Phase transformation and liquid density redistribution during solidification of Ni-based superalloy Inconel 718

Abstract: The influences of chemical segregation and phase transformation on liquid density variation during solidification of Ni-based superalloy Inconel 718 were investigated using SEM and EDS. It was found that significant segregation in liquid prompts high Nb phase to precipitate directly from liquid, which results in the redistribution of alloy elements and liquid density in their vicinity. The term “inter-precipitate liquid density” is therefore proposed and this concept should be applied to determine the solidification behavior of superalloy Inconel 718.

Key words: Inconel 718; Nb segregation; phase transformation; inter-precipitate density inversion

1 Experimental details

The nominal chemical composition of investigated Inconel 718 is 0.021%C, 0.97%Ti, 0.56%Al, 2.98%Mo, 5.36%Nb, 17.72%Cr, 19.93%Fe (by weight) and balanced with Ni.

The re-melting treatment process was designed according to the freezing range of Inconel 718, which is 1,260–1,336 °C. All samples were columns with the dimension of Ф25 mm

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Recently, more aggressive jet engines and industrial gas turbine designs have increased the demand for large diameter superalloy ingots used in rotating components. However, ingot diameter has been limited by the strong tendency of forming melt-related defects, such as freckles, in these complex alloys. Over the past four decades, there have been substantial efforts in both industry and academia to reduce macro-segregation. It has been widely accepted that the freckle defect is formed in accordance with “density inversion theory” proposed by McDonald, Giamei, and Copley, et al

Density inversion theory claims that the density of the interdendritic liquid depends on both the thermal and solute effects. On the one hand, the liquid density increases with the decrease in temperature; on the other hand, it also changes as the solute elements vary. When the effects on the density of negative segregation of heavier elements or positive segregation of lighter elements exceed the temperature effects, the liquid density will decrease as the solidification continues. And the inverse density distribution becomes thermodynamically unstable when the gravity force acts against the growth direction of solid. As a result, the fluid flow may occur due to the density inversion.

This theory can successfully explain why the freckle defect forms in simple binary alloys, such as Ni-Al and Pb-Sn systems

In this paper, the solidification process of Inconel 718 was investigated. Due to segregation, the composition of residual liquid deviated from the original composition, and the content of Nb in liquid reached 20%, which agreed with the reported data in reference [12]. Laves, MC, and d precipitate directly from such liquid during consequent solidification. These precipitates change the distribution of the alloy elements and the density of the interdendritic liquid, resulting in a low Nb and low density area between two precipitates, which is called the inter-precipitate in this paper. Accordingly, the local liquid area is called the inter-precipitate liquid and the local density is named as the inter-precipitate liquid density. The liquid of all interdendritic areas, including both the inter-precipitate areas and liquid-precipitated phase, is named the average liquid and the density is called average liquid density. The density difference between the inter-precipitate liquid and the average interdendritic liquid can generate a slight density inversion in local areas of the mushy zone. This paper is aimed to study the effect of phase transformation on the liquid density. Based on the experimental results, the term “inter-precipitate liquid density” was proposed in order to accurately demonstrate the liquid density variation in the mushy zone of Inconel 718.
× 35 mm, and were placed in alumina crucibles before heat treat- ment. These samples were heated to 1,400 °C, holding for 15 min, and then cooled in furnace to a set temperature in freezing range, holding for 20 min, quenched in salt water. The temperature (°C) at which the samples were quenched \( (T_q) \) is: (1) 1,360, (2) 1,340, (3) 1,320, (4) 1,300, (5) 1,280, (6) 1,260, (7) 1,240, (8) 1,200, (9) 1,180, and (10) 1,140. Soaking in the freezing range for 20 min ensured sufficient diffusion of solute elements in liquid, which makes the solidification condition closer to that in the industrial ingot processing.

