Effect of Solidification Rate on the Microstructure of a Ni-Base Superalloy

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The effect of solidification rate on the solidified structure, solute segregation and microstructures such as carbide, \( y'/y \) eutectic, \( y' \) phase and dendrite arm spacing was experimentally investigated employing a method of partially directional solidification and subsequent quick quenching. Three types of the solidified structure were identified: cellular, cellular-dendritic and developed dendrite-type, and the width of a mushy zone was narrowed when solidification rate increased from 2.5 \( \mu \text{m/s} \) to 125 \( \mu \text{m/s} \). The carbide morphologies were affected by both solidified structure and solidification rate, it formed bar-type in the cellular structure, and Chinese script-type in the dendrite structure. The increase of solidification rate caused a lot of \( y'/y \) eutectic and the change of \( y' \) phase from cubic into cubic-round. The dendrite arm spacing decreased and the segregation of Cr, Al, Co, Mo, Ti was alleviated with increasing solidification rate.

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I. Introduction

Unidirectional solidification along a temperature gradient can result in improved properties in superalloys, mainly in strength and ductility, so it was widely used in producing gas-turbines, because the dendrite arm spacing, porosity and non-metallic inclusion size can be significantly reduced\(^{(1)} \) compared to conventional solidification. The mechanical properties of the gas-turbine depend closely on the size of dendrite\(^{(2)-(4)} \), the carbide characteristics\(^{(5)} \) and the solute segregation\(^{(6)} \) etc. In general, the dendrite is refined at high solidification rate, so the mechanical properties can be improved. Fatigue life in alloys, especially in Ni-base superalloys, was found to be greatly affected by the size of preexisting cracks in MC-type carbide. The crack initiation and propagation often depend on the shape and size of carbide. The large blocky carbide that speeds up crack propagation usually deteriorates the mechanical properties. The diffusion of solute is fast when the concentration gradient that caused by solute segregation is far larger than the driving force of diffusion, and it results in unstable microstructure. For example, \( \text{M}_{23}	ext{C}_{6} \) or \( \text{M}_{23}	ext{C}_{4} \) carbide formed in some superalloys.

The purpose of the investigation is to examine the microstructure at various solidification rates, such as the carbide characteristics, dendrite arm spacing and solute segregation. Directional solidification makes the correlation between growth rate and the microstructure particularly easy. The relation between the solidification rate and the carbide morphology, \( y' \)-phase and solidified structure, in this new superalloy was elucidated.

II. Experimental Procedure

The virgin alloy was remelted and cast into bars in an induction furnace. The composition of the alloy is 0.16 mass\%C, 5.34 mass\%Al, 0.75 mass\%V, 4.46 mass\%Ti, 8.58 mass\%Cr, 3.0 mass\%Mo, 10.17 mass\%Co, 0.018 mass\%B, and the rest is Nickel. All bars were machined into 8 mm in diameter and directionally solidified under high-purity argon flow in an induction furnace equipped with a bottom water-cooled chill and a graphite susceptor minimizing induction stirring of the melt and homogenizing the temperature distribution. The sample was placed in an alumina crucible, heated to 1773 K for 10 min, and then pulled downward at a uniform rate of 2.5 \( \mu \text{m/s} \), 17 \( \mu \text{m/s} \) or 125 \( \mu \text{m/s} \), respectively. The thermal gradient in the liquid in front of the solid-liquid interface was 15 K/mm. For this particular set-up (shown in Fig. 1), the growth rate of the solid in the direction of heat flow was equal to the rate at which the crucible was pulled\(^{(7)} \). The sample was pulled down by 30 mm and then quenched quickly into water. The longitudinal section of the specimen was polished and etched in a medium of \( \text{CuSO}_{4}(20 \text{ g}) + \text{HCl}(50 \text{ mL}) + \text{H}_{2}\text{SO}_{4}(5 \text{ mL}) + \text{H}_{2}\text{O}(100 \text{ mL}) \) at room temperature. The morphology of the solidified structure, the width of mushy zone and the dendrite arm spacing (DAS) were examined using optical microscopy. A large number of dendrite arms were counted in order to get high precision, and the average was chosen as the final result. The profiles of solute distribution were established by electron probe microanalysis (EPMA), using the linear scanning technique across the interdendritic region. SEM was used to determine the shape of the \( y' \) phase, and optical microscope was used to examine the solidified structure and \( y'/y \) eutectic. The
The parameter of shape (PS) is defined as following:

\[ PS = \frac{4\pi S}{l^2} \]

\( l \): the perimeter of carbide,
which is a measure of shape, \( 0 < PS < 1 \), and PS tends to
1 as the shape becomes more circular.

