model for the more complex casting superalloys. An example of this approach lies in the role of TiN precipitation and is described below.

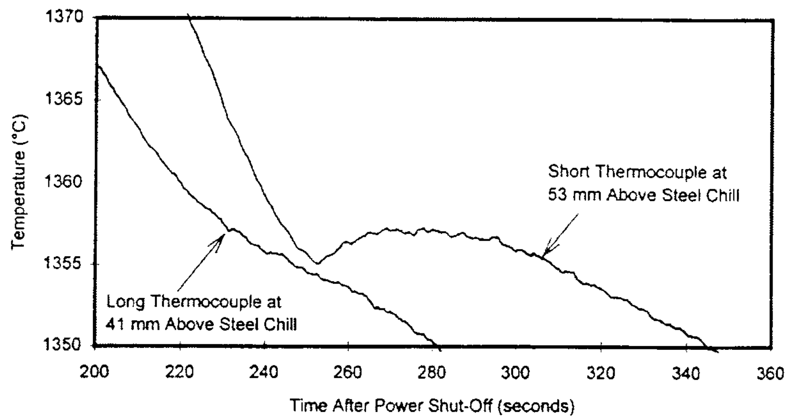

Figure 3: Comparision of thermal histories measured by long and short thermocouples as the CET is approached showing the difference between the enthalpy releases at the liquidus in columnar dendritic solidification and the equiaxed region.

The nitrogen solubility in IN718 is represented by a solubility product for the relation;

$$[Ti] + [N] = TiN(s) \quad \ldots\ldots\ldots\ldots \qquad (1)$$

in which the equilibrium constant, K is;

$$K = 1/[Ti]x[N]$$

K is a strong function of temperature and a somewhat weaker function of alloy composition, principally in relation to the Cr content in the normal range of superalloys although strong nitride-formers such as Zr, and Hf have a great influence when they are present in significant quantity. The value of K for IN718 is shown in Fig 5 and Table 1(8,9) as a function of temperature and it can be seen that upon entering the solid+liquid region, compositions with [N] > 40ppm will commence to precipitate TiN particles. The particles act as nuclei for carbide precipitation, but also can act as nuclei for the precipitation of solid i.e. as grain nucleators, since the face-centred cubic structure of TiN has lattice parameters which match those of the superalloy gamma phase. The match is not perfect and using the theory of Hunt, we may estimate that an undercooling of approximately 19°C would be required to force precipitation on the interface TiN/gamma. Since the experimental value at the CET for solidification rates common in remelting practice is much less than this value we may infer that TiN does not nucleate the CET in remelt ingots. However, values of at least 19°C are computed to occur in single crystal casting practice (10) and in that case TiN could potentially be a nucleating agent for random grains. This theory has been tested experimentally (11) with results outlined below.

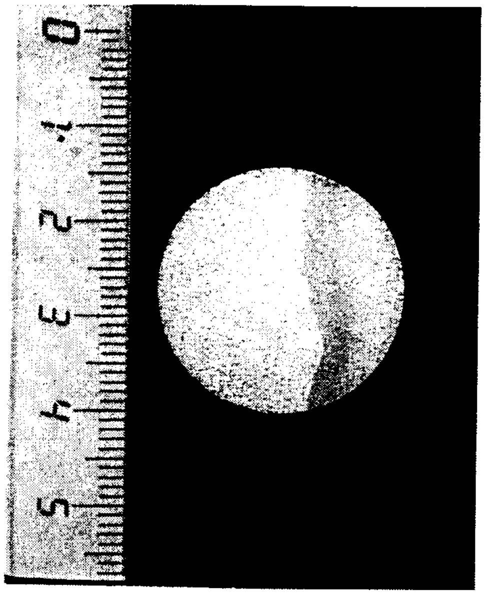

Figure 4: A random grain (right) observed on the cross section area of the top part of a single crystal IN718 inogt.

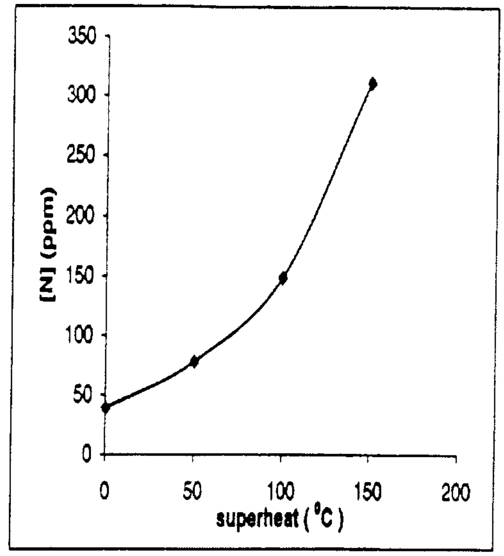

Figure 5: The solubility of TiN in alloy IN718 as a function of Suprheat.

