

Homogeneous Microstructure of Bulk K4169 Superalloy Obtained by Stable Undercooling

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Abstract: By improving the method of B₂O₃ glass purification combined with cycle superheating based on traditional undercooling method, a stable undercooling above 200 K of 100 g bulk K4169 superalloy was obtained, and the largest undercooling went to 271 K. The effects of purification and superheating temperature on undercooling have been discussed. Moreover, the three-dimensional numerical analysis of temperature field inside the undercooled melt has been presented, and the maximum temperature deviation in different parts is only 14 K before nucleation. In contrast with the as-solidified microstructure, the grain size will increase with the increment of nucleating temperature. Generally, the difference of microstructure in 100 g undercooled K4169 superalloy is tiny and the average grain size of the superalloy with 271 K undercooling is 12±2 μm.

Key words: K4169 superalloy; undercooling; purification; temperature field; microstructure; homogeneity

The microstructure of undercooled melt after rapid solidification is one of the most important fundamental subject in various materials [1-3]. The so-called undercooling refers to the phenomenon of pure liquid metal or alloy below a certain temperature range without crystallization or solidification. Molten glass purification combined with cycle superheating is one of the methods which can achieve reasonable undercooling successfully [4-6].

To date, high undercooling in bulk alloys has been widely investigated [7,8]. Previous researches only focused on the relationship between superheating, holding time and undercooling. However, some details of the undercooling process have not been studied systematically yet, such as the replacement of purification and the way of cycle superheating, and thus the undercooling degree is obtained randomly. Furthermore, with the increase of melt size, the melt needs longer time to cool down and the external part cools faster than the center. So the inhomogeneous temperature field inside the undercooling melt leads to the forming of inhomogeneous microstructure [9].

As one of the most widely used superalloys in modern industry, K4169 superalloy shows outstanding performance in elevated temperature environment, and it's widely used as the critical structural components in gas-turbine engines. Therefore, lots of investigations have been carried out for a better understanding on K4169 superalloy [10-13] and the research of undercooled solidification of K4169 is indispensable. In the present work, the high undercooling of K4169 superalloy has been achieved by a method of replacement of molten glass combined with optimized cycle superheating. And the temperature field in the cooling process of large size melt was simulated to figure out the way how the temperature distribution affects the uniformity of microstructure.

1 Experiment

The undercooling experiment was conducted by a glass purification method in a high frequency induction unit with a coil mounted in atmosphere. The glass flux was B₂O₃ which was dehydrated at 1073 K for 5 h in advance. In each

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experiment, a bulk K4169 superalloy of 100 g was placed in a quartz crucible of 20 mm diameter and covered with B_2O_3 powder on the top and the bottom. Then the crucible was placed in the coil of the high frequency induction unit. Firstly the sample was heated to 773~873 K until completely enwrapped by the molten B_2O_3 . Then the temperature increased to 1821~1881 K which was 200~260 K above the liquidus temperature (T_L) and held for 3~5 min. After that the temperature decreased to T_L+30 K and held for 3~5 min. The process was cycled 2~3 times to generate different undercooling.

In each cycle, the negative pressure suction device was used to replace the molten B_2O_3 , as illustrated in Fig.1. The device can extract molten B_2O_3 from the upper edge of the quartz crucible, following by addition of same amount of fresh B_2O_3 . When the interface between alloy melt and B_2O_3 was stable and there were no air bubbles, it was time to stop heating. The thermal behaviors of samples were monitored by a double-color pyrometer with ± 5 K accuracy and 100 ms response time.

The solidified samples were cut along the longitudinal section, polished and etched using a solution of 10 g $CuCl_2$ +100 mL HCl +100 mL alcohol. The as-solidified microstructures of 5 parts on the longitudinal section were observed by Olympus PMG3 metallographic microscope (OM), which are marked by a, b, c, d and e as shown in Fig.2. The B_2O_3 was analyzed by X-ray diffraction (XRD).

