Postprint of Research on Solidification Characteristics and Typical Solidification Defects of Single Crystal Superalloys

Authors: Zhang Jun, Huang Taiwen, Liu Lin, FU Hengzhi

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Abstract

Single crystal superalloys are complex multi-component, multi-phase materials. With the continuous increase in alloying level, the addition of more refractory elements, and the increasing complexity and scaling-up of blade structures, control of solidification defects has become critical for improving blade quality and performance. The solidification microstructure and defects of single crystal alloys depend not only on alloy composition, but also on their solidification characteristics and processing conditions. This paper elaborates on the features and variation patterns of solidification characteristics—including solid/liquid phase transition temperature and solidification partition coefficient—of advanced single crystal alloys, with emphasis on analyzing the formation mechanisms of two typical solidification defects, namely crystal orientation deviation and stray grains, and their relationships with solidification characteristics and processing conditions. It also discusses approaches and strategies for mitigating typical defects in complex single crystal blades, and evaluates the effectiveness of various control methods.

Full Text

Preamble

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Research on Solidification Characteristics and Typical Casting Defects in Single Crystal Superalloys

ZHANG Jun, HUANG Taiwen, LIU Lin, FU Hengzhi

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi' an 710072

Correspondent: ZHANG Jun, Professor, Tel: (029)88494825, E-mail: zhjscott@nwpu.edu.cn

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Abstract

Single crystal (SC) superalloys are complex, multi-phase materials. With increasing degrees of alloying, higher refractory element contents, and increasingly complex and large-scale blade structures, controlling solidification defects has become critical for improving blade quality and performance. The solidification microstructure and defects in single crystal alloys depend not only on alloy composition but also on solidification characteristics and processing conditions. This paper summarizes the features and variation patterns of solidification characteristics in advanced single crystal alloys, including solid/liquid phase transformation temperatures and partition coefficients. It focuses on analyzing the formation mechanisms of two typical directional solidification defects—crystallographic orientation deviation and stray grains—and their relationship with solidification characteristics and processing parameters. Methods and approaches for suppressing such defects in complex single crystal blades are discussed, and the effectiveness of different control methods is evaluated.

Keywords: single crystal superalloy, solidification characteristic, solidification defect

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Nickel-based single crystal superalloys are widely used in hot-section components of aero-engines and industrial gas turbines due to their excellent high-temperature mechanical properties, and their development level has become one of the important indicators of a country's materials development capability. The advancement of high-performance aero-engines demands higher temperature capability and mechanical properties from nickel-based single crystal superalloys. With the evolution of alloy design concepts, single crystal superalloys have now developed to the fifth generation. Optimizing alloy composition design and manufacturing processes are currently the main approaches to improve superalloy performance.

A notable feature of alloy composition changes is the increase in refractory element content. Adding large amounts of refractory elements such as Ta, Mo, W, and Re can effectively improve the alloy’ s temperature capability and high-temperature mechanical properties. However, the addition of refractory elements not only significantly increases material costs and alloy density but also intensifies elemental segregation, crystal defects, and the precipitation probability of topologically close-packed (TCP) phases [?, ?]. Therefore, for new single crystal superalloys, there is an urgent need to optimize composition design and develop new melting and solidification processes to improve alloy microstructure and reduce segregation and defect formation.

Among aero-engine hot-section components, turbine blades operate in the most severe environments, have the most complex structures, and face the most stringent requirements. They widely employ advanced single crystal superalloy materials and complex cooling structures [?, ?]. Complex single crystal hollow turbine blades have become a core technology for current high thrust-to-weight ratio engines. The research and application of advanced single crystal alloy materials and the emergence of double-wall super-cooled single crystal blade manufacturing technology have enabled single crystal preparation technology to play a key role in today’ s most advanced military and commercial aero-engines. The complexity of double-wall cooling structures makes the manufacturing process more complicated, leading to a significant increase in solidification defects related to both processing and casting complexity.

In summary, the development of superalloys and changes in blade structure have made defect control a key factor in improving blade quality and performance. This paper reviews the formation mechanisms of typical solidification defects in advanced single crystal superalloy blades from the perspective of their solidification characteristics and behavior, discusses control methods for solidification defects in advanced single crystal superalloy blades in combination with casting structure and process condition effects, and evaluates the implementation effectiveness of different control methods.

1. Solidification Characteristics of Single Crystal Superalloys

The solidification characteristics of single crystal superalloys (including solidification path, characteristic temperatures, partition coefficients, etc.) significantly influence casting process performance, solidification microstructure, segregation, and defects, thereby affecting subsequent heat treatment processes, microstructural stability, and mechanical properties. Solidification characteristics depend on alloy composition and are also closely related to processing parameters. With the continuous development of single crystal superalloy compositions, refractory element contents continue to increase, particularly Re and Ru, which have become the main compositional features for distinguishing generations of advanced single crystal superalloys. Additionally, the roles of trace elements such as C and Hf have received more attention, with their addition levels becoming more sensitive. Investigating the effects of Re, Ru, and trace element additions on the solidification characteristics of advanced single crystal superalloys provides important guidance for further exploiting alloy potential, optimizing composition design, and reducing solidification defects.

1.1 Effect of Alloying Elements on Solidification Characteristics

During solidification, single crystal superalloys first precipitate a Ni-rich γ solid solution from the liquid phase. When the temperature decreases to about 10°C below the liquidus temperature, C-containing single crystal superalloys also precipitate primary MC-type carbides (MC+γ). As temperature further decreases, γ' phase-forming elements such as Al, Ta, and Ti enrich in the residual liquid phase, and the solidification process finally ends with the eutectic reaction L $\rightarrow$ γ+γ '. With increasing Re and Ru contents in single crystal superalloys, a series of new phases have been discovered in the solidification microstructure, such as the δ phase, Ru2AlTa-based Heusler phase [?, ?], or new phase transformations such as the L+γ $\rightarrow$ γ' peritectic reaction [?]. For alloys containing Hf and B, M3B2 and Ni5Hf may also precipitate from the residual liquid phase after the eutectic reaction [?]. Due to the small amounts of these phases, their influence on defect formation is not significant.

