Rare Metal Materials and Engineering
Volume 46, Issue 6, June 2017
Online English edition of the Chinese language journal

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(6): 1530-1535.

ARTICLE

Designing of the Homogenization-Solution Heat Treatment for Advanced Single Crystal Superalloys

Yue Xiaodai, Li Jiarong, Shi Zhenxue, Wang Xiaoguang

Science and Technology on Advanced High Temperature Structural Materials Laboratory, Beijing Institute of Aeronautical Materials, Beijing 100095，China

Abstract: An advanced single crystal superalloy was studied with different homogenization-solution heat treatments. The alloy microstructures and elements segregation were analyzed. The results show that no incipient melting appears when the alloy is directly heated up to 1338 ℃; when it is directly heated up to 1350 ℃, obvious incipient melting occurs at the beginning while gradually fades away with holding time; for 1328 ℃, although there is no risk of incipient melting, the homogenization efficiency is far from satisfactory. It is concluded that for advanced single crystal superalloys, elevating temperatures of each step is much more effective than prolonging duration to get better heterogeneous effect; as the single crystal superalloy owns a dynamic homogenization-solution heat treatment window, there is no need to always keep the temperature below the incipient melting temperature of the as-cast condition, but keeping it below the incipient melting temperature of the alloy at the temporal homogenous state is necessary. Based on above conclusions, a new approach is introduced to design effective homogenization-solution heat treatments for advanced single crystal superalloys, and it has been successfully used on the alloy in this study.

Key words: single crystal superalloy; homogenization; solution; heat treatment; designing

To cater for the continuous development of high temperature performance of advanced turbine blades and vanes, increasing amounts of dense refractory elements, including Mo, Re, Ta, W and Nb, are added to newer generations of single crystal superalloys[1]. However, other than solid solution strengthening, those dense refractory elements also lead to severe dendrite segregation, which greatly influence the strengthening effect of those alloying agents and the alloy properties[2,3].

A proper homogenization-solution heat treatment can efficiently eliminate segregation and promote chemical homogeneity. For the first and second generation single crystal superalloys, it is not so difficult to design a suitable homogenization-solution heat treatment thanks to the small quantity of refractory elements addition[1,4-7]. However, with higher refractory element content, it becomes increasingly more difficult for higher generations of single crystal superalloys to acquire satisfactory compositional and microstructure homogeneity. Designing more efficient homogenization-solution heat treatments becomes a new challenge[3,5,8,9].

To design efficient homogenization-solution heat treatments for advanced single crystal superalloys, an advanced single crystal superalloy was studied with different homogenization-solution heat treatments in this paper. After analyzing the experimental results by aid of dynamics and thermodynamics calculation, a suggestion about designing the homogenization-solution heat treatment was offered, which might be a more promising choice for the advanced single crystal superalloys.

1 Experiment

To cater for the segregation characteristic of advanced single crystal superalloys[10-12], 21.0wt% of refractory elements, including 6.0wt%Re, were added into the single crystal superalloy. A certain amount of Ru was also employed to promote the dissolving of those refractory elements in the matrix and restrain the precipitating of unstable phase. The single crystal

---

Received date: May 15, 2016

Corresponding author: Yue Xiaodai, Candidate for Ph. D., Science and Technology on Advanced High Temperature Structural Materials Laboratory, Beijing Institute of Aeronautical Materials, Beijing 100095, P. R. China, Tel: 0086-10-62498309, E-mail: yuexiaodai0126@126.com

bars of Φ15 mm×170 mm were cast with a crystal selection method in a directionally solidified furnace with high temperature gradient. DSC specimens of Φ4 mm×2 mm and homogenization-solution heat treatment specimens with Φ15 mm ×10 mm were cut from above mentioned single crystal bars. The heating curve of as-cast alloy was obtained using DSC, whose prepared heating rate was 10 ℃/min. The DSC curve is showed in Fig.1.

Generally, there are two methods to determine the starting temperature of γ' solution[13,14]:

1) Directly read the temperature where the first endothermic peak starts to climb up, which is usually referred to as $T_{\rm i}$. According to Fig.1, the value of $T_{\rm i}$ is 1338 ℃.