2 Results and Discussion

2.1 Influencing factors of purification

2.1.1 Influence of B_2O_3 on purification



1-negative pressure suction device, 2-molten B_2O_3 , 3-alloy melt

Fig.1 Principle diagram of negative pressure suction device

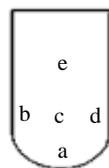


Fig.2 Longitudinal section of the superalloy

The selection of purification agent is very important for achieving high undercooling^[14]. The reason why B_2O_3 is widely used can be ascribed to that the molten B_2O_3 in amorphous state won't provide heterogeneous nucleus, meanwhile the sticky molten B_2O_3 can eliminate heterogeneous nucleation particles through physical absorption, and it can also melt some impurities through chemical reaction to achieve physicochemical purification^[15]. In addition, the molten B_2O_3 can not only protect the melt from atmosphere to avoid the formation of oxide film, but also work as a high-damping isolation layer to eliminate the interference from external vibration. However, the amorphous B_2O_3 will be crystallized at high temperature by absorbing large numbers of metal ions such as Fe^{2+} and Fe^{3+} in alloy melt, and the viscosity of molten B_2O_3 will be decreased. To some extent, the crystallization of B_2O_3 provides heterogeneous nucleuses which may lead to the large decrease of undercooling^[16]. Fig.3 shows the XRD patterns of B_2O_3 after and before the undercooling experiment. It can be seen that a crystallization peak appears obviously in the used B_2O_3 , however, in the unused B_2O_3 there appears a broad diffraction peak which is a typical symbol of amorphous state. It suggests that B_2O_3 will be seriously crystallized after participating the purification for a long time. Thus, it is not sufficient to add B_2O_3 in bulk alloys only once during the undercooling experiment and it is indispensable to replace the molten B_2O_3 by adopting the negative pressure suction device as shown in Fig.1.

2.1.2 Influence of superheating on purification

Normally it is difficult to get a desirable undercooling by superheating only once, and thus the method of cycle superheating is usually adopted, which means that the alloy is superheated for a few minutes and then cooled down till solidification in each cycle. Nevertheless, this kind of cycle superheating is not most suitable, due to the fact that the alloy will be segregated with B_2O_3 during solidification and exposed to the air during the process of reheating. In order to avoid the oxidation, the temperature of alloy melt should be cooled to T_L+30 K for 1~3 min and then reheated to

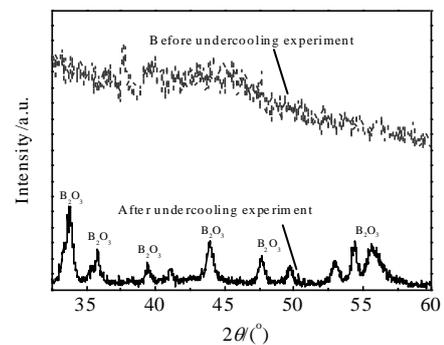


Fig.3 XRD patterns of B_2O_3 before and after undercooling experiment

$T_L+200\sim 260$ K for 1~3 min. At the same time, the interface between the alloy melt and B_2O_3 can be changed by temperature. When the temperature is high, the alloy melt shows a shape of sharp elliptic ball on the top; on the other hand when the temperature is low, the alloy melt shows a shape of flat ball which can be completely covered by the molten B_2O_3 . In this procedure, the alloy melt will make full attachment with molten B_2O_3 and the cohesive adsorption will be achieved sufficiently. Meanwhile the impurities dissolved and adsorbed in the molten B_2O_3 will be rejected far away from the interface, so that the content of impurities is greatly reduced near the interface. Eventually high undercooling can be obtained by this optimized cycle superheating method.

Thus the replacement of molten glass combined with optimized cycle superheating method (the optimized method) can obtain a stable and high undercooling. Previous reports confirmed that the solidification of the undercooled melts was initiated by heterogeneous nucleation [17,18]. The nucleation particles always appeared in the interface of purified alloy and molten glass. The heterogeneous nucleation rate J_a in the melt surface can be expressed as [19]:

$$J_a = 10^{21} \zeta \varphi_0 \eta^{-1} \exp[-\Delta G^* f(\theta) (kT)^{-1}] \quad (1)$$

where ζ refers to the activating factor, φ_0 the area fraction of heterogeneous nucleation particle, η the viscosity of liquid metal or alloy, ΔG^* the nucleation activation energy, $f(\theta)$ the heterogeneous nucleation factor, and k the Boltzmann constant. When the system is confirmed as K4169 superalloy, $f(\theta)$ is mainly determined by the oxides of Ni, Fe and Cr. Thus k , η and $f(\theta)$ are all constants, and J_a is just related with ζ , φ_0 and ΔG^* . The optimized method will improve the passivation effect of the heterogeneous nucleation particle (i.e. reduce ζ), accelerate the dissolution of oxide substrate in the replacement of molten B_2O_3 (i.e. reduce φ_0), and increase the cluster size to promote the melt homogenization of structure and composition (i.e. increase ΔG^*). Thus the heterogeneous nucleation rate J_a can be decreased.