Alloying elements have significantly different effects on characteristic solidification temperatures. Reed [?] compiled the solidus and liquidus temperatures for Ni-X binary systems, showing that increasing Re, W, Ru, and Co contents raises the liquidus and solidus temperatures of these binary alloys, while Al, Ti, Ta, Mo, etc., lower them. Among these elements, Re, W, Ti, and Ta have particularly significant effects. However, these patterns differ in complex alloys. Murakami et al. [?] studied the Ni-19Al-xRu ternary alloy system and demonstrated that Ru addition increases the liquidus temperature of ternary alloys. Kearsey et al. [?] analyzed differential thermal analysis (DTA) curves of several alloys and found that refractory element Re addition significantly increases alloy liquidus and solidus temperatures. Feng et al. [?] showed that only when Re and Ru contents exceed certain levels do they significantly increase liquidus temperature, while Co addition lowers liquidus temperature, as shown in [Figure 1: see original paper][?]. Heckl et al. [?] argued that Re addition significantly increases alloy liquidus temperature but has little effect on solidus temperature, while Ru has a smaller effect on alloy solidification temperatures compared to Re. Hobbs et al. [?] performed differential scanning calorimetry (DSC) analysis on several single crystal superalloys, indicating that Ru addition lowers solidus temperature while having essentially no effect on liquidus temperature, thereby expanding the solidification temperature range. These research results show significant differences, indicating that the solidification characteristic temperatures of single crystal superalloys are closely related to alloy system and composition, and their patterns are not yet fully understood.

Liu et al. [?] designed a series of model alloys based on a third-generation single crystal superalloy by adjusting Re and Ru contents to systematically investigate their effects on solidification characteristics. [Figure 2: see original paper] shows the effects of Re (<6%, mass fraction) and Ru additions on alloy characteristic temperatures. The results indicate that as Re content increases (3%~6%), the liquidus temperature of single crystal superalloys changes little, while the solidus temperature decreases by about 12.5°C, expanding the solidification temperature range. The critical nucleation undercooling ΔT' decreases by about 3°C. Ru content increase (0~3%) has no obvious effect on solidus and liquidus temperatures, but reduces critical nucleation undercooling by about 3°C. Re and Ru additions significantly reduce alloy critical nucleation undercooling, intensifying stray grain formation tendency and reducing alloy castability.

Advanced single crystal superalloys also contain trace elements such as C, B, and Hf to improve tolerance to low-angle grain boundaries. These trace element additions significantly affect solidification characteristics. Early research [?] using In100 alloy as a model established the relationship between liquidus temperature TL and alloying element mass fraction w as:

$$TL = 1508 - 258Al - 4.94B - 51.5Mo - 2.14C - 32.2Cr - 1.63Zr - 17V - 0.72Co\cdots$$

Equation (1) shows that adding trace elements C and B lowers liquidus temperature. Liu et al. [?] found that as C content increases, the alloy' s incipient melting temperature gradually decreases, while other phase transformation temperatures show no obvious change pattern. Al-Jarba et al. [?] showed that when C content is less than 0.05%, liquidus temperature does not change with increasing C content; when C content exceeds 0.05%, liquidus temperature decreases with increasing C content, while other phase transformation temperatures show no obvious change pattern. Hu et al. [?] used DSC to study the effect of different C contents on solidification characteristic temperatures of single crystal superalloys, with results shown in . They found that C addition lowers liquidus, solidus, and carbide precipitation temperatures, with liquidus temperature variation consistent with Equation (1). When C content increases to 0.15%, liquidus, solidus, and carbide precipitation temperatures all show abrupt increases. C addition makes γ' phase precipitation temperature first increase then decrease, reaching maximum at 0.045% C content.

Solute partitioning of alloying elements between liquid and solid phases inevitably causes elemental segregation during solidification, with the partition coefficient being an important indicator for measuring element segregation. In recent years, extensive research has been conducted on the effects of refractory elements on segregation in single crystal superalloys. Kearsey [?] found that Re addition increases segregation of Cr, Mo, and Re, while Ru addition reduces segregation of these refractory elements; Feng et al. [?] reached similar conclusions. Hobbs et al. [?] studied the effects of refractory elements on segregation behavior in SRR300 series single crystal superalloys, concluding that Cr, Mo, and Ru additions reduce segregation of Re, W, and other elements to varying degrees, but interactions among Cr, Mo, W, and Re are significant. Caldwell et al. [?] showed that Co and Mo can reduce segregation of other elements, while increasing Ru, Cr, and Re contents increases segregation of other elements, which differs significantly from previous findings. Liu et al. [?] found that Re and Ru have relatively obvious effects on equilibrium partition coefficients of

Al, Ta, Re, and W. Re addition increases segregation tendency of Al and Ta to the liquid phase while reducing segregation tendency of Re and W to the solid phase. As Ru content increases, segregation tendencies of Al, Ta, Re, and W all increase to varying degrees. Re addition increases microsegregation of Al, Ta, W, and Re; Ru addition increases segregation of Al and Ta, has little effect on Re segregation, and slightly reduces W segregation. Trace elements have little effect on segregation of other alloying elements. However, Tin and Pollock [**?**] showed that C addition reduces Re segregation. Al-Jarba et al. [**?**] indicated that except for Re, partition coefficients of other elements do not change significantly with C content variation, which may be related to different experimental conditions and alloy systems. Hu et al. [**?**] investigated the role of trace elements in third-generation single crystal superalloys, finding that as C content increases, segregation of most elements including Re, W, Cr, and Ta first increases then decreases, with C content having the greatest effect on Re segregation. B addition increases segregation of Re and W but has little effect on other elements. Additionally, solute segregation under dendritic solidification conditions depends not only on alloy composition but also on solidification process parameters, casting geometry, liquid flow, and crystal orientation. Solute segregation is the comprehensive result of solidification thermodynamics and kinetics.

Changes in single crystal alloy composition and solidification characteristics affect solidification microstructure, including primary dendrite spacing, eutectic content, precipitate size, and carbide morphology. With increasing Re and Ru contents, the content of coarse γ/γ' eutectic in interdendritic regions increases ([Figure 3: see original paper][**?**]), but dendrite morphology shows no obvious change, with Ru having a more significant effect [**?**, **?**]. C reduces eutectic content. AM3 alloy containing 0.001%C has large amounts of eutectic microstructure, which gradually decreases with increasing C content [**?**]. Metal elements in carbides are mainly Ti, Nb, and Ta, which are also the main elements in γ' phase in eutectic. Clearly, carbide formation consumes eutectic-forming elements, thereby reducing eutectic content.

