Incipient Melting Behavior of a High-Boron Directionally Solidified Alloy and Its Effect on Mechanical Properties: Postprint

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Abstract

This study systematically investigated the incipient melting behavior of high-boron DZ444 directionally solidified alloy and its influence on mechanical properties. The results show that in the as-cast alloy, the interdendritic regions contain a large amount of / ’ eutectic, MC carbides, and “agglomerated phases” composed of borides, Ni5Hf, and phases. During solution treatment, the matrix significantly influenced by borides around the agglomerated phases undergoes incipient melting first. Borides are not nucleation sites for incipient melting, but play a critical role in its formation. The higher boron content results in a lower incipient melting temperature for the alloy, ranging between 1160-1170 °C, which is significantly lower than that of normal alloys. Increasing temperature or prolonging holding time exacerbates the incipient melting phenomenon. With water cooling (WC), the incipient melt tends to solidify as typical dendrites and numerous fine precipitate particles, whereas with air cooling (AC), the incipient melt solidifies sequentially as agglomerated phases, matrix, and / ’ eutectic phases, with the morphology of agglomerated phases showing no significant difference from that in the as-cast condition. During complete heat treatment, when the solution temperature is increased from 1210 °C to 1230 °C, incipient melting increases slightly, but when the temperature reaches 1250 °C, the size and area fraction of incipient melting increase dramatically, causing catastrophic damage to the alloy. Due to the relatively low temperatures, high- and low-temperature aging of the alloy does not significantly affect the incipient melting microstructure. Finally, the study found that with increasing size and area fraction of incipient melting, the tensile properties of the alloy decrease slightly, while the stress-rupture properties are significantly reduced.

Full Text

Incipient Melting Behavior and Its Influences on the Mechanical Properties of a Directionally Solidified Ni-Based Superalloy with High Boron Content

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Abstract

The incipient melting behavior and its effects on mechanical properties of a high-boron DZ444 directionally solidified superalloy were systematically investigated. The results show that the as-cast alloy contains numerous interdendritic / eutectics, MC carbides, and "constituent phases" composed of borides, Ni Hf, and phase. During solution treatment, incipient melting first occurs in the matrix surrounding the multi-phase constituent, significantly influenced by the presence of borides. Borides are not nucleation sites for incipient melting but play a critical role in its formation. The higher boron content lowers the incipient melting temperature to between 1160–1170 °C, which is noticeably lower than that of normal alloys. Increasing temperature or extending holding time exacerbates incipient melting. With water quenching, incipient melting tends to solidify as typical dendrites and numerous fine precipitate particles, whereas with air cooling, it solidifies successively as constituent phases, matrix, and / eutectic, with the constituent phase morphology showing no obvious difference from the as-cast condition. During complete heat treatment, raising the solution temperature from 1210 °C to 1230 °C slightly increases incipient melting, but at 1250 °C, both the size and area fraction of incipient melting increase dramatically, causing severe damage to the alloy. Due to the relatively low temperatures, high and low temperature aging treatments have minimal effect on the incipient melting microstructure. As the size and area fraction of incipient melting increase, the incipient melting regions consume substantial solid solution strengthening elements while simultaneously promoting microcrack initiation within these regions, resulting in a slight decrease in tensile properties and a significant reduction in creep-rupture properties.

Keywords: directionally solidified superalloy, solution treatment, incipient melting, multi-phase eutectic-like constituent, mechanical property

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1. Introduction

Directionally solidified Ni-based superalloys require heat treatment before service. During heat treatment, strengthening phases precipitated during solidification dissolve or partially dissolve and then reprecipitate as uniformly fine and dispersed strengthening particles, reducing or eliminating elemental segregation present in the as-cast condition—particularly segregation caused by composition deviations between the eutectic phase and surrounding regions formed during the final stages of solidification [1,2]. The areas adjacent to eutectic fronts concentrate low-melting-point phases or components. Literature reports have identified low-melting-point phases such as Cr-Mo borides and Ni-Zr compounds at eutectic fronts [3–9]. The formation of low-melting-point phases makes alloys susceptible to incipient melting during heat treatment, which significantly affects mechanical properties [10–13].