The optimized method and the traditional superheating method are both adopted in a series of undercooling experiments for bulk K4169 superalloy. Compared with the optimized method, the traditional superheating method is an undercooling process which has fixed superheating temperature, holding time and it always cools till solidification in each cycle [5,7,20]. The distributions of undercooling under different superheating are shown in Fig.4, in which gray scatters are from the optimized method and the black scatters are from the traditional method. It can be noticed that the distribution of undercooling in the traditional method is very fragmented and random, even under the same degree of superheating, the undercooling is still different, and it presents a rising trend with the increase of superheating. On the other hand, the distribution of undercooling in the

optimized method is so stable that the undercooling always stays above 200 K, even if the superheating is only 130 K. The largest undercooling is 271 K.

2.2 Microstructure of bulk undercooled K4169 superalloy

In the traditional researches of undercooling, the melt usually cools down from high superheating temperature ($T_L+200\sim 260$ K) directly to get a large dynamics undercooling. Under this condition, the size of a sample is small and the thermal dissipation is homogeneous. Thus it's feasible for small sample to get a high undercooling [21,22]. However, with the increase of the sample size, it's more difficult to obtain a stable high undercooling (>200 K) and homogeneous microstructure. This is because the surface of the melt is cooled faster than the center which will result in a large temperature gradient when the melt cools from high superheating ($T_L+200\sim 260$ K) directly. In order to make the solidified microstructure more homogeneous in bulk alloy, the cooling temperature is supposed to be as low as possible, meanwhile the nucleation should also be forbidden. As aforementioned, a stable high undercooling can be achieved easily upon choosing an appropriate purification method even in low superheating temperature. Based on this, the high superheated melt can be cooled to T_L+30 K for 2~5 min after all cycle superheating processes to reduce the cooling time dramatically, and then a more homogeneous microstructure can be obtained theoretically.

For the quantitative discussion, the temperature-time relationship of an undercooled 100 g K4169 superalloy during the solidification was measured by infrared thermometer (as shown in Fig.5), and T_N is the nucleation temperature. The temperature was only measured at point b in Fig.2. The curve has no solidification platform and the whole solidification process finished in rapid recalescence. However, many other parts of temperature especially in the center could not be measured by the infrared thermometer, and the information obtained from the curve is too rare to analyze the whole undercooled alloy. Under this condition, ANSYS software was adopted to simulate the temperature field of the whole

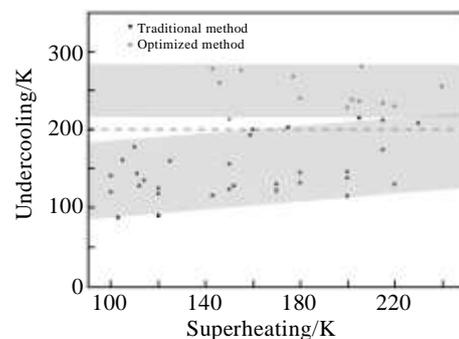


Fig.4 Distribution of undercooling in different superheating obtained from the traditional method and the optimized method

melt which was cooled from $T_L + 30$ K to the nucleation temperature T_N , so it can shed light on the way how temperature field influences its microstructure. The parameters of considered undercooled melt are shown in Table 1 and the boundary conditions are considered as the thermal radiation and convection [23].

From the simulation result presented in Fig.6, one can notice that the maximum temperature deviation in different parts is only 14 K, as well as the highest temperature in the center (Fig.6e) and lowest in the upper (Fig.6g). In different cross sections, the temperature deviation between the center and the surface is also different. The deviation is only 4 K in the middle (Fig.6e, 6f) and bottom (Fig.6c, 6b), as well as 8 K in the upper (Fig.6h, 6g). In generally, there is only tiny difference in the distribution of temperature at nucleation temperature. In the size of K4169 superalloy, the temperature is homogeneous in the melt which is about to nucleate.