The industrial samples with the dimension of 10 mm × 10 mm × 10 mm cubic block were cut from the rim, mid-radius, and center of a \( \Phi \) 508 mm Inconel 718 ingot. SEM specimens were mechanically ground, polished, and further electro-polished 10 s at a voltage of 10 V in a mixed solution of CrO₃, H₂SO₄, and H₃PO₄. Composition analysis of the dendritic and interdendritic areas of ingots, and of that of residual liquid, as well as some phases formed during the solidification of remelting samples, were carried out by means of EDS attached to the SEM. All major alloying elements (>5wt.%, except for carbon) were semi-quantitatively analyzed. The chemical compositions presented in this paper are average values over five or more direct EDS measurements. Standard deviation observed in the multiple measurements always fell within the expected precision of EDS system, namely ±5% for major alloying elements and up to ±15% for minor alloying elements (content usually lower than 5wt.%).

2 Results

Figure 1 shows the liquid microstructure of Inconel 718 quenched at three different temperatures. The liquidus of Inconel 718 is below 1,340 °C, and there was only liquid present in the microstructure of the sample quenched at 1,340 °C in salt water. When these samples were water quenched at a temperature between liquidus and solidus, the morphology and composition of the formed solid and the residual liquid were preserved. Macrostructures of these samples consisted of the primary \( \gamma \) solid phase and the residual liquid. The lower the temperature, the more the primary \( \gamma \) and the less the residual liquid present. This tendency is clearly demonstrated in Fig. 1 and the liquid fraction at different temperatures is summarized in Fig. 2. The quenched residual liquid consisted of \( \gamma \) phase and precipitates (consist of Laves, MC, \( \delta \) or their eutectic or pseudo-eutectic according to the cooling rate and the resultant local liquid composition), as shown in Fig. 1. As the temperature decreased, the residual liquid volume reduced, and the eutectic phase became more prevalent in the quenched liquid microstructure. The residual liquid became eutectic as the quenching temperature fell below 1,280 °C (Fig. 1b), this corresponded to about 80% solid and 20% residual liquid.

Segregation of alloy elements during solidification is shown in Fig. 3. It can be seen that the content of Nb increased rapidly as the solidification proceeded. There was more than 20%Nb in the final liquid although there was only 5%Nb in the
nominal composition. The increase in the content of Nb was concentrated at temperatures below 1,300 °C when the liquid fraction decreased to 20%. The concentration of Mo and Ti in the liquid showed a small increase during the solidification. The variation of Al in the liquid was not remarkable.

Alloy element segregation changed the composition of the residual liquid and led to complex phase transformations. The equilibrium phase diagrams of these alloys were calculated using the Thermo-calc program. Figure 4(a) shows the partial enlarged diagram of the alloy with nominal composition. In the calculation, complete diffusion in both solid and liquid was assumed, which is similar to the condition of slow cooling as in the industrial practice. The MC phase was shown to precipitate at temperatures above the solidus. In comparison with Fig. 4(a), Fig. 4(b) shows the phase diagram of alloy with segregated composition in liquid quenched at 1,320 °C, whose liquid fraction is about 31% with 10.05wt.%Nb. Due to large changes in composition (compared with the nominal composition) resulting from segregation, the phase transformation is quite different in the residual liquid regime, and the solidus and liquidus temperatures are greatly decreased. In addition to a small amount of MC, more than 5% Laves forms in liquid above the solidus. When the temperature and the liquid quantity decrease, there are more Laves formed in the freezing range of these diagrams, and \( \delta \) begins to precipitate in the liquid as well. In the phase diagrams of segregated liquid quenched at 1,280 °C, there was about 15% Laves and 20% \( \delta \) precipitated directly from the liquid.

It can be seen from these experimental and calculated results that Nb concentration in the residual liquid increased quickly and greatly with the decrease in the temperature and the quantity of liquid due to the redistribution of solute between solid and liquid. Alloy element segregation in the residual liquid, mainly Nb, changed the solidification sequence of Inconel 718.

In order to define the effect of phase transformation on the distribution of liquid density in interdendritic liquid, the average liquid density and inter-precipitate density were further investigated in experimental samples.

The average interdendritic liquid density at different temperatures was calculated in accordance with the method provided in the literature [13, 14]. The error resulting from this approximation is less than 2.5%. Figure 5 shows the calculated liquid density as a function of temperature. It can be seen from Fig. 5 that the liquid density increased slowly at the beginning of solidification, but increased quickly below 1,300 °C when the liquid fraction fell to less than 20%. The liquid density increases monotonically with the decrease of temperature through the freezing range, and there was no density inversion observed.