2) Make the extension of DSC baseline and the tangent line through the maximum slope point on the first endothermic peak. The intersection of those two lines is regarded as the extrapolating starting point of γ' solution, which can be referred to as $T_{\rm e}$. The value of $T_{\rm e}$ is 1350 ℃ according to Fig.1.

On the basis of above DSC curve, 1338 and 1350 ℃ were chosen for this research. As comparison, another lower temperature, 1328 ℃, was also picked, which was closer to those general temperature of first homogenization-solution heat treatment.

The specimens were directly heated up to 1328, 1338 and 1350 ℃. After preserving for 2 h and 6 h at each temperature, the specimens were taken out rapidly and air cooled to room temperature. Microstructures of the specimens were examined by metallographic and field emission microscope. The results were analyzed by the aid of dynamics and thermodynamics calculation.

2 Results

Fig.2 shows the metallographic structures after different homogenization-solution heat treatments. With duration time, the dendrite boundary gets fuzzy and eutectic decreases gradually. This speed gets more rapid at higher temperature. When heat treated at 1328 ℃ and 1338 ℃, no incipient melting occurs, and eutectic still exists after 6 h. At 1350 ℃, a mass of incipient melting appears after 2 h, while largely disappear after 6 h.

Fig.3 shows γ/γ' microstructure at interdendrites after different homogenization-solution heat treatments. After being heat treated at 1328 ℃ for 2 h, the γ' at interdendrites can be divided into three parts based on different size scales: (1) extremely coarse γ' existing in the eutectic; (2) very fine γ' far from eutectic; (3) intermediate section between above two regions where γ' with medium size spreads. After 6 h, the specimen still contains considerable eutectic, while

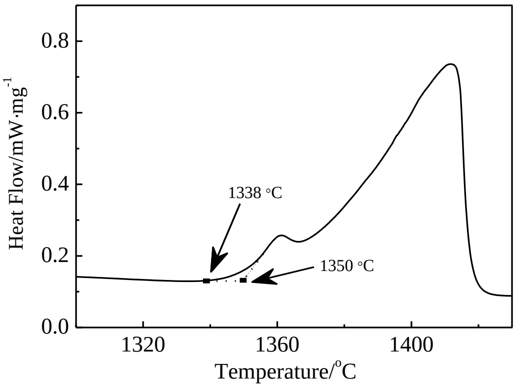

Fig.1 DSC curve of the as-cast alloy

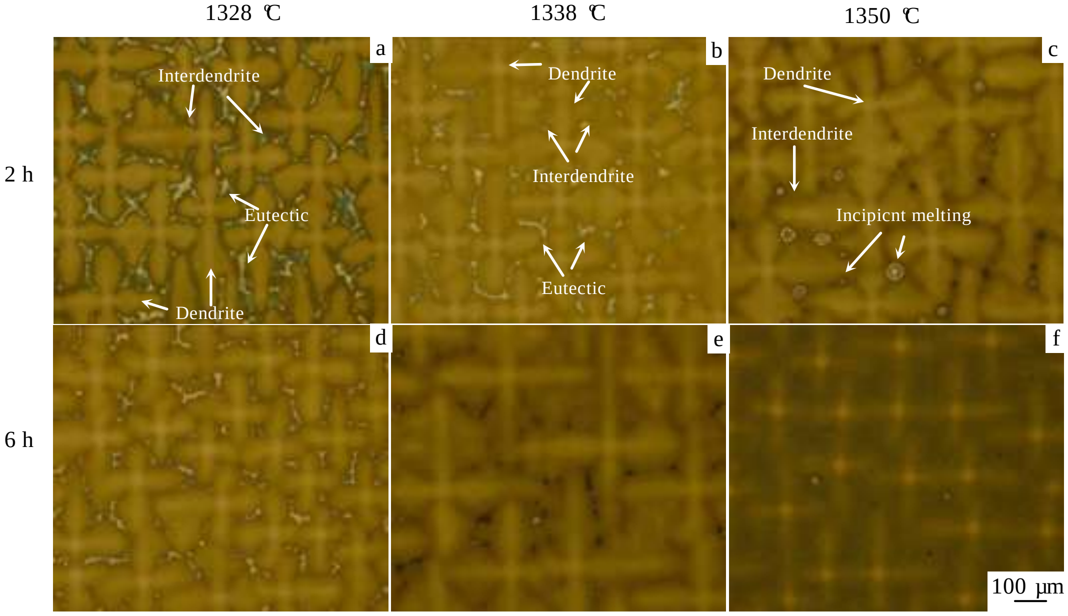

Fig.2 Metallographic structures of specimens after different homogenization-solution heat treatments