1.2 Effect of Process Parameters on Solidification Behavior

In addition to intrinsic alloy properties, directional solidification microstructure depends on melt thermal history, temperature gradient, and growth rate. By controlling directional solidification parameters such as temperature gradient and solidification rate, primary dendrite spacing can be controlled to optimize mechanical properties of single crystal superalloys. Achieving high-gradient directional solidification to reduce solidification defects is an effective method to improve single crystal superalloy performance, especially for large castings [**?**].

Melt structure affects solidification characteristics. In metallic and alloy melts, atomic clusters of different sizes exist, whose changes are related not only to alloy type and composition but also to melt state. These atomic clusters are sub-units in nucleation and growth processes during solidification. Therefore, melt treatment can change melt solidification characteristics, thereby affecting casting microstructure and comprehensive performance. In recent years, domestic research has been conducted on improving single crystal superalloy solidification microstructure, reducing solidification segregation, and suppressing defects through melt thermal history approaches. DTA curves for a third-generation single crystal superalloy at different melt superheating temperatures are shown in [Figure 4: see original paper][**?**]. As superheating temperature increases from 1450°C to 1780°C, critical nucleation undercooling continuously increases from about 32°C to about 78°C. When melt superheating is low, dissolution of some refractory particles reduces nucleation cores, increasing undercooling. As melt temperature increases, medium-range ordered atomic clusters gradually dissociate into short-range ordered clusters, increasing nucleation cores. This effect is opposite to refractory particle dissolution, so undercooling does not change significantly. When melt is superheated to very high temperatures such as above 1700°C, short-range ordered atomic clusters further dissociate and surround small refractory particles through electrostatic interaction, forming new multi-atomic cluster structures that are difficult to serve as nucleation cores, leading to further increase in nucleation undercooling.

Superheating treatment also affects elemental segregation. As shown in [Figure 5: see original paper], as superheating temperature increases, partition coefficients of heavily segregated elements such as Re, Al, W, and Ta in a third-generation single crystal superalloy approach 1, indicating decreasing segregation during solidification. Changes in other elements like Mo, Co, and Cr are not obvious. Segregation is one of the important causes of solidification defects. Melt superheating treatment can reduce segregation, which is significant for improving casting quality and reducing defects. The effect of superheating treatment is also related to holding time. As shown in [Figure 5b: see original paper], as holding time extends from 15 min to 60 min, partition coefficients of various components approach 1, meaning solute segregation weakens. Changes in alloy melt structure have hysteresis; when holding time reaches a critical value, the alloy melt can achieve equilibrium at that superheating temperature. With extended holding time, the alloy melt reaches equilibrium, and elemental segregation changes little.

As superheating temperature and time change, microstructural features such as dendrite spacing and γ' phase size also change. Establishing appropriate melt superheating treatment directional solidification thermal history regimes is key to effectively utilizing melt property effects on solidification characteristics to improve microstructure, reduce solidification defects, and enhance single crystal superalloy performance.

2. Solidification Defects and Control in Single Crystal Superalloys

During solidification of single crystal superalloys, refractory elements, especially negative segregation elements like Re and W, enrich in dendrite cores, while positive segregation elements like Ti, Nb, and Ta enrich in interdendritic regions. Thermal-solutal convection caused by liquid density inversion in the mushy zone can cause solidification defects such as freckles and stray grains. Additionally, defects can form due to casting structure reasons [**?**]. Typical casting defects in single crystal blades are shown in [Figure 6: see original paper]. This work focuses on studying the formation mechanisms and control methods of orientation deviation and stray grains.

2.1 Crystallographic Orientation Deviation

Nickel-based single crystal superalloys have an fcc structure with a preferred growth direction of <001>, which has the lowest elastic modulus and provides the best high-temperature mechanical properties. Since turbine blades mainly bear axial loads, single crystal blades can only fully exploit their advantages when the <001> preferred growth direction of primary dendrites is parallel to the blade axis. Therefore, controlling crystal orientation of single crystal superalloys and reducing deviation between <001> and blade axis has important engineering significance.

2.1.1 Orientation Control by Grain Selection Single crystal superalloy blades are generally manufactured using the spiral grain selection method, which utilizes competitive growth and geometric blocking of grains with different orientations in the spiral selector to finally obtain single crystals with <001> preferred orientation. During single crystal growth, orientation changes with temperature and solute fields, but the variation is small. Previous studies show that crystal orientation mainly depends on the grain selection process, so orientation deviation control should start with grain selection.

Grain selector structure significantly affects orientation control \cite{27~30}. Analysis of the grain selection process [**?**] shows that the starter block determines alternative grains and their orientation characteristics, making it the key to orientation control. As shown in [Figure 7: see original paper][**?**], as starter block height increases and diameter decreases, grain orientation deviation continuously decreases. When starter block height is 20 mm, over 95% of grains have orientation deviation within 15° of <001>. When height reaches 30 mm, all grains have orientation deviation within 15°. Therefore, the starter block should have sufficient length, but its diameter should not be too large.

Zhang Xiaoyue [**?**] further investigated the effect of starter block height-to-diameter ratio on selected grain orientation, with results shown in [Figure 8: see original paper][**?**], where d and h are starter block diameter and height, respectively. The figure shows that as the height-to-diameter ratio increases, the angle between the single crystal <001> direction and specimen axis gradually decreases. When starter block height increases, it provides more space and time for <001>-oriented grains to eliminate other orientations. As starter block diameter decreases, temperature gradient at the solid/liquid interface gradually increases, enhancing the advantage of preferentially oriented grains in competitive growth and facilitating orientation optimization within the starter block.

Directional solidification process parameters such as withdrawal rate and mold temperature also significantly affect orientation control because they influence grain competitive growth and elimination processes [**?**, **?**]. [Figure 9: see original paper][**?**] shows orientation deviation of selected single crystals at different solidification rates and mold insulation temperatures. As solidification rate and mold insulation temperature increase, single crystal orientation deviation angle gradually decreases, favoring orientation optimization. Increasing both solidification rate and mold insulation temperature increases cooling rate, intensifying grain competitive growth in the starter block and optimizing grain orientation. Zhou et al. [**?**] conducted detailed studies and discussions on the effect of cooling rate on grain competitive growth. However, if solidification rate is too high (e.g., >200 mm/s), severe concavity of the solid/liquid interface may cause alloy melt undercooling, preventing stable single crystal growth.