Sidhu et al. [10] studied the directionally solidified superalloy Rene80 and found that incipient melting was caused by Cr-Mo borides, Ni-Ti phases, and Ni-Zr phases in regions surrounding the / eutectic formed during the final stages of solidification. Zheng et al. [11,12] investigated incipient melting in the Hf-containing directionally solidified alloy DZ22 and demonstrated that melting of the Ni Hf phase was the primary cause. Alloys with incipient melting volume fractions exceeding 3% showed significant degradation in both creep-rupture and high-temperature tensile properties, with fracture surfaces exhibiting features of cracking along the edges of / eutectics within incipient melting zones. Zheng et al. [11,12] and Chen et al. [13] effectively controlled incipient melting by adjusting alloy composition and heat treatment regimes to eliminate or reduce low-melting-point phases. Jahangiri et al. [14] studied the cast Ni-based superalloy IN939 and found that adjusting the heat treatment regime could effectively avoid incipient melting, thereby improving hot workability.

The DZ444 alloy is a low-cost, hot-corrosion-resistant directionally solidified Ni-based superalloy developed based on the equiaxed K444 alloy. Its service temperature is approximately 30 °C higher than K444, with mechanical properties comparable to the foreign alloy MGA1400DS and superior to GTD111DS and IN792DS alloys. It is used to manufacture high-temperature components such as turbine blades operating at temperatures not exceeding 930 °C in modern marine and industrial gas turbines [15,16]. Since this alloy contains trace B (0.01 wt%) and minor Hf (0.5 wt%), it theoretically has a tendency to form low-melting-point phases under severe segregation conditions. Therefore, this work intentionally added a higher B content (0.09 wt%) to investigate the incipient melting behavior during solution treatment, its close relationship with B or borides, and its effects on mechanical properties. The results provide guidance for chemical composition design and heat treatment process selection in cast Ni-based superalloys.

2. Experimental

The experimental alloy had a chemical composition (wt%) of: C 0.07, B 0.09, Cr 15.8, Co 10.7, W 5.3, Mo 2.0, Al 3.0, Ti 4.7, Ta 0.5, Hf 0.5, Ni balance—equivalent to DZ444 alloy with excess B. Master alloy was melted in a vacuum induction furnace, and directionally solidified bars were prepared in a directional solidification furnace. Small specimens were cut from the bars and subjected to solution treatment at different temperatures (1150, 1160, 1170, 1180, 1190, and 1200 °C) for various times (5, 10, and 30 min), followed by cooling via two methods: water quenching (WQ) and air cooling (AC).

The bars were divided into three groups for solution treatment at 1210, 1230, and 1250 °C for 2 h, followed by air cooling to room temperature and then two-stage aging (1080 °C/4 h/AC + 850 °C/24 h/AC). These three complete heat treatment regimes are designated HT1, HT2, and HT3 in order of increasing solution temperature. After heat treatment, tensile properties at 900 °C and stress-rupture properties at 930 °C/275 MPa were tested.

Microstructure observation and composition analysis were performed using a GX51 optical microscope (OM) and a JEM 6340 field emission scanning electron microscope (FESEM) equipped with an energy dispersive spectrometer (EDS). Elemental distribution was measured using an EPMA-1610 electron probe microanalyzer (EPMA). Specimens were etched electrolytically using two solutions: Solution A (HNO :HCl:glycerol = 1:3:5 by volume) to remove the phase, and Solution B (10% H CrO aqueous solution, 10 g CrO + 90 mL H O) to remove the matrix. TEM samples were prepared by twin-jet electropolishing using a solution of 10% HClO + 90% C H OH. The size and area fraction of incipient melting were measured using Image Pro Plus 6.0 software, with results averaged from at least 30 images.

2.1 As-Cast Microstructure

Figure 1 [Figure 1: see original paper] shows typical as-cast microstructures of the high-boron DZ444 alloy. At low magnification, the as-cast alloy exhibits a typical dendritic structure with numerous interdendritic / eutectics surrounding dendrites like bead chains (Fig. 1a). At higher magnification, the / eutectic displays a sunflower-like morphology, with phase size gradually increasing from the center outward—particularly the outermost phase, which is much larger than that in the center. Borides, Ni Hf, phase, or MC carbides frequently appear around the eutectic (Figs. 1b–f). MC carbides exhibit blocky morphologies in two forms: one rich in Ti and W (gray, denoted as MC(1)) and another primarily rich in Hf (bright white, denoted as MC(2)). Borides mostly show skeletal morphologies and can be divided into two types: one with a (W+Mo)/Cr ratio of approximately 1 (light gray) and another with a ratio of about 2.6 (white) (Fig. 1c and Table 1). Compared with borides, honeycomb-like or blocky Ni Hf phases are fewer in number and smaller in size, making them difficult to observe (Fig. 1d). In superalloys, both borides and Ni Hf phases are low-melting-point phases. For example, in K5 or K19H alloys, borides (M B) begin to melt at approximately 1200–1220 °C, while the melting temperature range for Ni Hf phase is about 1135–1160 °C [17]. In Fig. 1d, phase co-precipitates with borides, Ni Hf, and phases at the front of / eutectic, which we term "constituent phases." In some literature [3,4,18], these are referred to as multi-phase eutectic-like constituents.

