Grain refinement of superalloys K3 and K4169 by the addition of refiners
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Abstract

Grain refinement of superalloys K3 and K4169 is achieved by adding refiners A, B, or mixed refiner (A + B) into the melt of alloy K3, and refiner C into the melt of alloy K4169 under different casting parameters. Results indicate that the mixed refiner (A + B) produces the best refining effect for alloy K3. In this case, the average equiaxed grain size is reduced from 4.9 to 1.5 mm, i.e. to ASTM M9, and the proportion of equiaxed grains at traverse cross-section has been improved from 40 to 84%. Moreover, the average main axis length of dendrites reduces, and the morphologies of MC carbides change from rod-like and Chinese-script type to discrete block type after grain refinement. For alloy K4169, adding C into the melt can refine the grains to the order of ASTM M9.5. Meanwhile, the proportion of equiaxed grains increases 31% and the average main axis length of dendrites reduces 2.85 mm. In addition, the amount and size of both Laves phase of eutectic morphology and MC carbides reduce. Interdendritic segregation level of elements of both alloys is reduced. © 2001 Published by Elsevier Science Ltd.

Keywords: Superalloy K3; Superalloy K4169; Refiner; Grain refinement

1. Introduction

The main disadvantages of conventional investment cast superalloys are microstructural coarseness and non-uniformity of grain size, which reduce the fatigue performance and reliability of cast turbine blades and wheels within the medium temperature ranges. In recent years, integral fine-grained cast techniques [1,2] have been extensively progressed, which has resulted in improved uniformity in properties, homogeneous microstructures and morphology of precipitates such as carbides and γ’ phase.

Refinement of cast structures requires that nucleation occurs at a large number of sites and that extensive growth of crystals be avoided. The existing methods of grain refinement include [3] rapid cooling, dynamic methods, growth-hindering additions, nucleating additions, and denucleation. It has been considered that refiners are not often used with superalloys because of their high inclusion sensitivity. In the present study, by considering the principle of grain refinement and the melting characteristics of superalloys, several refiners which do not change the phase constitution freezing characteristic and structural stability of superalloys, have been chosen to investigate their effects on the grain structures of cast superalloy K3 and K4169.

2. Materials and experimental procedures

2.1. Preparation of refiners

The ingots of refiners A, B, and C, which are intermetallic compounds, were prepared by melting an appropriate proportion of the constituents in a vacuum furnace in an argon atmosphere. They were ground into powder before they were added to the alloy melt.

2.2. Superalloy K3

Superalloy K3 has the chemical composition illustrated in Table 1 and its melting and solidification properties were determined by differential thermal analysis (DTA). The equilibrium liquidus and solidus of 1362 and 1311°C were respectively obtained.

The melt was firstly superheated to 1550°C for 4 ~ 6 min to remove the effects of the previous processing history of the alloy. Then, the melt was cooled down to a predetermined pouring temperature. After that, refiners A, B, or mixed refiner (A + B) was added into the melt under the chosen process parameters. The mould preheating temperature was 900°C in all cases.

2.3. Superalloy K4169

The chemical composition of superalloy K4169 is shown as Table 1. Its equilibrium liquidus and solidus temperature
are determined to be 1339 and 1256°C by DTA. Two cast procedures were used to prepare the samples: (1) the melt was superheated to 1550°C for 4 ~ 6 min, then cooled down to 1420°C and poured; (2) the melt was superheated to 1420°C for 4 ~ 6 min, then refiner C was added into the melt and the melt was subsequently poured. The preheated temperature of ceramic mould was kept at 850°C for both cases.

For both alloys K3 and K4169, a vacuum melting and casting unit, consisting of an induction furnace and a mould preheating furnace, which are installed within a stainless vessel connected to vacuum pumps, was used to cast the samples. In order that the refiner can be dispersed in the melt uniformly, an appropriate agitation was needed.

2.4. Structural examination

The alloy ingots were sectioned at different heights and specimens were ground, polished and subsequently etched. The average equiaxed grain size and proportion of equiaxed grains were determined by quantitative metallographic techniques. The grain size was also estimated with reference to the ASTM standard. For alloy K3, the etching treatment was carried out in a solution consisting of H₂O (80 ml), HCl (40 ml), and H₂O₂ (20 ml) to expose the microstructure of specimens. In order to reveal the microstructure, the specimens were etched with HCl (50 ml), HNO₃ (5 ml), and H₂O (50 ml) solution. For alloy K4169, the solution mixed with H₂O₂ (120 ml), HCl (20 ml), and FeCl₃ (5 g) was used to reveal the macrostructure of specimens. If the specimens were etched with a solution composed of HCl (50 ml), HNO₃ (5 ml), and H₂O (50 ml), the microstructure can be seen.