### III. Results and Discussion

#### 1. Solidified structure

As shown in Fig. 2, the solid-liquid interface morphology can be classified into three types, i.e. cellular, cellular-dendritic, and developed dendritic and when the solidification rate is up to 125 \( \mu m/s \), the dendrite somewhat deviated the direction in which the temperature gradient lay. Table 1 shows the width of the mushy zone of the specimens at different solidification rates. Here, the distance from the cell/dendrite tip to the bottom was defined as the width of mushy zone. It was evident that the value decreased with increasing solidification rate. At the higher solidification rate, the mushy zone was widened and out of the measurement.

On the basis of the constitutional supercooling argument of Tiller et al.\( ^{[9]} \), a criterion for developing dendritic growth in binary alloy can be stated as

\[
d = \sqrt{\frac{S}{\pi}}
\]

\( d \): equivalent diameter of carbide, \( \mu m \)
\( S \): area of the cross-section of carbide, \( \mu m^2 \)

<table>
<thead>
<tr>
<th>Growth rate (( \mu m/s ))</th>
<th>Width (( mm ))</th>
<th>PDAS (( \mu m ))</th>
<th>SDAS (( \mu m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>cellular</td>
<td>cellular</td>
<td>cellular</td>
</tr>
<tr>
<td>17</td>
<td>3.97</td>
<td>227.8</td>
<td>52.4</td>
</tr>
<tr>
<td>125</td>
<td>3.00</td>
<td>171.7</td>
<td>27.0</td>
</tr>
</tbody>
</table>

Fig. 2  Morphology of solid-liquid interface for different solidification rates. (a) 2.5 \( \mu m/s \), (b) 17 \( \mu m/s \), (c) 125 \( \mu m/s \).
\[
\frac{\Delta G}{R} = \frac{m_c c_0 (k-1)}{D_k}
\]  

(1)

where \( G \) is the thermal gradient in the liquid near the solid-liquid interface, \( R \) is the solidification rate, \( m_c \) is the inclination of liquidus, \( C_0 \) is the solute concentration, \( k \) is the partition coefficient and \( D_k \) is the effective diffusion coefficient of atom in the liquid, which is believed relatively constant. Although eq. (1) was originally developed to give the critical conditions for the development of dendrite growth in dilute binary alloys, it can also be approximately applied to give an upper limit for the \( G/R \) to form dendrite, and it can be deduced from eq. (1) that the higher the solidification rate is, the more developed dendrite forms.

2. Dendrite arm spacing

The values of primary dendrite arm spacing (PDAS) and secondary dendrite arm spacing (SDAS) were listed in Table 1. It was found that both PDAS and SDAS decreased with increasing solidification rate. The similar result on other alloy was described in Ref. (10). The primary and secondary dendrite arm spacing depended on both the property of alloy and the solidification parameter. When the rate increased, the dendrite was suppressed and dendrite arm spacing decreased because of the short local solidification time in this case.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Characteristics of carbide.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth rate (( \mu m/s ))</td>
<td>Size (( \mu m ))</td>
</tr>
<tr>
<td>2.5</td>
<td>6.9</td>
</tr>
<tr>
<td>17</td>
<td>6.5</td>
</tr>
<tr>
<td>125</td>
<td>2.7</td>
</tr>
</tbody>
</table>

3. Pattern of the primary MC carbide

As shown in Table 2, with increasing of solidification rate, the content and size of the MC carbide decreased and the PS of MC carbide reduced but one case at 2.5 \( \mu m/s \). The morphology of primary carbide was given in Fig. 3. The growth of the primary carbide was affected by both the chemical potential of carbide-form elements and the available room for the carbide to develop. When the rate was at 2.5 \( \mu m/s \), the segregation of Ti was a little lighter than that at 17 \( \mu m/s \), so only when the local concentration of Ti was accumulated large enough for the carbide to precipitate, but at that time, the cellular had grown up, and the carbide growth was constrained to the narrow cell boundaries, so PS was smaller than that in dendritic solidification. This is in good agreement with the results described in Ref. (11). For the growth of the carbide was always behind the growth of the dendrite, it

Fig. 3 Morphology of primary carbide in different specimens.
4. \(\gamma'\) phase precipitation

Figure 4 shows the pattern of \(\gamma'\) phase in the interdendritic region at the same temperature for different specimens. The result of PS measurement was listed in Table 3. It indicated that the \(\gamma'\) phase was cubic form and local distribution at 2.5 \(\mu\)m/s, while the \(\gamma'\) phase turned cubic-round form and fully dispersed distribution when the solidification rate went up to 125 \(\mu\)m/s.