During single crystal growth, orientation can also be slightly affected by temperature and solute fields [**?**]. Inconsistent deviation among dendrites can lead to low-angle grain boundaries between dendrite arrays. Overall, using the grain selection method to prepare single crystal superalloys with specific orientations mainly depends on controlling grain selector structure and solidification process parameters.

2.1.2 Orientation Control by "Seeding + Selection" Method The grain selection method is simple but inevitably results in random single crystal orientations. Secondary dendrite orientation and dendrite deviation direction also significantly affect stray grain formation at blade platforms and airfoils. Therefore, to further improve quality of advanced complex single crystal blades, orientation control requirements may include not only deviation angle but also secondary dendrite orientation and deviation direction. The "seeding + selection" method provides a solution \cite{34~37}.

The difference between the "seeding + selection" method and the grain selection method is replacing the starter block with a seed block for orientation control; the difference from the seeding method is adding a spiral grain selector between the seed and casting. [Figure 10: see original paper][**?**] reveals microstructure evolution in the seed and selector sections during single crystal blade model preparation using the "seeding + selection" method. Grain orientation analysis shows that seed crystal orientation basically determines the three-dimensional crystal orientation of the directional solidification microstructure.

The "seeding + selection" method experiences a spiral grain selection process after successful seeding, with continuously changing temperature gradient direction in the spiral selector section. Therefore, it is necessary to evaluate whether crystal orientation at the selector outlet is consistent with seed orientation. [**?**] shows orientation changes between three different seeds and corresponding single crystals at selector outlets. The results show that after experiencing the spiral selection process, three-dimensional orientation change of the single crystal is very small, further demonstrating that the "seeding + selection" method can effectively control three-dimensional orientation.

Overall, in the "seeding + selection" process, crystal orientation obtained from seeding is basically consistent with seed orientation, and crystal orientation does not change significantly after the selection process. In engineering applications, specific seed orientation can first be set according to actual needs; then an initial single crystal with consistent orientation can be grown epitaxially; after experiencing the grain selection process, other grains formed during the initial seeding stage are eliminated, finally obtaining single crystal superalloy castings with precisely controlled orientation.

2.2 Stray Grains

Stray grain defects easily appear in single crystal superalloy castings. Stray grains generally refer to randomly oriented grains with different crystal orientations from the single crystal casting, which easily form high-angle grain boundaries with the original grains. Stray grains often occur at special locations such as abrupt cross-sections \cite{38~43} and near seed remelting zones \cite{35,36,44~46}. When base grain orientation deviation is too large, stray grains may also form at locations near the shell at the blade airfoil [?]. Avoiding and controlling stray grain formation in single crystal castings to improve casting yield has become an important research topic in superalloys.

With the development of experimental methods and numerical simulation technology, especially the continuous advancement of Cellular Automaton (CA) models, direct observation and analysis of thermal-solutal convection, microstructure evolution, and defect formation during directional solidification have become possible, promoting research on stray grain formation inside abrupt cross-sections. Currently, extensive research has been conducted on competitive growth mechanisms of stray grains [?] and the effects of alloy composition \cite{37~43}, process parameters \cite{39~43}, and casting geometry \cite{37~43} on stray grain nucleation. However, control technology for stray grains in large, complex castings is not yet mature.

Dendrite growth in abrupt cross-sections is shown in [Figure 11: see original paper][?]. During directional solidification, when dendrite growth encounters a protruding cross-section, secondary dendrite branches grow into the protruding platform while tertiary and even higher-order dendrite branches also grow. When the platform is sufficiently long, stray grains begin to nucleate and grow at platform edges before dendrites of the original grain reach the platform edge. The essence of stray grain formation at cross-section changes is that single crystal growth occurs in both x and y directions at this location, while directional solidification processes generally only control temperature gradient in the y direction. Temperature gradient in the x direction is difficult to control and cannot guarantee directional solidification conditions.

De Bussac and Gardin [?] performed mathematical derivation of stray grain nucleation in abrupt cross-sections based on the KGT model and numerous assumptions, obtaining a criterion for stray grain formation inside abrupt cross-sections:

$$\Delta \mathrm{Tnucl} - \Delta \mathrm{T} = (\mathrm{A} \cdot \mathrm{vL}\hat{}\mathrm{n} + 1) \cdot \mathrm{L} \cdot (\cos\ )$$

where A and n are dendrite growth kinetic parameters in the KGT relationship, is the deviation angle between dendrite <001> direction and axial direction, G and vL are temperature gradient and liquidus velocity, ΔTnucl is critical nucleation undercooling, and f is platform structural size. Equation (2) shows that process parameters G and vL, alloy composition-determined A, n, and ΔTnucl, and crystal orientation-determined affect stray grain nucleation tendency by influencing temperature and solute field distribution in abrupt cross-sections. This criterion reveals that temperature field, alloy composition, orientation deviation angle, process parameters, and platform structural size all affect stray grain nucleation. However, due to numerous assumptions, this criterion cannot reflect actual casting processes.

To directly observe stray grain formation during casting, many researchers have used cellular automaton combined with finite element analysis or finite difference methods (CAFE and CAFD) to simulate grain growth during directional solidification. Rappaz et al. [?] used 2D CAFE technology to simulate directional solidification of a single crystal blade cross-section, directly observing temperature field changes during solidification and predicting grain structures under different process parameters.

Research on the effect of crystal orientation deviation on stray grain nucleation in blade abrupt cross-sections [?, ?] found that deviation boundaries tend to generate larger undercooling, and as deviation angle increases, stray grains form more easily. Structural dimensions of abrupt cross-sections directly affect temperature field distribution during directional solidification. Compared with the airfoil, longer or thinner platforms have better heat dissipation, thus increasing concavity of the liquidus line and leading to larger undercooled melt volume and increased probability of heterogeneous nucleation sites, making stray grains more likely to appear. Zhang Xiaoli et al. [?] and Meng et al. [?] verified this experimentally and found that due to asymmetric temperature fields, the probability of stray grain formation varies at different positions on the same platform. In actual production, multiple samples are often drawn in one furnace, so temperature field distribution is generally not symmetrical left-right. The side of the sample near the furnace wall and the side near the center have different concavity in temperature field, resulting in different stray grain formation tendencies.