3. Results and discussion

3.1. Macrostructure

3.1.1. Alloy K3

The alloy pouring temperature was kept at a constant value of 1400°C, and different refiners were added into alloy K3 its macrostructure being shown in Fig. 1. Table 2 illustrates the process parameters and characteristic parameters of the grain structures. It can be seen that the addition of refiners produces structural refinement. Among them, the mixed refiner (A + B) produces the best grain refinement effect. The average equiaxed grain size reduces from 4.9 to 1.5 mm, i.e. to ASTM grain size M9. Moreover, the proportion of equiaxed grains at traverse cross-section increases progressively from 40 to 84%.

3.1.2. Alloy K4169

The process parameters and the corresponding characteristic parameters of the grain structures of alloy K4169 are listed in Table 3. It can be seen that the addition of refiner makes the average equiaxed grain size reduce drastically from 4.3 to 1.2 mm. That is, the grain size can be as fine as ASTM M9.5. Furthermore, the proportion of equiaxed grains increases from 50 to 81%.

3.2. Grain refinement mechanisms by the addition of refiners

It is known that the process of nucleation and growth generates crystals. The refiners can act as the nucleation substrata of the γ matrix [4,5]. The presence of a large number of active refiners in the melt would cause enormous heterogeneous nucleation of several crystallites, which would collide with each other and restrict crystal growth.

Because of multi-components, multi-phases, high

| Alloy | C  | Cr | Co | W  | Mo | (Nb + Ta) | Al | Ti | Fe | B  | Ce | Zr | Ni |
|-------|----|----|----|----|----|----------|----|----|----|----|----|----|----|
| K3    | 0.15 | 11 | 5.3 | 5.2 | 4.2 | –        | 5.6 | 2.6 | <2 | 0.02 | 0.02 | 0.1 | Remainder |
| K4169 | 0.08 | 21 | 1.0 | –  | 3.3 | 5.4      | 0.7 | 1.15 | Remainder | 0.006 | – | – | 55 |

Fig. 1. Macrostructure of alloy K3 under various additions: (a) without addition; (b) addition of refiner A; (c) addition of refiner B; (d) addition of mixed refiner (A + B).
melting point and inclusion sensitivity of superalloys, it is difficult to choose appropriate refiners. Therefore, good refiners should have high melting points and good thermal stability. In addition, their densities and crystal structures should be close to that of the melt. Also, their components are the basic constituents of the superalloy, which means they do not bring inclusion into the melt. That is to say, the refiners do not change the phase constitution, freezing characteristics and structural stability of the alloy. Generally, the less the lattice disregistry between the refiner and the γ matrix the better the refinement effect of the refiner [6]. In the present study, the crystal structures of the refiners are similar to that of the primary phase [7], and the refiners have a low lattice disregistry of less than 12% with the primary phase (shown in Table 4). Hence, the grain structures can be refined by the addition of refiners.

Moreover, the mixed refiner has a better refinement effect, which can be attributed to the enlarged effective nucleation temperature range, resulting from the cooperation of two refiners.

### 3.3. Microstructure

#### 3.3.1. Alloy K3

The dendritic morphologies of samples a and d are shown in Fig. 2 and the average main axis length of dendrites (L) was measured. It can be seen that L reduces from 1.688 to 0.927 mm because of grain refinement. This is due to the addition of mixed refiner (A + B) to the melt. In such a case, a large amount of effective heterogeneous nucleation sites occur. Therefore, a large number of crystals form, which soon impinge on one another and prevent further growth, resulting in the growth of dendrites being hindered by other dendrites.

Moreover, the secondary dendrite arm spacing (SDAS) of samples a and d is 0.035 mm, indicating that the grain refinement has little effect on the SDAS, which relates to the melt pouring and mould temperature, i.e. to the cooling rate, which is kept almost constant throughout the present study.

While the grain size is reduced along with grain refinement, the size of MC carbides decreases and the morphologies of it change from the rod-like and script-like type to small blocks. One of the reasons is that refiner (A + B) contains trace Zr, which is capable of changing the morphologies of MC carbides into block type [8]. In addition, the number of nucleating centres increases and growth is inhibited after adding refiner, leading to the restriction of the growth of every dendrite. Hence, the interdendritic region for the growth of MC carbides is limited, which causes MC carbides not to be extended randomly. Furthermore, it is found that the interdendritic segregation of elements Mo, Al, Ti reduces whereas that of Cr increases slightly along with grain refinement. That is, the region and elements used for MC carbides’ growth are all reduced with grain refinement, resulting in variation of MC carbides in size and morphologies.