The individual coherent \(\gamma'\) precipitate has an energy state which can be expressed by the following equation

\[
E_{\text{total}} = E_{\text{str}} + E_{\text{surf}} + E_{\text{int}}
\]  

(2)

where \(E_{\text{str}}\) is the elastic strain energy due to the lattice mismatch between \(\gamma'\) precipitate and the matrix \((\gamma\) phase), \(E_{\text{surf}}\) is the surface energy of \(\gamma'\) precipitate and \(E_{\text{int}}\) is the elastic interaction energy between \(\gamma'\) precipitates. In the initial stage of \(\gamma'\) precipitation, \(\gamma'\) particles are far away from each other, so \(E_{\text{int}}\) can be regarded as zero, and the shape of \(\gamma'\) precipitate is determined by minimizing the sum of \(E_{\text{str}}\) and \(E_{\text{surf}}\). At that stage, the effect of surface tension resulted in the round-like form because the sphere had the smallest surface energy if the volume was constant. The subsequent growth which was controlled by diffusion was usually in some crystallographically optimal orientation, so it grew into cubic form under the low solidification rate.

5. \(\gamma'/\gamma\) eutectic

As shown in Fig. 5, only a thin layer of \(\gamma'\) covered on the cellular surface, when the solidification rate was 2.5 \(\mu\)m/s and several large fan-like \(\gamma'/\gamma\) eutectic cells were found in the interdendritic region in the specimen of 17 \(\mu\)m/s. But when the rate went beyond 125 \(\mu\)m/s, a large number of small chrysanthemum \(\gamma'/\gamma\) eutectic cells emerged in that region. This result is in good agreement with Ref. (5).

The \(\gamma'/\gamma\) eutectic was a primary phase which formed in the latter stage of solidification. If the rate was very low, the \(\gamma'\)-form element may be well-distributed through diffusion and only a thin layer of \(\gamma'/\gamma\) eutectic formed over the cellular. If the solidification rate increased, the local concentration of those elements increased and the available time of being well distributed was relatively insufficient, so much \(\gamma'/\gamma\) eutectic cells formed, and the size of the cell depended on the interdendritic spacing.

<table>
<thead>
<tr>
<th>Growth rate ((\mu)m/s)</th>
<th>Size ((\mu)m)</th>
<th>Content (Area %)</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.69</td>
<td>34.7</td>
<td>0.71</td>
</tr>
<tr>
<td>17</td>
<td>0.57</td>
<td>32</td>
<td>0.75</td>
</tr>
<tr>
<td>125</td>
<td>0.19</td>
<td>26</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Fig. 4 Morphology of \(\gamma'\)-phase in different specimens.
6. Microsegregation of solute

The electroprobe microanalysis (EPMA) by linear scanning across the interdendritic region in the bottom of the mushy zone was employed to determine the solute concentration profiles for each specimen. The results were shown in Fig. 6. It was found that Al, Mo, Cr, Co, Ti were enriched whereas V had no distinction in the interdendritic region. Though a big negative peak for Al emerged in its concentration profile as the growth rate was 2.5 μm/s, it was still a positive segregation element, because γ' phase around the cellular used up much Al.

![Fig. 5 Morphology of γ/γ' eutectic different specimen. (a) 2.5 μm/s, (b) 17 μm/s, (c) 125 μm/s.](image_url)

![Fig. 6 Compositional profiles across grain boundaries by line scanning.](image_url)
(see Fig. 5(a)), and it can be verified by the positive peak on the left side of the big negative peak in Fig. 6(a). It was also found that the segregation of other elements apart from Ti was mitigated with increasing of solidification rate. It might be caused by the suppression of the dendrites at the high rate. This result is in good agreement with Refs. (14) and (15).

**IV. Conclusion**

The relation between solidification rate and the microstructure such as the morphology of liquid-solid interface, $\gamma'$ phase and primary carbide in the new superalloy was studied in this work. As the solidification rate increased, the solidified structure changed from cellular to fully dendritic and the mushy zone was narrowed, the dendrite arm spacing was also reduced, the carbide turned from bar or blocky into Chinese script-type, the $\gamma'$ phase changed from cubic to cubic-round and the size reduced, the segregation of solute element was mitigated apart from Ti.

**REFERENCES**