Jiao Juanjuan [?] analyzed conditions for stray grain formation based on temperature field simulation of variable cross-section castings, as shown in [Figure 12: see original paper]. Vertical arrows represent primary dendrite growth direction, horizontal arrows represent secondary branch growth direction within the platform, and the red curve represents the isotherm at dendrite tip front at time t, with point B being the isotherm inflection point. It is well known that alloy melt can nucleate only when actual temperature Tq is lower than critical nucleation temperature TN, i.e., only when melt undercooling ΔT = TL - Tq is greater than critical nucleation undercooling ΔTnucl = TL - TN. Similarly, stray grains in the platform must satisfy ΔT0 > ΔTnucl (ΔT0 is undercooling at platform edges before dendrite tips reach the platform). Melt in platform edge region (region BCDB) is in thermal undercooling state with large undercooling ΔT, making platform edges prone to stray grain formation. Assuming primary dendrites of the base grain just grow to point A, temperature of undercooled melt in region BCDB is recorded as TA. If no stray grains form in the platform after directional solidification is complete, time required for secondary branches growing along platform edges (green horizontal lines in [Figure 12: see original paper]) to reach platform edge C is recorded as tAC = tAB + tBC, where tAB is time for secondary branches to grow from A to B. Temperature gradually increases from A to B, making secondary branch growth decelerate along AB, following the KGT model. tBC is time for secondary branches to grow from B to C. Based on isotherm shape, temperature gradually decreases from B to C, making secondary branch growth accelerate along BC, following the LGK model. Thus, secondary branch growth along platform edges is very complex. Time for undercooled melt temperature to decrease from TA to TN during solidification is recorded as tAN. If tAC > tAN, stray grains form in the platform; if tAC < tAN, no stray grains form throughout solidification.

The above analysis shows that platform stray grains nucleate under undercooled conditions. Changing processes, casting structure, and cooling conditions to reduce local undercooling, or increasing maximum melt undercooling, and changing dendrite growth direction can all control stray grain formation.

2.2.1 Adjusting Alloy Composition Alloy composition affects stray grain formation. Zhang Xiaoli et al. [?] experimentally found that different alloy compositions have different stray grain formation tendencies under the same solidification conditions. Because different alloy compositions, especially refractory element (Re, W, Ta, and Hf) contents, change alloy liquidus temperature, they affect stray grain nucleation. In heterogeneous nucleation, critical nucleation undercooling is proportional to wetting angle; smaller wetting angle means smaller critical nucleation undercooling and stronger nucleation capability. Under otherwise identical conditions, alloy composition becomes the main factor affecting wetting angle, so different alloys have different critical nucleation undercoolings. Nucleation is jointly determined by undercooling and critical nucleation undercooling; larger difference between them makes nucleation easier.

Recently, Chen Xianzhou [?] studied the effects of refractory element Re and trace elements C and B on stray grain formation at platforms. Experimental alloy compositions are shown in [?], where alloys 1-1 and 1-2 compare Re effects, alloys 2-1 and 2-2 compare C effects, and alloys 3-1 and 3-2 compare B effects. Experimental results are shown in [Figure 13: see original paper][?]. The section line in [Figure 13e: see original paper] shows sampling position, arrows indicate single crystal growth direction, region A is initial single crystal region, region B is single crystal region expanded through secondary and tertiary branches, and region C shows stray grains. The results show that Re makes stray grains appear more easily, while both C and B can suppress stray grain formation to some extent. This effect relates to changes in solidification characteristics. Re reduces nucleation undercooling, favoring stray grain nucleation. As C and B contents increase, liquidus temperature TL significantly decreases, reducing undercooling ΔT of undercooled melt and decreasing possibility of $\Delta T > \Delta$Tnucl, thus reducing stray grain formation tendency at platform positions. Additionally, Tin and Pollock [?] believed that carbides can suppress solutal convection in interdendritic liquid, thereby improving alloy castability and reducing grain defects. Therefore, during alloy composition design, while ensuring alloy performance, stray grain nucleation during solidification should be minimized, i.e., while maintaining constant undercooling (constant liquidus temperature), critical nucleation undercooling should be increased as much as possible to reduce stray grain nucleation capability.

2.2.2 Changing Solidification Parameters Solidification parameters (especially withdrawal rate) significantly affect stray grain formation in directional solidification of single crystal superalloys. Napolitano and Schaefer [?] showed that shape of solidification interface at plate edges is closely related to stray grain formation; increasing withdrawal rate increases concavity of solidification interface, making stray grains more likely to appear. Lu Yuzhang et al. [?] obtained consistent experimental results. At high withdrawal rates, peripheral parts of castings begin solidifying first, while core heat cannot dissipate in time, making core temperature higher than periphery and causing concave solidification interface. When edge plate temperature falls below liquidus temperature, stray grains begin nucleating and growing, with growth direction perpendicular to the solid/liquid interface. From the solute field perspective, according to the classic constitutional undercooling criterion, increasing withdrawal rate V and decreasing temperature gradient G make constitutional undercooling more likely at solidification front, obviously increasing stray grain nucleation tendency. Additionally, increased V hinders solute diffusion at dendrite tips (diffusion boundary layer thickness δ = 2DL/V decreases), further increasing constitutional undercooling near dendrite tips and promoting stray grain nucleation and growth. Increased G reduces mushy zone width H, making base grains more likely to catch up with stray grains nucleated here, which is unfavorable for stray grain nucleation and growth. Therefore, increasing temperature gradient is an effective method to control stray grain defects. Gao Sifeng [?] compared the effects of two processes–high rate solidification (HRS) and liquid metal cooling (LMC) –on stray grains, with experimental results shown in [Figure 14: see original paper][?]. Since temperature gradient in LMC process (110 K/cm) is nearly double that in HRS process (45 K/cm), critical withdrawal rate for stray grain appearance increases under LMC conditions. Stray grains appear at 9 mm/min in LMC process but at 6 mm/min in HRS process.