In order to understand the relationship between the microstructure and temperature field, the microstructures in different parts were observed. As shown in Fig.7, there are five microstructures of different parts on a, b, c, d and e in Fig.2 for 271 K undercooling K4169 superalloy. By calculating, the grain sizes are (a) 10.9 μm , (b) 11.5 μm , (c) 12 μm , (d) 11.5 μm and (e) 14 μm . It can be found that the microstructures are nearly homogenous, which only have tiny difference, and the average grain size is about 12 ± 2 μm . To compare the temperature and the microstructure of each point, the temperature of point e is the highest and point a is the lowest. Based on this temperature distribution point e has the largest grain size (14 μm) and point a has the smallest grain size (10.9 μm). Besides this, points b and d have the same grain size due to the equal nucleating temperature 1350

Table 1 Parameters of considered undercooled melt

$(T_L+30 \text{ K})/\text{K}$	t_c/s	δ/mm	d/mm	h/mm
1651	55	3	20	40

Note: $(T_L+30 \text{ K})$ -initial temperature, t_c -cooling time, δ -wall thickness of quartz crucible, d -inside diameter of quartz crucible, h -height of K4169 superalloy

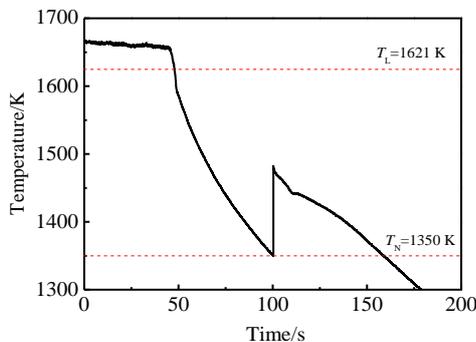


Fig.5 Temperature-time relationship of an undercooled 100 g K4169 superalloy

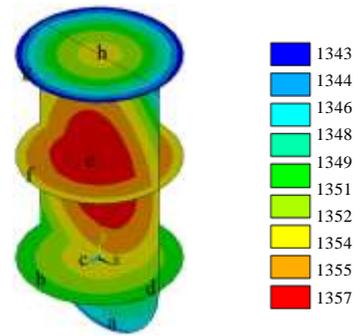


Fig.6 Three-dimensional temperature distribution of K4169 superalloy melt at nucleation temperature

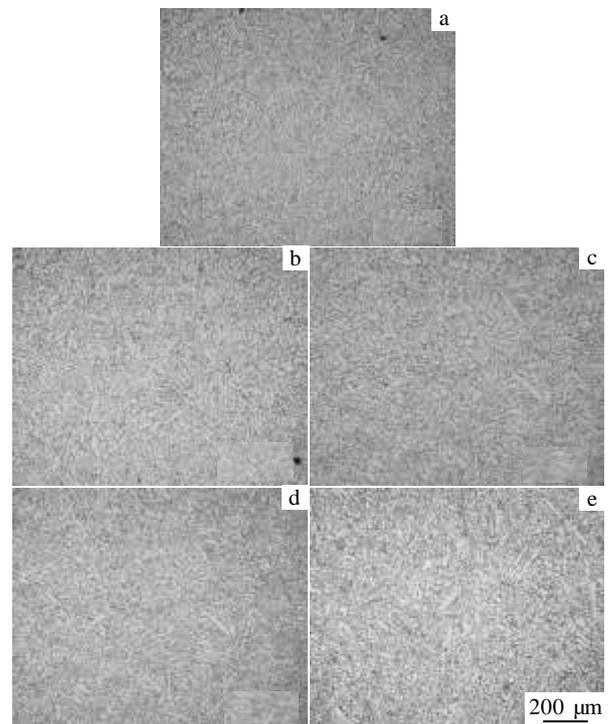


Fig.7 Microstructures of different points in Fig.2 for K4169 superalloy

K. It can be concluded that the grain size increases with increasing of nucleating temperature. Based on the classical nucleation theory [24], the lower the nucleation temperature is, the higher undercooling can be obtained, which increases the nucleation rate in the undercooled melt. As soon as the nucleation activates from nucleus, the dendrite will grow rapidly and radically. Meanwhile, the dendrite tip radius will decrease with increasing of undercooling [25]. For the effect of remelting and the inter stress from melt shrinkage on solidification dendrite, the dendrite with different sizes can be distorted and fragmented into granular grain.

By integrating the work we have done, the experimental results are in good agreement with the simulation of temperature field: uniform temperature field will lead to a

uniform microstructure; conversely, different nucleating temperatures will generate different microstructures. So the experimental results can provide theory support for further research on high undercooling of bulk alloys.

3 Conclusions

1) The molten B_2O_3 should be renewed by the negative pressure suction device during the process of cycle superheating to avoid crystallization.

2) The replacement of molten glass combined with optimized cycle superheating method is adopted in the undercooling experiment for 100 g K4169 superalloy, a stable undercooling above 200 K is obtained and the highest undercooling goes to 271 K.