In order to further demonstrate the liquid density variation, the relationship between local Nb segregation and liquid density was analyzed in detail. Figure 6(a) shows the microstructure of liquid quenched in salt water, and Fig. 6(b) shows the content of Nb and the density at the locations 1 to 3, where 1 is on the precipitate, 2 is at the \( \gamma \) matrix near the \( \gamma \)-precipitate interface, and 3 is at or about the mid-distance between two precipitates. It can be seen that the closer to the precipitate, the higher the content of Nb, and the higher the density. It is also noted that the lowest density area is at the mid-distance between two precipitated phases (inter-precipitate). The average liquid
density which is higher than that of the inter-precipitate is also given in Fig. 6 for reference.

The effect of phase transformation on the density distribution was also confirmed in an Inconel 718 ingot with a diameter of 508 mm. The microstructure and alloy element segregation in the interdendritic region were investigated using SEM and EDS as well. The contents of Nb in the interdendritic area at the rim, mid-radius, and center of the ingot were analyzed by EDS and were determined to be 6.01wt.%, 7.24wt.%, and 6.99wt.%, respectively. It can be seen that the segregation level at the center was close to that at mid-radius and both of them were heavier than that at the ingot rim. The microstructure and segregation at the center can be used to represent the industrial ingot; the microstructure is shown in Fig. 7. The dark area indicates γ dendrites, and the lighter areas are the interdendritic, whose area fraction is about 30%. Those island-like phases in the interdendritic area are mainly Laves. Obviously, these islands of Laves transformed directly from the liquid. The content of Nb in the interdendritic region is about 7%.

Figure 8(a) shows the Laves microstructure in the interdendritic area at a higher magnification. The δ plates and γ'' disks precipitated in the vicinity of Laves. The measured Nb concentration between two Laves islands and the calculated density at locations 1, 2, and 3 are shown in Fig. 8(b), where 1 is at the location of Laves precipitate, 2 is at the location of γ matrix in close proximity with the interface of γ-Laves at the interdendritic area, and 3 is between two precipitates of Laves. For comparison, the average content of Nb and the average interdendritic density are also given in Fig. 8(b). From these results, it can be seen that the farther from the Laves, the lower the content of Nb and the lower the density. The content of Nb and the density at the mid-distance between two precipitates of Laves were the lowest compared with that at other locations. Similar to the above-mentioned experimental samples, the distribution of the density was similar to that of Nb, and the inter-precipitate area had the lowest density. The increase in the density at the location 2 was probably related to
the fact that the analyzed zone was on the Laves or the density was affected by other alloy elements besides Nb, such as Mo, during the slow solidification of the ingot.

Due to the slow cooling in the solidification of the industrial ingots, especially in the ingot center, the redistribution of alloy elements occurred and the alloy segregation was severe. The serious segregation of Nb and Mo in the interdendritic liquid made the phase transformation at those locations/regions deviate from the equilibrium. In the interdendritic region, there were a large quantity of Laves and $\delta$ precipitated from the segregated liquid during solidification. These high-Nb precipitates (mainly Laves) changed the distribution of alloy elements and resulted in the liquid density variation in the interdendritic region. The inter-precipitate region had a lower density and thus there would be a slight density inversion between the inter-precipitate liquid and the average interdendritic liquid.

3 Discussion

3.1 Segregation and phase transformation during solidification of Inconel 718

During solidification of Inconel 718, the alloy elements were redistributed between solid and liquid and the elements of positive segregation, such as Nb, Mo, and Ti, were ejected into the liquid. Therefore, their concentrations in the liquid increased with the decreasing of liquid fraction. On the other hand, the negative segregation elements, such as Fe and Cr, would congregate in the solid. Because of large atom size and low diffusion coefficient, Nb segregation was the most serious and the concentration of Nb could reach 20wt.% in the final solidified liquid in a nominal 5.36wt.% concentration alloy. Mo is another positive segregation element behaving similarly as Nb. Segregation of Al and Ti was not remarkable because the total content of these elements in the nominal composition was no more than 1wt.%. The content of Nb in the interdendritic region of the cast ingot was lower than that in liquid of the experimental samples, and this was related to further diffusion in solid during the slow cooling of the ingot. When Laves begins to form in liquid, the liquid fraction was similar to the volume fraction of the interdendritic region in the ingot.