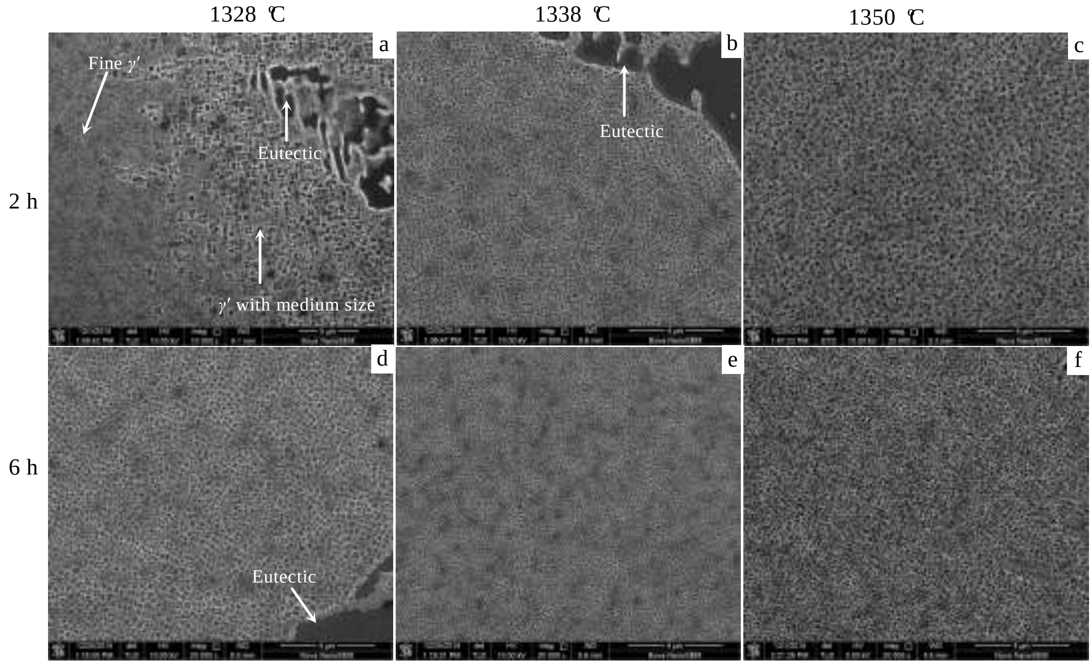

Fig.3 γ/γ' at interdendrites after different homogenization-solution heat treatments

there no longer exists any obvious boundary to distinguish γ' with different size scales. Meanwhile, when the specimens are homogenization-solution heat treated at 1338 ℃ and 1350 ℃ such boundary also can't be observed.

It is worth mentioning that although a mass of incipient melting appears after holding at 1350 ℃ for 2 h, that defect fades away with holding time. After 6 h, not only the quantity of incipient melting points decreases, the size of an individual incipient melting also shrinks, seen in Fig.2.

3 Discussion

For the as-cast single crystal superalloys, the components are highly segregated and the γ' precipitates are coarse, irregular shaped and incoherent. As the γ/γ' interface plays a major role in the high temperature properties, it's always desirable to have fine, uniformed cubical shaped precipitates throughout the alloy. For this reason, the solidified alloys need to undergo homogenization-solution heat treatments.[8] For newer generations of single crystal superalloys, good homogenizations can also reduce the precipitation of TCPs.[15] However, with increasingly more refractory elements are added into newer generations of single crystal superalloys, the homogenization becomes more difficult [3,5,8,9]. As a result, the homogenization-solution heat treatments of newer generations of single crystal superalloys have to be particularly studied to tap the most potential of those alloys.

3.1 Dynamic window of homogenization-solution heat treatments

As the principal purpose of homogenization-solution heat treatment is to dissolve the irregular γ' and homogenize alloy elements, the temperature of homogenization-solution heat treatment has to be above the γ' solvus end temperature and below the melting point of the alloy. The temperature range between the lower and upper bound is known as the window of homogenization-solution heat treatment [16].