Table 1 Solubility of TiN as a Function of Temperature During Solidification in Alloy IN718

T °C	[wt.% Ti]	[N] ppm with Ti segregation
1340	1	39
1320	1.5	19
1300	1.6	14
1280	1.7	9
1240	2	4

Single crystals of IN718 were cast under controlled conditions of G and R which were in the range commonly used in commercial SX casting i.e. G = 26 °C/cm, R = 2 mm/min. The alloy used was of three nitrogen levels, 100ppm, 40ppm and <10ppm. The first case would precipitate TiN at temperatures well above the liquidus, the second at temperatures close to the liquidus and the third composition would not precipitate TiN until the alloy was almost completely solid. It was found that the onset of random grain nucleation in these three compositions was a function of R, at a constant value of G i.e. that it was a function of undercooling at the liquidus. The two compositions in which TiN was present at the equilibrium liquidus temperature produced grain nucleation at values of R which were less than half that required for the third composition, indicating that TiN is a nucleating agent under these conditions. Although this finding has little implication for the manufacture of IN718, it does suggest that the single-crystal superalloys should be best made with nitrogen contents which are lower than saturation solubility of nitrogen to at least 20°C below the equilibrium liquidus value. In the case of a high-Ti alloy such as

CMSX4, this value would be less than 3ppm N, obviously presenting some commercial difficulties.

Interdendritic Segregation

The superalloys are well-known for their extensive properties of interdendritic segregation, which play a major role in determining the melting, casting and homogenisation processes used in their manufacture. This segregation has been shown on numerous occasions (12,13) to limit the possible ingot diameters which may be made by the conventional remelting processes by the appearance of unacceptable local macrosegregation. The segregation is produced when local density changes in the liquid + solid zone create instability in the local fluid flow. The resultant local concentration changes may appear as "freckles", "centre segregation", "A-segregates" and "V-segregates" depending on the alloy and the process used. In the case of IN718, the composition changes which take place in the solid and liquid during solidification have been closely studied, and are well-defined, as shown in Fig 6 (18) . The principal segregating elements which affect the bouyancy forces are Nb, Si and C. These elements influence the liquid density in differing ways. Nb has a density which is quite similar to that of the Ni-Fe-Cr base liquid, and a change in Nb concentration even though severe, would not in itself produce a serious change in the liquid density. However, the interaction of Nb and C controls the precipitation of the primary carbide, NbC; also since the NbC and TiN are isomorphous, this precipitation reaction to some extent (14) also involves the local concentration of Ti and N. The primary carbide precipitation start-temperature lies approximately 40C below the equilibrium liquidus of IN718 for the normal carbon concentration of 300ppm. As the carbide precipitates, it removes both C and Nb from the liquid, thus changing the bulk density in a direction which continuously increases the density relative to that at the liquidus. The interdendritic liquid thus becomes "heavier" with respect to the overlying liquid and any fluid-flow instabilities introduced by melting or freezing irregularities tend to produce liquid percolation in a downward direction through the dendrite mesh. This mechanism is responsible for the "centre segregation" often encountered in large IN718 remelt ingots. When the precipitation reaction is suppressed, either by reducing the carbon content, or by eliminating the TiN precipitation (which removes the necessary carbide nucleation sites through reducing the nitrogen content), the bouyancy force is reduced and the tendency to centre segregation is less marked. This technique has been used in the manufacture of large ingots in both IN718 and other similar alloys. The method is limited in respect of nitrogen by the practicality of reducing the nitrogen content to the necessary value of 5ppm (8), and in respect of carbon by the limit set through the necessity of retaining enough carbon to generate the secondary carbides required for satisfactory mechanical properties, which is approximately 80ppm carbon in IN718.

The effect of silicon is more direct. Silicon segregates strongly in superalloy compositions, as indicated by the appropriate phase diagrams, and is identified with the production of Laves phases in the last liquid to solidify. It is normal practice to specify silicon contents in the superalloys at values which are as low as is practically acceptable in the alloy formulation. However, this maximum acceptable limit has been progressively lowered over the years and with that lowering a reduced frequency of occurrence of "freckle" defect has been experienced in remelt ingots. The reason for this link is probably contained in the strong influence of Si on the liquid density. When the Si content of the liquid is increased, a density inversion can occur during solidification creating the necessary condition for the classical freckle mechanism of upward fluid flow from the dendrite mesh (Fig7) (15,16). The effect has been demonstrated by directionally solidifying IN718 of varying Si content under conditions where upward and downward flow can be separately observed (16).