The enrichment of elements Nb and Mo in liquid and the leanness of elements Fe and Cr make the residual liquid density increase greatly through the freezing range. The lower the temperature at which the samples were quenched, the higher the residual liquid density. There was no density inversion during solidification from the view of average liquid density.

On the other hand, the segregation of alloy elements in liquid changed the solidification sequence. High content of Nb in liquid prompts Laves to precipitate directly from the liquid. Thus, the content of Nb in the liquid surrounding the high-Nb phase could be notably decreased. The densities calculated in such inter-precipitate regions were lower than that of the average liquid at the same temperature. During the slow cooling of large industrial ingots, there were many blocks of Laves formed in the interdendritic region and the inter-precipitate region had a lower density as well.

3.2 Density variation in the mushy zone of Inconel 718

During the solidification of high Nb-containing superalloy, heavy Nb segregation prompts the precipitation of high-Nb phase (mainly Laves) in liquid and thus, the density of the adjacent liquid decreases significantly. Therefore, the liquid density does not increase monotonically in the mushy zone from the top to the bottom during an upward directional solidification. There was a density inversion between the inter-precipitate liquid and the average interdendritic liquid, which is called “inter-precipitate density inversion” in this work. Figure 9 shows schematically the model for the density variation in the mushy zone of Inconel 718. To simplify the situation, it is assumed that there is only Nb segregation in the mushy zone, and the phase transformation in the mushy zone is only limited to that of high-Nb precipitates. The density profile of liquid in the mushy zone is similar to the concentration profile of Nb. In Fig. 9, $\rho_o$ and $\rho_e$ are the densities corresponding to that of original composition and that of eutectic, respectively. $\rho_s$ and $\rho_l$ are the densities of solid and liquid compositions, respectively, at temperature corresponding to horizontal location AB in the mushy zone. $\rho_p$ is the density of high-Nb precipitates.

![Fig. 9: Model of inter-precipitated liquid density inversion](image-url)
Due to a higher concentration level of Nb in liquid, the high-Nb phase precipitated at a lower location in the mushy zone, as shown in Fig. 9(a), which consumed the Nb nearby. Therefore, there was a low Nb/density area surrounding them especially in the inter-precipitate region between two precipitates of high-Nb phase. Figure 9(b) is the density profile along the horizontal direction of AB in Fig. 9(a). There is a minimum value of liquid density at the midpoint between two precipitates, which is called the inter-precipitate. The liquid density distribution along the vertical direction of CD in Fig. 9(a) is presented in Fig. 9(c). The average content of Nb in liquid and the average liquid density are increasing from up to bottom, as indicated by the dash dot line in Fig. 9(c), if there is no high-Nb precipitates formed during the solidification \([11,15-17]\). However, the formation of high-Nb precipitates generates some fluctuations in the density curve, as indicated by the solid line. The inter-precipitate density is lower than that of the average liquid density at a higher temperature or higher location, resulting in a density difference \((\Delta \rho)\) between them and producing a local density inversion. However, a quantitative evaluation of the magnitude of the inter-precipitate density inversion and the relationship with its Rayleigh number still needs more detailed work.

4 Summary

The segregation behavior and the influence of phase transformation on the liquid density variation during the solidification of Ni-based superalloy Inconel 718 have been experimentally investigated using SEM and EDS. As the solidification of Inconel 718 proceeds, the segregation of Nb in liquid prompts the precipitation of high-Nb precipitates. The formation of these precipitates consumes Nb in the surrounding region and results in the redistribution of alloy elements and liquid density in the vicinity. A low density area forms between two precipitates and therefore, the term “inter-precipitate density” is proposed in this paper. This concept should be applied to determine the solidification behavior (including the influence of phase transformation on the liquid density variation) of superalloy Inconel 718.

References


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