DSC curve of as-cast alloy is shown in Fig.1. During heating process, there are two obvious endothermic peaks. The first smaller peak indicates the solution of γ', including the γ' in dendrites and interdendrites. The following larger one indicates the melting of the γ. These two endothermic peaks have a large scale of overlap whose width can't be distinct from the curve. That is because the refractory elements such as Mo, Re, Ta, W are prone to participate in dendrites and elements like Al, Ta, Nb are prone to participate in interdendrites. The severe segregation makes the phase transformation temperatures of $\gamma'\rightarrow\gamma$ and $\gamma\rightarrow$L vary a lot from dendrites to interdendrites. This is one of the reasons why it is more difficult to design a proper homogenization-solution heat treatment regime for advanced single crystal superalloys.

However, according to this paper, the temperature intervals of $\gamma'\rightarrow\gamma$ and $\gamma\rightarrow$L phase transformation can vary with the homogenization process. When the alloy is homogenization-solution heat treated at 1350 ℃, a large scale of incipient melting appears after 2 h, while after 6 h, the incipient melting degree decreases apparently. Not only the quantity of incipient melting points decreases, the size of an individual incipient melting also shrinks with holding time.

That is because the refractory elements diffuse from dendrites to interdendrites and other elements diffuse in the opposite direction, inducing the increase of melting temperature of interdendrites.

The variation of γ' solvus end temperature and incipient melting temperature with the homogenization at 1338 ℃ was calculated with a simulating software JMatPro, see Fig.4. It is demonstrated that both the γ' solvus end temperature and the incipient melting temperature increase with homogenization. That is to say, the homogenization-solution heat treatment window is dynamic for single crystal superalloys.

The dynamic characteristic of homogenization-solution heat treatment window doesn't draw much attention for the first and second generation single crystal superalloys since their solutes are easy to diffuse and alloying elements can be homogenized sufficiently at temperatures below the melting temperatures of the as-cast alloys. However, with increasingly more refractory elements added, the alloying elements can't diffuse sufficiently at the temperatures lower than as-cast melting points. That dynamic characteristic has to be brought to the forefront. To acquire a more efficient homogenization-solution heat treatment, the temperature can be set below the melting point of the alloy at the temporal homogenous state, other than always set it below the melting point of the as-cast condition.

3.2 First step temperature of homogenization-solution heat treatments

For the single crystal superalloy containing a high amount of refractory elements, there is a large overlap scale of the γ' solution peak and γ melting peak owing to severe segregation. That scale can't be distinct from the DSC curve. Even at a temperature slightly higher than the starting point of the first endothermic peak, incipient melting may occur. It is one of the reasons why most newer generations of single crystal superalloys are homogenization-solution heat treated with first stage temperatures close to 1300 ℃ [6,10,16,17], which are followed by stages coming towards the top temperature step by step. However, such long-term and complicated homogenization-solution heat treatments may not be so necessary.

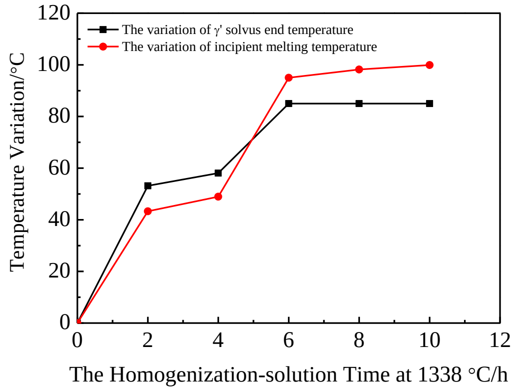

Fig.4 Variation of γ' solvus end temperature and incipient melting temperature after being homogenized at 1338 ℃ for different durations

According to Fick's second law (seen eq.1[18]) and the computational formula of diffusion coefficient (seen eq.2[19]),

$$\partial C/\partial t = D\cdot(\partial^2 C/\partial^2 x) \tag{1}$$

where D is diffusion coefficient; t is diffusion time; C is the volume concentration of solute; x is diffusion distance.

$$D = D_0\cdot\exp(-\Delta E/kT) \tag{2}$$

where D_0 is solute diffusion constant; ΔE is the activation energy of element diffusion; T is absolute temperature.