Due to the low diffusion coefficients of refractory elements such as W, Mo, Hf, and Ta, their segregation in the alloy melt is severe [19–22]. During the final stages of solidification, massive precipitation of / eutectic exacerbates segregation of these elements, causing them to precipitate collectively as borides, Ni Hf, or phases. Since segregation degrees vary at different locations, different types of MC carbides and borides appear in the alloy (Table 1). These phases distributed around / eutectics consume large amounts of strengthening elements (W, Mo, Ti, Al, etc.) during solidification. Moreover, because of their low melting points, they are prone to incipient melting during heat treatment, which is detrimental to mechanical properties. Figure 2 [Figure 2: see original paper] shows EPMA elemental mapping of various phases, clearly revealing elemental distributions within each phase and the surrounding matrix. The matrix around constituent phases is significantly depleted in Cr but enriched in Ni, Al, and Ti—opposite to the composition of borides, particularly Boride(1), which is Cr-rich but Ni-, Al-, and Ti-poor. Therefore, we can infer that the elemental distribution characteristics around constituent phases are closely related to interdiffusion occurring during boride precipitation.

2.2 Effects of Solution Temperature and Time on Incipient Melting

No incipient melting occurred in as-cast specimens held at 1150 and 1160 °C for various times (5, 10, and 30 min). At 1170 °C, no incipient melting was observed after 5 min (Fig. 3a [Figure 3: see original paper]), but when the time reached 10 min, an almost closed incipiently melted circle (IMC) appeared around the constituent phases, enclosing phase, borides, and Ni Hf (Fig. 3b). Notably, incipient melting did not occur at borides or Ni Hf phases with low melting points as described in some literature [11–13,23], but rather first appeared in the matrix surrounding the multi-phase constituent significantly influenced by borides. This indicates that although borides do not directly cause incipient melting, they are intimately associated with its formation. The formation of the / eutectic circle confirms both the enrichment of -forming elements (Ni, Al, Ti) around constituent phases and the critical contribution of borides to incipient melting formation. Extending the holding time to 30 min at 1170 °C caused the incipient melting circle to erode and expand toward the constituent phases, melting most of the matrix within the circle. However, due to the relatively low treatment temperature, the constituent phases themselves (phase, borides, Ni Hf, etc.) showed no obvious melting signs (Fig. 3c). Rene80 alloy [10], IN738 alloy [3], and IN939 alloy [14] all exhibit incipient melting after holding at 1160 °C, 1155 °C, and 1150-1160 °C, respectively, occurring around constituent phases similar to those in this alloy (Cr-Mo borides, Ni-Ti phases, or Ni-Zr phases).

When the treatment temperature increased from 1180 °C to 1200 °C and holding time extended from 5 min to 30 min, the matrix within the incipient melting circle melted first, followed by successive dissolution or melting of constituent phases, eventually transforming all original structures within the circle into molten liquid—forming an incipiently melted pool (Fig. 4 [Figure 4: see original paper]). Water quenching preserves the high-temperature state and clearly reveals differences between unmelted and melted structures within the incipiently melted region (IMR). The unmelted structures, though not melted, dissolve substantial amounts of W, Mo, and Hf released from dissolving constituent phases, forming a supersaturated solid solution, while the melted structures consist of rapidly solidified structures with various new precipitates (Figs. 4b and c). After holding at 1200 °C for 30 min, all original structures within the IMR completely melted into liquid. During water quenching, this liquid rapidly solidified to form fine dendritic structures [24-28]: besides star-shaped dendrite cores, several relatively large and complete dendrites with clear primary and secondary arms are visible, while other areas are covered by needle-like or flocculent precipitates. The original structures within the IMR are complex, typically containing borides, Ni Hf, phase, / eutectic, and matrix. These numerous phases fuse together at high temperature, allowing composition redistribution, and finally form dendrites and numerous fine precipitates during water quenching. Due to their small size and mixed nature, these precipitates are difficult to identify and distinguish (Fig. 4d).

Etching with Solution A reveals overall IMR morphology, size, and melting degree of original structures but cannot resolve changes in constituent phases during incipient melting (Figs. 3 and 4). To observe individual phases more clearly, Solution B was used. This method effectively reveals the size, morphology, and distribution of constituent phases (including phase, borides, and Ni Hf) as shown in Fig. 5 [Figure 5: see original paper].