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**Table 2**
Process parameters and characteristic parameters of gain structures for conventional and fine-grained castings of alloy K3 (T_p, melt pouring temperature; P, proportion of equiaxed grains)

| Sample | Refiner | Content (wt.%) | T_p (°C) | Grain size (mm) | ASTM grade | P (%) |
|--------|---------|----------------|----------|----------------|-------------|-------|
| a      | –       | –              | 1400     | 4.9            | M5.5        | 40    |
| b      | A       | 0.2            | 1400     | 2.8            | M7          | 55    |
| c      | B       | 0.4            | 1400     | 3.7            | M6.5        | 64    |
| d      | A + B   | 0.6            | 1400     | 1.5            | M9          | 84    |

**Table 3**
Process parameters and characteristic parameters of gain structures for conventional and fine-grained castings of alloy K4169 (T_s, melt superheating temperature; T_p, melt pouring temperature; P, proportion of equiaxed grains)

| Sample | Refiner | Content (wt.%) | T_s (°C) | T_p (°C) | Grain size (mm) | ASTM grade | P (%) |
|--------|---------|----------------|----------|----------|----------------|-------------|-------|
| g      | –       | –              | 1550     | 1420     | 4.3            | M6          | 50    |
| h      | C       | 0.4            | –        | 1420     | 1.2            | M9.5        | 81    |

**Table 4**
Lattice disregistry between refiners and primary phase

| Refiner | Room temperature lattice parameters | Orientation relationship | Lattice disregistry |
|---------|-------------------------------------|--------------------------|---------------------|
|         | a_0 (nm) c_0 (nm) γ (deg.) | (010)_γ/(011)_γ | 5.341 |
| A       | 0.4837 0.7884 120 | (010)_γ/(111)_γ | 3.971 |
| B       | 0.6951 0.9000 120 | (001)_γ/(001)_γ | 2.430 |
| C       | 0.2881 0.3884 120 | (001)_γ/(001)_γ | 11.80 |
3.3.2. Alloy K4169

The dendritic morphologies of samples g and h can be observed in Fig. 3. The average length of the main axis decreases from 3.9 to 1.05 mm after grain refinement. In addition, the SDAS remains 0.05 mm.

At the same time, both the amount and the size of Laves phase decrease after grain refinement. It is revealed by electron micro-probe analysis that for K4169 alloy, the segregation of elements Nb and Ti is relatively severe, but that of Al and Mo is not serious under conventional casting conditions. However, the segregation of Nb and Ti is reduced and that of Al and Mo has been ameliorated along with grain refining treatment. The reduction of segregation of Nb — the main component of Laves phase — makes it difficult for Laves phase to form. Because Laves phase is brittle, its decrement is beneficial to ameliorate the mechanical properties of alloy K4169. The amount and size of MC carbides also decrease for fine grains. In addition, the MC carbides are distributed homogeneously.

4. Conclusions

From the above experiments, the following conclusions can be drawn:

1. By adding refiner to the melt of alloy K3, the grain structures can be refined considerably. The best refinement effect can be obtained by addition mixed refiner (A + B). In such a case, the average equiaxed grain size reduces from 4.9 to 1.5 mm. Moreover, the proportion of equiaxed grains increases intensively from 40 to 84%, and the average main axis length of dendrites is reduced from 1.688 to 0.927 mm.

2. Grain refinement causes the variation of the MC carbides morphologies from rod-like or script-like type to small block type for alloy K3.

3. The addition of refiner C into alloy K4169 makes the average equiaxed grain size reduce drastically from 4.3 to 1.2 mm, the proportion of equiaxed grains increase progressively from 50 to 81%, and the average main axis length of dendrites reduce from 3.9 to 1.05 mm.

Fig. 2. Dendritic morphologies of alloy K3: (a) sample a; (b) sample d.

Fig. 3. Dendrites of alloy K4169: (a) sample g; (b) sample h.
4. Both the amount and size of Laves phase and MC carbides in alloy K4169 decrease along with grain refinement, which is helpful in the improvement of the mechanical properties.

5. The grain refinement has an effect on the average main axis length of dendrites but has almost no influence on the secondary dendrite arm spacing, which is sensitive to the cooling rate.

6. The mechanism of grain refinement by the addition of refiners is that the refiner can act as the nucleation substrata of the γ matrix so as to promote nucleation and prohibit growth. The fact that the mixed refiner has a higher refinement effect can be attributed to the enlarged effective nucleation temperature range, which is the result of the cooperation of the two refiners.

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