Eq.3 can be acquired:

$$\partial C/\partial t = D_0\exp\left(\Delta E/kT\right)\cdot\left(\partial^2 C/\partial^2 x\right) \tag{3}$$

From equation (3), such information can be got: with a constant concentration gradient, the element concentration at a certain point in the diffusion process is proportional to the diffusion time, while the increase of temperature causes an exponential increase of diffusion coefficient. Hence it can be seen that to get a better homogenizing result, elevating temperature is much more effective than prolonging time.

We measured the solute concentrations at dendrites and interdendrites with electron probe and calculated the partition coefficients with formula (4):

$$k_i = C_{\mathrm{D},i}/C_{\mathrm{ID},i} \tag{4}$$

where $C_{\mathrm{D},i}$ and $C_{\mathrm{ID},i}$ are the atomic concentrations of alloying element i at dendrite and interdendrite, respectively.

The variations of partition coefficients with temperature are shown in Fig.5.

From Fig.5, it can be seen that the homogenization degree can be promoted by increasing homogenization time and temperature. For W, Mo, Ta and Nb, it is hard to identify which is more important, time or temperature. However, for the element Re, which is considered to be the most difficult to diffuse [20,21], prolonging homogenization-solution time for 4 h doesn't make any difference on partition coefficients, and elevating temperature is more effective apparently. This agrees very well with the previous thermodynamic analysis.

3.3 Designing of the homogenization-solution heat treatment for advanced single crystal superalloys

Basing on above analysis, a new procedure can be introduced to design an effective homogenization-solution heat treatment for an advanced single crystal superalloy, as shown in following steps: (1) decide the starting point of the γ' solution endothermic peaks on the DSC heating curve, denoted by T_s; (2) set the temperature of the first step below T_s. Test the temperature to see if it can induce incipient melting; (3) quickly heat specimens to temperatures higher than T_s and hold for 6 h, which is the general duration for the highest temperature of homogenization-solution heat treatment; (4) observe the microstructures of above specimens. Decide the temperature range without incipient melting. The highest temperature can be set as the top temperature of homogenization-solution heat treatment, denoted by T_m; (5) set several steps between T_s and T_m to keep the heating rate within an acceptable range. With above approach, a homogenization-solution heat treatment regime is designed as follows:

1338 ℃/2 h+1345 ℃/2 h+1350 ℃/6 h+air cooling

The microstructures after homogenization-solution heat treatment are shown in Fig.6. It can be seen that no eutectic and incipient melting exist. The γ' is fine and homogeneous throughout the alloy. What’s more, the total duration time is only 10 h, which are much less than those convention ones.