Due to the effect of solidification rate on stray grain formation, researchers have attempted to use variable withdrawal rates to increase single crystal productivity while suppressing stray grain formation at blade platforms. That is, normal withdrawal rate is used for the airfoil section, and withdrawal rate is reduced near the platform to keep the solid/liquid interface flat. Chen Chun [?] used variable withdrawal rate directional solidification and found no stray grain defects at platform edges. Thus, variable withdrawal rate directional solidification can effectively suppress stray grain defect formation during single crystal blade preparation. However, solid/liquid interface position is difficult to determine, making variable-rate processes uncertain. Additionally, non-steady-state microstructure evolution during rate changes can easily cause dendrite coarsening and increased eutectic [?], affecting casting quality consistency.

2.2.3 Changing Local Temperature Field Local temperature field changes caused by casting structure are the main reason for stray grain formation at special locations. Therefore, researchers have adjusted temperature fields through other means to offset temperature field changes favorable for stray grain formation, thereby reducing or suppressing stray grain formation. Ma et al. [?, ?] used local cooling by setting graphite blocks at the junction between airfoil and platform to improve heat transfer conditions at “hot spot” locations, reducing undercooling at platform edges, decreasing undercooled region, making liquidus line smoother, and effectively reducing stray grain formation tendency at platforms. Meyer et al. [?] added insulating material SiO2-Al2O3 at platform edges to prevent heat loss. Although these two methods have opposite approaches, their effects are consistent: both make isotherms in the platform flatter and suppress stray grain nucleation.

[Figure 15a: see original paper][?] shows simulated temperature field evolution with graphite blocks added at the airfoil-platform junction. After adding graphite blocks, liquid phase isotherms become smoother on the graphite block side, preventing microstructure 突变 caused by solid/liquid interface 突变. [Figure 15b: see original paper] shows CAFE results with graphite blocks [?], demonstrating that graphite block addition effectively weakens hot spot effects, making heat at abrupt cross-sections dissipate along solidified airfoil parts and effectively preventing stray grain formation at platform edges. [Figure 15c: see original paper] shows experimental results [?], where red arrows indicate stray grains and white arrows indicate graphite addition positions. Analysis shows no stray grain formation on the side with graphite block local cooling, while stray grains appear on the other side of the casting. Experimental and simulation results agree well. However, it should be noted that graphite block addition method and size are complex issues that are currently unclear.

2.2.4 External Physical Fields As an external physical field, magnetic fields typically act on directional solidification processes in a contactless manner through force and energy, affecting diffusion, flow, and solidification interface, thereby influencing solidification microstructure and composition distribution. This makes them important means for improving alloy and crystal properties. Xuan Weidong et al. [?] experimentally found that applying magnetic fields during directional solidification of superalloy variable cross-section specimens can reduce stray grain tendency. At certain withdrawal rates, applying magnetic fields of certain intensity results in no stray grain formation at variable cross-sections. This can be attributed to magnetic fields increasing solid/liquid interface energy, lowering liquid nucleation temperature (increasing critical nucleation undercooling), thereby suppressing stray grain formation at variable cross-sections. However, the reliability and mechanism of this method need further clarification, and its application prospects are also questioned.

2.2.5 Grain Continuator-Assisted Seeding Meyer et al. [?] designed two grain continuators at the junction between blade airfoil bottom and selector top to guide dendrite growth, directly guiding the single crystal to the region outside the abrupt interface where stray grains easily form, thus avoiding stray grain formation. During directional solidification, solidification interface positions in the airfoil and grain continuators are the same. When dendrites in the airfoil grow to the platform intersection, dendrites in the continuators also grow to the abrupt cross-section, leaving no space for stray grain nucleation. Combined simulation and experimental verification of continuator effects are shown in [Figure 16: see original paper][?]. Continuator size and angle both affect seeding effectiveness. When properly designed, continuators can prevent stray grain formation at platforms; when improperly designed, they may even cause stray grains. Moreover, when crystals growing separately in continuators and airfoil converge, small-angle grain boundaries can easily form.

2.2.6 Suppressing Stray Grains by Superheating Treatment Both the analytical model of Bussac [?] and qualitative models based on temperature field and melt undercooling analysis demonstrate that nucleation characteristics of the melt itself significantly affect stray grain formation. Since different thermal histories can obtain different melt structures, thereby affecting melt nucleation and growth kinetics, superheating treatment is a possible method to control stray grain formation. As shown in [Figure 4: see original paper], when melt superheating treatment temperature increases from 1450°C to 1780°C, nucleation undercooling increases from 32°C to about 78°C, significantly increasing undercooling required for stray grain nucleation and correspondingly reducing stray grain formation probability.

2.2.7 Suppressing Stray Grains by Three-Dimensional Orientation Control Yang et al. [?] found that if the seed [001] direction is not parallel to the withdrawal direction, i.e., deviating from or converging with the mold, significant local undercooling exists at deviation and convergence locations between single crystal and mold. Both situations promote stray grain formation, but undercooling at deviation interfaces is greater than at convergence interfaces, and stray grains at deviation interfaces grow more easily. D' Souza et al. [?] and Stanford et al. [?] also observed this phenomenon. Additionally, Yang et al. [?] and Zhou [?] experimentally showed that not only do seed-mold deviation locations easily generate large undercooling, but large undercooling also easily occurs between stray grains and seeds growing away from each other, generating new stray grains. Partition coefficients and diffusion coefficients determined by alloy composition also significantly affect stray grain nucleation. Increased partition coefficient and solute diffusion coefficient significantly increase constitutional undercooling at dendrite tips, promoting stray grain nucleation. Dendrite competitive growth studies show that orientation relationships between adjacent dendrites affect competition results. Since different three-dimensional orientations of single crystals form different angular relationships with the mold, three-dimensional orientation of single crystals also significantly affects stray grain formation. Jiao Juanjuan used the scheme shown in [Figure 17: see original paper][?] to investigate effects of different angular relationships between single crystals and molds on stray grains, where 1 is the angle between primary dendrite orientation and casting axis, and 2 is the angle between secondary dendrite orientation and platform edge. [Figure 17a: see original paper] shows secondary dendrite growth schematic, [Figure 17b: see original paper] and c compare effects of primary dendrite axis deviation angle, and [Figure 17b: see original paper], d~f compare effects of secondary dendrite-platform angle.