After treatment below 1190 °C for various times, no obvious melting signs appeared in constituent phases within the IMR (Figs. 5a and b). However, at 1200 °C for only 10 min, most constituent phases disappeared, either melting or dissolving into the supersaturated matrix (Fig. 5c); after 30 min, constituent phases completely disappeared, and numerous fine phase, boride, and Ni Hf particles reformed during water quenching (Fig. 5d). This indicates that the melting temperature of constituent phases lies between 1190 °C and 1200 °C. Some constituent phases melt first, becoming high-temperature liquid that erodes unmelted phases, causing them to melt or dissolve until all constituent phases disappear—this is the typical process of incipient pool formation. During water quenching, the liquid in the incipient pool rapidly solidifies into fine precipitates identified as borides, Ni Hf, and phases, essentially the same types as the original constituent phases. In DZ22 and K19H alloys, constituent phase melting begins with the low-melting-point Ni Hf phase, followed by successive melting of borides and / eutectic, finally forming an incipient pool [11,12]. In this alloy, constituent phases contain more types of phases with more complex distributions, making their melting sequence difficult to determine.

Compared with water quenching, air cooling provides sufficient solidification time, allowing precipitates adequate time for nucleation and growth (Figs. 6c [Figure 6: see original paper] and d), resulting in final sizes much larger than those formed during water quenching (Figs. 5c and d). Interestingly, under air cooling, the morphology and size of new precipitates show almost no difference from the original constituent phases (Fig. 1d). This phenomenon has two main causes: (1) the incipient melting region is relatively independent from the surrounding matrix, and its chemical composition theoretically remains consistent before and after incipient melting occurs; (2) the air cooling method used here is essentially the same as the cooling method during alloy solidification preparation. Under these conditions, the solidified structure of incipient melting remains basically consistent with the original structure (as-cast structure).

2.3 Evolution of Incipient Melting During Heat Treatment and Its Effect on Mechanical Properties

The standard heat treatment for DZ444 alloy (with 0.01% B) is 1210 °C/2 h/AC + 1080 °C/4 h/AC + 850 °C/24 h/AC. In this study, DZ444 alloy with 0.09% B was subjected to similar heat treatments but with solution temperatures of 1210, 1230, and 1250 °C to investigate changes in incipient melting during heat treatment and their effects on mechanical properties.

Figure 7 [Figure 7: see original paper] shows microstructures of the high-boron DZ444 alloy after solution treatment at different temperatures, etched with Solution B. This etching method primarily reveals constituent phases within the IMR, so the incipient melting shown represents only the area occupied by constituent phases within the region. Low-magnification images (Figs. 7a, c, and e) show that as solution temperature increases, the distribution and morphological characteristics of constituent phases change little, but their size increases significantly. Since constituent phases are the most important component of incipient melting, their size increase implies increased incipient melting size—i.e., erosion and expansion of incipient melting boundaries into the surrounding matrix. High-magnification images (Figs. 7b, d, and f) reveal that constituent phases within the IMR are mainly borides, Ni Hf, and phases, essentially the same as those in Fig. 6. In Fig. 7b, an incipient melting circle surrounds the constituent phases, which may represent the true boundary of incipient melting, with the region between the boundary and constituent phases being the matrix [12].

Etching with Solution A clearly reveals the overall morphology of incipient melting (Fig. 8 [Figure 8: see original paper]). Figures 8a and b show that the IMR can be subdivided into three regions from inner to outer: constituent phases, matrix, and / eutectic, which likely represents the solidification sequence of incipient melting. The formation mechanism is: as the molten pool gradually cools, constituent phases first precipitate and grow from the supersaturated liquid; then the matrix forms extensively, releasing certain amounts of -forming elements into the surrounding liquid; combined with the already Ni-, Al-, and Ti-rich residual liquid (Fig. 2), eutectic formation conditions are easily satisfied, leading to final formation of / eutectic. Thus, the boundary of incipient melting is actually the interface between / eutectic and the alloy matrix. With increasing temperature, phases at the boundary continuously coarsen and connect, gradually forming a continuous chain that significantly coarsens the boundary. Meanwhile, the boundary morphology suggests multiple protrusions eroding into the alloy matrix, indicating that the IMR is expanding outward and increasing in size (Figs. 8a and b). At 1250 °C, incipient melting size increases dramatically and no longer consists of the three typical regions (constituent phases, matrix, and boundary). Instead, multiple "matrix islands" appear within the melted region. When incipient melting erodes and grows into the matrix, local matrix regions with higher melting points do not melt and become surrounded by molten liquid, finally forming so-called matrix islands. In fact, matrix islands also appear at 1230 °C, but they are few in number and small in size, making them difficult to observe.