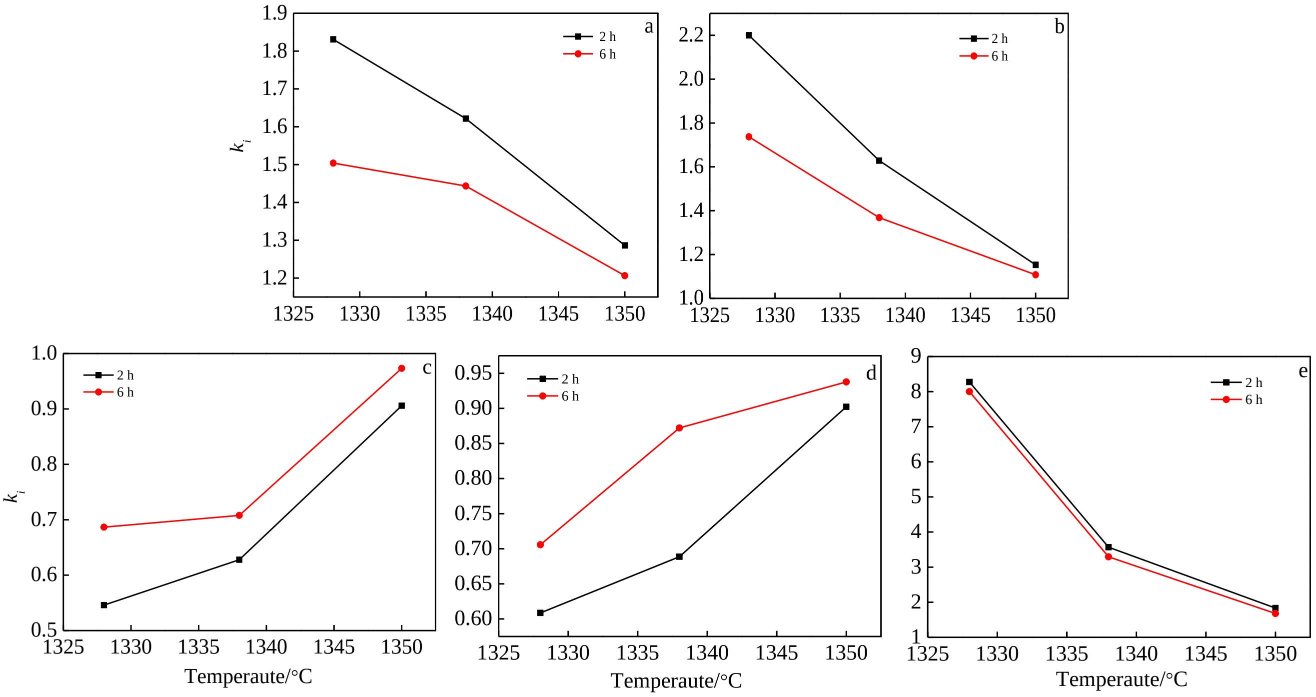

Fig.5 Variations of partition coefficients with temperature after solution heat treated for 2 h and 6 h: (a) W, (b) Mo, (c) Ta, (d) Nb, and (e) Re

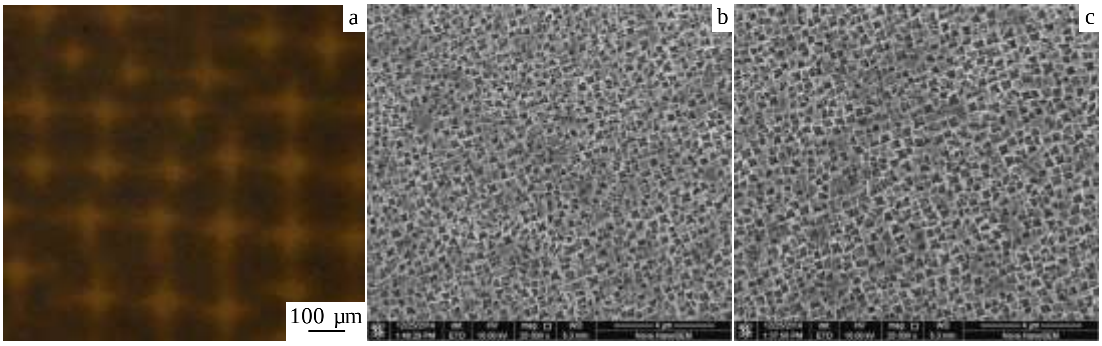

Fig.6 Microstructures after homogenization-solution heat treatment: (a) metallographic microstructure, (b) γ/γ' in the dendrite core, and (c) γ/γ' in the interdendrite

4 Conclusions

1) For the single crystal superalloy used in this study, when the temperature is directly raised to 1338℃, which is the practical starting temperature of γ' solution, the microstructure is homogenized rapidly and no incipient melting occurs.

2) As there is a large scale overlap of the γ' solution

endothermic range and the alloy melting endothermic range, which is difficult to distinguish, there is always risk of incipient melting when the alloy is directly heated up to any temperature above the practical starting temperature of γ' solution.

3) When the temperature is directly heated up to the extrapolating starting point of γ' solution, incipient melting occurs at the beginning. Then, with the homogenization process, the incipient melting would gradually fade away.

4) For an advanced single crystal superalloy, setting the first stage temperature at the practical starting point of γ' solution endothermic peak may drastically shorten the homogenization time.

5) There is no need to always keep the homogenization-solution heat treatment temperature below the incipient melting temperature of the as-cast condition, but keeping it below the incipient melting temperature of the alloy at the temporal homogenous state is necessary.