Experimental results show that when primary dendrite orientation is parallel to blade model axis ([Figure 17b: see original paper]), misorientation angle between microstructures on both sides of dendrite convergence location in the platform is 2.44°, forming a low-angle grain boundary. When primary dendrite orientation deviates 15° from the axis ([Figure 17c: see original paper]), at the side where primary dendrites converge with the platform, dendrite deviation angle is 2.88°, forming a low-angle grain boundary; at the side where primary dendrites diverge from the platform, obvious dendrite deviation occurs with angle of 13.99°, forming a high-angle grain boundary. The results indicate that larger deviation angle between primary dendrites and casting axis increases defect formation tendency, especially at the side where primary dendrites diverge from the platform. This is because secondary branches are farther from the platform edge on this side, requiring longer time to grow to platform edges, allowing longer cooling time at the platform far end and increasing undercooling in this region.

[Figure 18: see original paper][?] shows experimental results of crystal orientation at platforms for different secondary dendrite orientations [?]. As the angle between secondary dendrites and platform edge increases, the misorientation angle for sub-grain boundary formation at the platform increases, and stray grain formation tendency also increases. The mechanism of secondary dendrite orientation effect is similar to that of primary dendrite axial deviation. As the angle between secondary dendrites and platform edge increases, distance for secondary branches to grow to platform edges increases, making tAC longer for secondary or tertiary branches to grow to platform far ends, thus more easily satisfying stray grain formation condition: tAC > tAN.

Seed remelting zones are also prone to stray grains. Stanford et al. [?] found that when preparing single crystal castings by the seeding method, stray grains only appear at specimen edges during the initial withdrawal stage. As withdrawal proceeds, most generated stray grains are eliminated, with only a few able to grow. This indicates that stray grain nucleation is approximately a transient process occurring only during the initial withdrawal stage, with no stray grain nucleation after withdrawal rate stabilizes. Yang et al. [?] analyzed the effects of process parameters (withdrawal rate V and temperature gradient G), deviation angle between crystal orientation and casting axis, and alloy composition on stray grain formation near remelting zones during single crystal casting preparation by the seeding method. As V, , G, and refractory element content increase, stray grain nucleation tendency increases. Among these factors, stray grain nucleation in remelting zones is most sensitive to changes in V and , while G changes have no obvious effect on stray grain defect formation in remelting zones, and alloy composition effects are intermediate.

The "seeding + selection" process can also effectively solve remelting zone stray grain problems, as shown in [Figure 19: see original paper][?]. Numerous stray grains form at the seed remelting interface, located in gaps between seed and mold inner wall. Most stray grains are quickly eliminated, and a few may grow. However, since they originate from the surface, they are eliminated by mechanical blocking when passing through the constricted part of the selector, leaving only grains from the central part. Therefore, in the "seeding + selection" process, distance between remelting interface and spiral selector should be minimized to prevent remelting stray grains from growing into the center and being selected.

Through the above analysis, the "seeding + selection" method can control three-dimensional orientation of single crystals, such as reducing primary dendrite orientation deviation or reducing the angle between secondary dendrites and platform edges, effectively reducing platform stray grain defects. By appropriately controlling remelting interface position, the "seeding + selection" process can also effectively control stray grain defects.

3. Conclusions and Outlook

With continuous advancement in single crystal superalloy composition design, refractory element contents in alloys continue to increase, particularly Re and Ru additions, which have become markers for distinguishing generations of advanced single crystal superalloys. However, Re and Ru additions also bring a series of problems to alloy casting performance, heat treatment microstructure, phase stability, density, and cost. Especially in recent years, demand for large, complex industrial gas turbine blades has made these problems more prominent, becoming bottlenecks restricting alloy development.

Single crystal alloy development first leads to changes in solidification characteristics. With Re and Ru additions, eutectic content in as-cast microstructure significantly increases. Re addition has little effect on liquidus temperature but lowers solidus temperature, expanding the solidification temperature range. Re and Ru additions also significantly reduce alloy critical nucleation undercooling, intensifying stray grain formation tendency and reducing alloy castability. Re is also one of the most severely segregated elements. Trace elements C and B also significantly affect alloy solidification characteristics.

Good orientation control is the primary requirement for single crystal blades. Since orientation changes little during grain selection and single crystal directional growth, orientation control in grain selection-based single crystal manufacturing mainly depends on grain selector structure design, especially the starter block. Longer starter block and larger height-to-diameter ratio result in smaller orientation deviation. However, grain selection method has random orientation. The "seeding + selection" process can achieve three-dimensional orientation control of single crystals, not only controlling crystal orientation more precisely but also suppressing stray grain formation at casting abrupt cross-sections by controlling angular relationships between three-dimensional orientation and mold structure.

Platforms are concentrated areas for stray grain defects. Stray grain formation can be suppressed to some extent through alloy composition adjustment or trace element addition (e.g., B, C), variable-rate growth, high temperature gradient directional solidification, grain continuators, local cooling, external physical fields, melt superheating treatment, and other technologies. Challenges of local variable-rate processes include determining solid/liquid interface position; grain continuators may introduce stray grains and easily cause low-angle grain boundaries at "joint" locations; local cooling process challenges include determining graphite block shape, size, and position, with low process reliability. The seeding + selection process is an effective method to control stray grain defects. The selection process can completely eliminate stray grains in remelting zones, and precise seed arrangement can control three-dimensional grain orientation to suppress stray grain formation at airfoil and platform locations, thereby improving casting yield.