Statistics show that when temperature increases from 1210 °C to 1230 °C, the IMR changes little, but when temperature reaches 1250 °C, both its size and area fraction increase significantly (Table 2). The reason may be that at the former two temperatures, incipient melting occurs mainly within the incipient melting circle, while at 1250 °C, the incipient melting circle (or boundary) moves outward, greatly expanding the IMR. Thus, incipient melting severely damages microstructural continuity at temperatures above 1250 °C.

Research results indicate that during high-temperature aging (1080 °C/4 h/AC), the size, morphology, and distribution of the IMR do not change significantly. However, honeycomb-like Ni Hf phases in constituent phases disappear and are replaced by Hf-rich granular MC(2) carbides (Fig. 9 [Figure 9: see original paper]). According to literature [29], Ni Hf phase likely undergoes a decomposition reaction: Ni Hf + (C) → MC(2) + , where Ni Hf reacts with C in the matrix to form MC(2) carbide and a surrounding layer. Compared with high-temperature aging, changes in incipient melting during low-temperature aging (850 °C/24 h/AC) are even less noticeable and can be neglected due to the lower treatment temperature. Therefore, after high- and low-temperature aging treatments, the quantity, size, and morphology of the IMR remain essentially consistent with those after solution treatment. In other words, incipient melting originates during solution treatment and is primarily affected by solution temperature and time parameters, with little relation to subsequent high- and low-temperature aging.

After complete heat treatment (HT1, HT2, and HT3), tensile properties at 900 °C and stress-rupture properties at 930 °C/275 MPa were tested, with results listed in Table 3 . The data show that as solution temperature increases, tensile properties (including strength and ductility) decrease slightly, while stress-rupture properties decrease significantly—especially after HT3 treatment, where stress-rupture life drops to only half that after HT2. The main reasons are twofold: First, as solution temperature increases, the size and area fraction of the IMR increase (Table 2), consuming large amounts of solid solution strengthening elements (W, Mo, etc.) and weakening solid solution strengthening, thereby degrading mechanical properties. Second, during mechanical property testing, numerous phase interfaces exist within the IMR, making it easy for cracks to initiate at interfaces between various phases and the matrix, thus degrading mechanical properties. Figure 10 [Figure 10: see original paper] shows that cracks mainly initiate within the IMR. Due to the low interfacial bonding strength between skeletal or rod-like borides and the matrix within the IMR, temperature and external stress can directly cause cracking at boride/matrix interfaces during high-temperature tensile and creep tests, and borides themselves may crack to form crack sources. Hf-rich MC carbides and phases within the IMR are brittle phases with almost no plastic deformation capacity, and cracks easily initiate at their interfaces with the matrix. Moreover, cracks propagate rapidly along the IMR, accelerating fracture and degrading mechanical properties. Comparing Tables 2 and 3 reveals that incipient melting is the most important factor affecting mechanical properties: as the quantity and size of the IMR increase, creep-rupture life decreases almost linearly.

3. Conclusions

1. In the as-cast microstructure of high-boron DZ444 alloy, interdendritic regions contain numerous / eutectics, MC carbides, and "constituent phases" composed of phase, borides, Ni Hf, and phase. During solution treatment, incipient melting first occurs in the matrix surrounding the multi-phase constituent, significantly influenced by borides. Borides are not nucleation sites for incipient melting but play a critical role in its formation.

2. Higher boron content lowers the incipient melting temperature to approximately 1160–1170 °C. Increasing temperature or extending holding time exacerbates incipient melting. With water quenching, incipient melting solidifies as typical dendrites and numerous fine precipitate particles, whereas with air cooling, it solidifies successively as constituent phases, matrix, and / eutectic, with constituent phase morphology showing no obvious difference from the as-cast condition.

3. During complete heat treatment, raising the solution temperature from 1210 °C to 1230 °C slightly increases incipient melting, but at 1250 °C, incipient melting consumes large amounts of surrounding matrix, with dramatic increases in IMR size and area fraction, severely damaging mi-

crostructural continuity. Due to relatively low temperatures, high- and low-temperature aging have minimal effects on the incipient melting microstructure.

4. As IMR size and area fraction increase, the regions consume substantial solid solution strengthening elements, reducing solid solution strengthening effectiveness, while simultaneously promoting numerous microcracks within the IMR. This results in slight decreases in tensile properties and significant reductions in creep-rupture properties.

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Note: Figure translations are in progress. See original paper for figures.