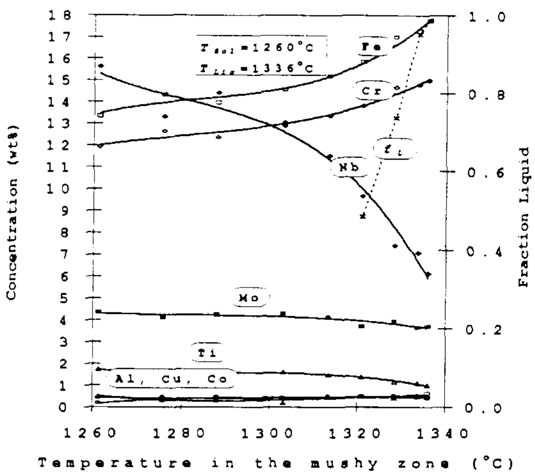

Figure 6: Interdendritic liquid segregation and fraction liquid profiles along the mushy zone in DSQ IN718.

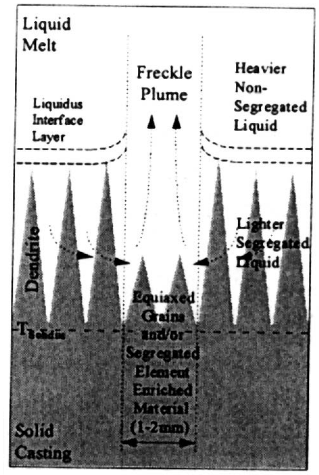

Figure 7: Schematic illustration depicting freckle formation and associated fluid flow pattern.

In respect of the above effects, IN718 presents the ideal "model" superalloy. The governing conditions of fluid flow can be accurately computed since we have an adequate knowledge of the appropriate solidification parameters. By using this approach, criteria have been developed for relating solidification conditions in respect of temperature gradient and solidification rate to the possibility for the formation of freckle and centre segregation (16), using the Rayleigh number (Ra) as the link dimensionless number to characterise the flow conditions. Using IN718 as the model base, the effect of composition changes can readily be shown and in principle used as a basis for developing alloys which are less sensitive to this form of segregation problem. The concept can also be used to predict ingot solidification behaviour, in particular in respect of the tendencies to segregation defects as we change size, shape and melting parameters. A combination of models describing "normal" solidification behaviour (for example, (17)) with the concept of segregation-driven interdendritic fluid flow provides us with a vehicle for establishing process routes for any superalloy composition, based on these experimental verifications using IN718.

Second-Phase Precipitation

Superalloys fall generally into two classes from the above viewpoint; those in which there is a precipitation reaction other than of primary solid during solidification, and those in which secondary precipitation does not occur until the eutectic composition is reached. In the case of IN718, the primary precipitation during solidification is that of NbC (an intentional component of the alloy) and TiN, arising from the nitrogen impurity. As solidification progresses, depending on the ratio of C;N in the alloy, the carbide nucleates on any pre-existing TiN, and at the later stages of the process may convert to a mixed (Nb+Ti) carbide. The various combinations of these compounds have generally been classed as "carbonitrides" in the alloy structure. Since IN718 has a relatively large solubility for TiN, it provides a convenient model for investigating the precipitation reactions. It has been shown, for example, (14), that when TiN is completely absent, in alloy refined by electron-beam melting in a high vacuum, carbide nucleation can be suppressed to the point that carbides are only found at the eutectic. This process substantially alters the eutectic reactions in favour of Nb-rich components. The implications of this finding in relation to other superalloys have not been investigated, but since many of the forging grade alloys experience similar carbide precipitation reactions, it is reasonable to assume that the same reactions will take place, giving the nitrogen content an indirect role in determining the basic structure of the alloy. The primary precipitation reactions are of particular concern in this alloy group due to the difficulty of altering the precipitate particle distribution by any industrially-acceptable solid-state heat treatments or homogenisation.

Conclusions

IN718 has been found to be a most useful model alloy for examining a variety of superalloy solidification reactions and processes. Knowledge has been gained from this work which throws light on single crystal manufacture; the removal of defects from ingots made by remelting processes; and the control of solidification structure. An underlying feature of the results is that the nitrogen content of superalloys is a critical component in several facets of their behaviour and hence should possibly be more carefully specified in future uses of the alloys.

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