References

[1] Reed R C, Tao T, Warnken N. Acta Mater, 2009; 57: 5898 [2] Biavette D, Caron P, Khan T. Scr Metall, 1986; 20: 1395 [3] Mottura A, Wu R T, Finnis M W, Reed R C. Acta Mater, 2008; 56: [4] Tin S, Pollock T M. J Propul Power, 2006; 22: 361 [5] Tryon B, Feng Q, Pollock T M. Intermetallics, 2004; 12: 957 [6] Feng Q, Nandy T K, Pollock T M. Scr Mater, 2004; 50: 849 [7] D' Souza N, Dong H B. Scr Mater, 2007; 56: 41 [8] Zheng Y R. Acta Metall Sin, 1986; 22: 119 [9] Reed R C. The Superalloys: Fundamentals and Applications. New York:

Cambridge University Press, 2006: 1 [10] Murakami H, Honma T, Koizumi Y, Harada H. In: Pollock T M, Kissinger R D, Bowman R R eds., Superalloy 2000, Warrendale: TMS, 2000: 747 [11] Kearsey R M, Beddoes J C, Jones P, Au P. Intermetallics, 2004; 12: 903 [12] Feng Q, Nandy T K, Tin S, Pollock T M. Acta Mater, 2003; 51: [13] Heckl A, Rettig R, Singer R F. Metall Mater Trans, 2010; 41A: [14] Hobbs R A, Tin S, Rae C M F, Broomfield R W, Humphreys C J. In: Green K A, Pollock T M, Harada H eds., Superalloys 2004, Warrendale: TMS, 2004: 819 [15] Liu G, Liu L, Zhao X B, Ge B M, Zhang J, Fu H Z. Metall Mater Trans, 2011; 42A: 2733 [16] Caldwell E C, Fela F J, Fuchs G E. In: Green K A, Pollock T M, Harada H eds., Superalloys 2004, Warrendale: TMS, 2004: 811 [17] Liu L R, Jin T, Zhao N R, Wang Z H. Mater Lett, 2004; 58: 2290 [18] Al-Jarba K A. PhD Dissertation, University of Florida, USA, 2003 [19] Hu Q, Liu L, Zhao X B, Gao S F, Zhang J, Fu H Z. Trans Nonferrous Met Soc China, 2013; 23: 3257 [20] Kearsey R M. PhD Dissertation, Carleton University, Canada, [21] Hobbs R A, Tin S, Rae C M F. Metall Mater Trans, 2005; 36A: [22] Tin S, Pollock T M. Mater Sci Eng, 2003; A348: 111 [23] Zheng L, Li S S, Xiao C B, Tang D Z, Gu C Q. Key Eng Mater, 2007; 353-358: 507 [24] Zhang J, Lou L H. J Mater Sci Technol, 2007; 23: 289 [25] Jiao S, Zhang J, Jin T, Wang C S, Wang H F, Liu L, Fu H Z. Rare Met Mater Eng, 2013; 42: 1028 [26] Seth Brij B. In: Pollock T M, Kissrnger R D, Bowman R R, Gree K A, McLean M, Olson S, Schirra J J eds., Superalloys 2000, Warrendale: TMS, 2000: 3 [27] Gao S F, Liu L, Wang N, Zhao X B, Zhang J, Fu H Z. Metall Mater Trans, 2012; 43A: 3767 [28] Gao S F, Liu L, Wang N, Zhao X B, Zhang J, Fu H Z. Mater Sci Technol, 2011; 27: 1783 [29] Dai H J, Dong H B, D' Souza N. Metall Mater Trans, 2011; 42A: [30] Esaka H, Shinozuka K, Tamura M. Mater Sci Eng, 2005; A413-414: 151 [31] Zhang X Y. Master Thesis, Northwestern Polytechnical University, Xi' an, 2013 [32] Zhou Y Z, Volek A, Green N R. Acta Mater, 2008; 56: 2631 [33] Zhang X L, Zhou Y Z, Jin T, Sun X F, Liu L. J Mater Sci Technol, 2013; 29: 879 [34] Jiao J J. Master Thesis, Northwestern Polytechnical University, Xi' an, 2015 [35] Stanford N, Djakovic A, Shollock B A, McLean M, Souza N D, Jennings P. In: Green K A, Pollock T M, Harada H eds., Superalloys 2004, Warrendale: TMS, 2004: 719 [36] Stanford N, Djakovic A, Shollock B A, McLean M. Scr Mater, 2004; 50: 159 [37] Chen X Z. Master Thesis, Northwestern Polytechnical University, Xi' an, 2014 [38] de Bussac A, Gandin C A. Mater Sci Eng, 1997; A237: 35 [39] Rappaz M, Gandin C A, Desbiolles J L. Metall Mater Trans, 1996; 27A: 695 [40] Napolitano R E, Schaefer R J. Mater Sci, 2000; 35: 1641 [41] Meyer T V, Dedecke D, Paul U, Sahm P R. In: Kissinger R D, Deye D J, Anton D L, Cetel A D, Nathal M V, Pollock T M, Woodford D A eds., Superalloys 1996, Warrendale: TMS, 1996: 471 [42] Zhang X L, Zhou Y Z, Jin T, Sun X F. Acta Metall Sin, 2012; 48: 1229 [43] Meng X B, LI J G, Chen Z Q. Metall Mater Trans, 2013; 44A: [44] Yang X L, Ness D, Lee P D, Souza N D. Mater Sci Eng, 2005; A413: 571 [45] Tin S, Pollock T M. Metall Mater Trans, 2003; 34A: 1953 [46] Gu J P, Beckermann C, Giamei A F. Metall Mater Trans, 1997; 28A: 1533 [47] Lu Y Z, Wang D W, Zhang J, Lou L H. Foundry, 2009; 58: 245 [48] Gao S F. PhD Dissertation, Northwestern Polytechnical University, Xi' an, 2012 [49] Chen C. Master Thesis, Northwestern Polytechnical University, Xi' an, 2013 [50]

Huang T W, Liu L, Zhang W G, Zhang J, Fu H Z. Acta Metall Sin, 2009; 45: 1225 [51] Ma D X, Bührig-Polaczek A. Metall Mater Trans, 2009; 40B: 738 [52] Ma D X, Zhou B, Bührig-Polaczek A. Adv Mater Res, 2011; 278: [53] Xuan W D, Ren Z M, Ren W L, Yu J B, Chen C. J Iron Steel Res, 2011; 23: 369 [54] Yang X L, Ness D, Lee P D. Mater Sci Eng, 2005; A413: 571 [55] D' Souza N, Jennings P A, Yang X L, Dong H B, Lee P D, McLean M. Metall Mater Trans, 2005; 36B: 657 [56] Yang C B, Liu L, Zhao X B, Sun D J, Zhang J, Fu H Z. Appl Phys, 2014; 114A: 979 [57] Zhou Y Z. Scr Mater, 2011; 65: 281

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