References

1 Li J R, Zhong Z G, Tang D Z *et al*. *Superalloys 2000*[C]. Warrendale: Seven Springs, 2000: 777

2 D'Souza N, Dong H B. *Superalloys 2008*[C]. Warrendale: Seven Springs, 2008: 261

3 Fuchs G E. *Materials Science and Engineering A*[J], 2008, 300: 52

4 Erickson G L. *JOM*[J], 1995, 47: 36

5 Cetel A D, Duhl D. *Superalloys 1988*[C]. Warrendale: Seven Springs, 1988: 235

6 Wukusick C S, Buchakjian L J. *UK Patent*, 2235697 A [P]. 1986

7 Duhl D N, Cetel A D. *US Patent*, 4719080 [P]. 1985

8 Hegde S R, Kearsey R M, Beddoesas J C. *Materials Science and Engineering A*[J], 2010, 527: 5528

9 Warnken N, Larsson H, Reed R C. *Materials Science and Technology*[J], 2009, 25: 179

10 Caron P. *Superalloys 2000*[C]. Warrendale: Seven Springs, 2000: 737.

11 Kawagishi K, Yeh A C, Yokokawa T *et al*. *Superalloys 2012*[C]. Warrendale: Seven Springs, 2012: 189

12 Sato A, Harada H, Yen A C *et al*. *Superalloys 2008*[C]. Warrendale: Seven Springs, 2008: 131

13 Tao Keming. *Physical and Chemical Examination of Trace Evidence in Forensic Sciences—Part 12: Thermoanalysis*, GB/T 19267.12-2008[S]. Beijing: China Standards Press, 2008: 3 (in Chinese)

14 Chen Yingchun, Deng Zhenning, Zhuo Ping *et al*. *Thermal Analysis Test Methods for Thermal Stability of Materials*, GB/T 13464-2008[S]. Beijing: China Standards Press, 2008: 3 (in Chinese)

15 Wilson B C, Hickman J A, Fuchs G E. *JOM*[J], 2003, 55(3): 35

16 Pang H T, Zhang L, Hobbs R A *et al*. *Metallurgical and Materials Transactions A*[J], 2012, 43A: 3264

17 Walston S, Cetel A. Mackay R *et al*. *Superalloys 2004*[C]. Warrendale: Seven Springs, 2004: 15

18 Xu Hengjun. *Fundamentals of Materials Science*[M]. Beijing: Beijing University of Industry Press, 2001: 119 (in Chinese)

19 Xu Hengjun. *Fundamentals of Materials Science* [M]. Beijing: Beijing University of Industry Press, 2001: 128 (in Chinese)

20 Karunaratne M S A, Carter P, Reed R C. *Materials Science and Engineering A*[J], 2000: 281: 229

21 Zacherl C L, Shang S L, Kim D E *et al*. *Superalloys 2012*[C]. Warrendale: Seven Springs, 2012: 455

先进单晶高温合金均匀化-固溶热处理的设计

岳晓岱，李嘉荣，史振学，王效光

(北京航空材料研究院 先进高温结构材料重点实验室，北京 100095)

摘　要：为设计更适用于先进单晶高温合金的均匀化-固溶热处理制度，研究了不同热处理温度和时间对一种先进单晶高温合金组织的影响。通过研究合金组织和元素分布发现，当温度直接升至γ'相溶解的实际起始温度1338 ℃时，合金不会发生初熔；当温度直接升至γ'相溶解的外推初始温度1350 ℃时，合金中出现了明显初熔，但初熔组织随着保温时间的延长逐渐减少；在1328 ℃固溶时，合金中虽然没有发生初熔，但均匀化效率明显降低。对实验结果进行了热力学和动力学计算与分析。结果表明，单晶高温合金的均匀化-固溶热处理窗口是一个动态的窗口，γ'相完全溶解温度和初熔温度均随着合金均匀化程度的提高而提高；高代单晶高温合金在均匀化-固溶热处理中，不须要将温度始终保持在铸态合金的初熔温度以下，只要保证温度低于合金所在均匀化状态对应的初熔温度即可；均匀化-固溶热处理中，提高每一台阶的温度可以得到的均匀化-固溶效果远优于延长热处理时间可达到的效果。根据实验及分析结果提出了一种适用于先进单晶高温合金的均匀化-固溶热处理制度设计方法，使合金在较短时间内得到了理想的合金组织和均匀化效果。

关键词：单晶高温合金；均匀化；固溶；热处理；设计

作者简介：岳晓岱，女，1984 年生，博士生，北京航空材料研究院先进高温结构材料重点实验室，北京 100095，电话：010-62498309，

E-mail: yuexiaodai0126@126.com