3) The three-dimensional distribution of temperature field from $T_L + 30$ K (1651 K) cooling to T_N (1350 K) can be simulated by ANSYS software. The maximum temperature deviation in different parts is only 14 K. In contrast with the solidification microstructure, the grain size will increase with the increment of nucleating temperature. But the difference in microstructure is tiny and the average grain size is $12 \pm 2 \mu\text{m}$.

References

- Lu Yiping, Lin Xin, Yang Gencang et al. *Journal of Applied Physics*[J], 2008, 104(1): 013 535
- Luo S B, Wang W L, Chang J et al. *Acta Materialia*[J], 2014, 69: 355
- Clopet C R, Cochrane R F, Mullis A M. *Acta Materialia*[J], 2013, 61: 6894
- Wang Pei, Liu Feng, Li Zhengxian. *Rare Metal Materials and Engineering*[J], 2010, 39(1): 482 (in Chinese)
- Wilde G, Sebright J L, Perepezko J H. *Acta Materialia*[J], 2006, 54: 4759
- Yang C L, Yang G C, Liu F et al. *Rare Metal Materials and Engineering*[J], 2009, 38(10): 1745 (in Chinese)
- Xi Zengzhe. *Thesis for Doctorate*[D], Xi'an: Northwestern Polytechnical University, 1998: 27 (in Chinese)
- Li Jinfu, Zhou Yaohe. *J Mater Sci* [J], 2000, 35: 5581
- Li Delin, Yang Gencang, Zhou Yaohe. *Trans Nonferrous Met Soc China*[J], 1994, 4(1): 64
- Li Xianghui, Zhang Yong, Hou Xueqin et al. *Rare Metal Materails and Engineering*[J], 2014, 43(1): 199 (in Chinese)
- Arrazola P J, Kortabarria A, Madariaga A et al. *Simulation Modelling Practice and Theory*[J], 2014, 41: 87
- Cheng L, Xue X, Tang B et al. *Materials Science and Engineering A*[J], 2014, 606: 24
- Parimi L L, Clark D, Attallah M M. *Materials Characterization*[J], 2014, 89: 102
- Zhou Shengyin. *Thesis for Doctorate*[D], Xi'an: Northwestern Polytechnical University, 2013: 35 (in Chinese)
- Wei Bingbo. *Thesis for Doctorate* [D], Xi'an: Northwestern Polytechnical University, 1989: 31 (in Chinese)
- Yang Changlin, Yang Gencang, Liu Feng et al. *Acta Metallurgica Sinica*[J], 2008, 44(8): 956 (in Chinese)
- Li J Z, Liu J, Zhang M X et al. *J Alloy Compd*[J], 2010, 499: 39
- Han X J, Yang C, Yang G C et al. *Material Science and Engineering A*[J], 2001, 307: 35
- Jacobson L A, McKittrich J et al. *Material Science and Engineering R*[J], 1994, R11: 355
- Zhou Jiankun, Li Jianguo. *J Alloy Compd*[J], 2008, 461: 113
- Yang Changlin, Liu Feng, Yang Gencang et al. *Journal of Crystal Growth*[J], 2009, 311: 404
- Chen Y Z, Liu F, Yang G C et al. *J Alloy Compd*[J], 2007, 427(16): L1
- Liu Tao, Yang Fengpeng. *Mastering ANSYS*[M]. Beijing: Tsinghua University Press, 2002: 345 (in Chinese)
- Turnbull D J. *Journal of Chemical Physics*[J], 1981, 18: 950.
- Liu Feng, Guo Xuefeng, Yang Gencang. *Materials Research Bulletin*[J], 2001, 36: 181

大体积 K4169 高温合金深过冷及其组织均匀性的研究

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摘要: 在传统深过冷工艺的基础上, 通过对传统工艺中 B_2O_3 玻璃净化法和循环过热方法的改进, 可使较大体积K4169高温合金稳定地获得200 K以上过冷度, 其中100 g合金熔体的最大过冷度达271 K。采用ANSYS软件模拟了100 g K4169高温合金冷却过程中熔体温度场的分布, 熔体形核前最大温差仅为14 K。在此基础上观察合金不同部位的凝固组织, 发现组织随着形核温度的升高而增大。总体来看组织只有微小差别, 其平均晶粒尺寸为 $12 \pm 2 \mu\text{m}$, 与模拟结果相吻合。

关键词: K4169高温合金; 深过冷; 净化机制; 温度场; 组织均匀

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