

Effect of Boron Microalloying on Casting Porosity in HK40 Alloy Postprint

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Date: 2023-03-19T00:00:00+00:00

Abstract

The formation mechanisms of casting porosity in HK40 alloy castings were analyzed by means of SEM, OM, XRD, and other techniques, and the influence of trace B addition on the solidification microstructure and porosity formation of HK40 alloy was investigated. The results indicate that HK40 alloy castings primarily exhibit two types of casting porosity defects, designated as Type A and Type B. Type A porosity is mainly caused by insufficient feeding in the regions between bridged dendrites, which results from rapid dendritic growth and bridging; Type B porosity arises from the blockage of interdendritic feeding channels by dendritic M₇C₃-type carbides that grow in the interdendritic regions. B microalloying can reduce the strong columnar grain growth tendency in HK40 alloy castings, refine the dendrites, and thereby suppress the formation of Type A casting porosity defects. Simultaneously, B microalloying increases the volume fraction of interdendritic eutectic phases in HK40 alloy, causing the transformation of interdendritic dendritic M₇C₃-type carbides to lamellar M₂₃C₆-type carbide precipitation, which prevents carbides from blocking the feeding channels between adjacent dendrites and thus also reduces the formation tendency of Type B casting porosity defects.

Full Text

Effect of B Micro-Alloying on Casting Porosity in HK40 Alloys*

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Supported by: National High Technology Research and Development Program of China (No.2012AA03A511), Program of Introducing Talents of Discipline to Universities of China (No.B12012) and Fundamental Research Funds for the Central Universities (No.FRF-TP-14-062A2)

Manuscript received: 2015-03-03, in revised form 2015-06-05

Abstract

The formation mechanisms of casting porosity in HK40 alloy castings were analyzed using SEM, OM, and XRD, and the effects of trace B addition on the solidification microstructure and porosity formation were investigated. The results show that two types of casting porosity defects, designated as Type A and Type B, exist in HK40 alloy castings. Type A porosity is mainly caused by insufficient feeding in the regions between bridging dendrites due to rapid dendritic growth and bridging. Type B porosity results from the blockage of interdendritic feeding channels by dendritic M₇C₃ carbides growing in interdendritic regions. Boron micro-alloying can reduce the strong columnar grain growth tendency in HK40 alloy castings, refine dendrites, and suppress the formation of Type A casting porosity defects. Meanwhile, B micro-alloying increases the volume fraction of interdendritic eutectic phases and transforms the dendritic M₇C₃ carbides into lamellar M₂₃C₆ carbides, preventing carbides from blocking interdendritic feeding channels and thus reducing the formation tendency of Type B casting porosity defects.

KEY WORDS HK40 alloy, B micro-alloying, casting porosity, boride, carbide

1 Introduction

Fe-Cr-Ni based HK40 alloys exhibit excellent high-temperature performance and have become key materials for industrial high-temperature furnace equipment in the steel, chemical, and thermal power industries[1~3]. Due to the metallurgical characteristics of the material, HK40 alloy castings are still prone to casting defects such as shrinkage cavities and porosity despite continuous adjustment of process conditions during casting production. The occurrence of casting defects not only significantly reduces the production yield of such casting products but

also affects the mechanical properties of castings, seriously threatening the service safety of alloy castings and representing a long-standing unresolved problem for HK40 alloy castings.

Casting defects such as shrinkage cavities and porosity inside castings are mainly caused by volume contraction during solidification. It is generally believed that increasing cooling rate and reducing the solidification temperature range (i.e., the solid-liquid two-phase region) are beneficial for promoting the feeding process, thereby reducing the tendency of casting porosity[4,5]. Casting studies on different alloy systems have shown that trace B addition can change the thermophysical parameters and solidification behavior of alloys. Although it leads to an increased solidification temperature range, the tendency for porosity is significantly reduced, which has attracted widespread attention from scholars[6-9]. Zhu et al.[10] investigated the relationship between B and porosity in nickel-based casting alloys and found that during solidification of high-boron alloys, the solid is surrounded by a layer of low-melting-point liquid with extremely high B content, forming spider-web-like feeding channels that expand the temperature range for feeding and reduce the amount of residual liquid that cannot be fed. Coutsouradis et al.[11] studied high-boron low-carbon superalloys and indicated that these alloys reduce the tendency for porosity formation by eliminating the blockage of feeding channels by carbide skeletons. Although many B-containing alloys with good casting performance have been developed in recent years, the mechanism by which B micro-alloying reduces casting porosity remains unclear due to differences in solidification behavior among different alloy types. Therefore, to improve the casting porosity of HK40 alloys, it is necessary to study the effect of B micro-alloying on casting porosity in HK40 alloys and enhance the performance and yield of industrial HK40 alloy castings.

In this work, Fe-Cr-Ni based HK40 alloy was taken as the research object. The formation mechanisms of casting porosity in industrially produced HK40 alloy castings were studied, and the effects of trace B addition on the solidification microstructure and porosity formation of HK40 alloy were investigated. The research results provide theoretical guidance for controlling casting defects in HK40 alloys.

2 Experimental Methods

The HK40 alloy castings used for casting defect analysis in this study were static sand mold castings. Samples for as-cast microstructure analysis and isothermal quenching experiments were obtained by remelting the above castings with Fe-B alloy (containing 22 wt% B) in a WZG-2 vacuum induction furnace under the same conditions, followed by metal mold casting. The dimensions of the remelted HK40 series alloy ingots were all 45 mm in diameter \times 100 mm in length. The chemical compositions of the ingots are shown in Table 1. Samples used for ingot microstructure analysis and isothermal quenching experiments

were all sectioned at approximately 25 mm from the bottom of the ingot and at the halfway point between the central axis and the outer surface of the ingot. Although there is some deviation between the measured B content and the nominal composition in the B-microalloyed HK40 series alloy ingots, this paper still designates them as HK40-0.1B and HK40-0.4B alloys.

To determine the initial melting temperature of the alloys and the precipitation temperature range of the precipitated phases, isothermal quenching experiments were conducted on the as-cast HK40 series alloys. Using a high-temperature resistance furnace, alloy samples were heated to 1210, 1250, and 1290 °C respectively, held for 15 min, then the furnace door was quickly opened and the samples were rapidly pushed into water for quenching. The quenched microstructures were observed.

Microstructural samples were prepared using standard metallographic sample preparation methods, and the samples were chemically etched using aqua regia solution with a volume ratio of $\text{HNO}_3:\text{HCl}:\text{H}_2\text{O} = 1:3:3$. The microstructures of the alloys were observed using a 4XC optical microscope (OM) and a SUPRA55 field emission scanning electron microscope (SEM) in secondary electron (SE) and backscattered electron (BSE) imaging modes. The composition of secondary phases was analyzed using the energy-dispersive spectrometer (EDS) attached to the SEM. It should be noted that the samples used for BSE microstructural observation and EDS composition analysis were not chemically etched.

A mixed solution of 90% CH_3OH + 10% HCl (volume fraction) + 1% tartaric acid (mass fraction) was used as the extraction solution to extract secondary phases from the alloys. Using a regulated DC power supply with a stainless steel plate as the cathode and the sample to be extracted as the anode, extraction was performed at a voltage of 3.0 V. The extracted powder was retained on filter paper through a filtration device. After drying, the three-dimensional morphology of the extracted phases was observed using SEM in SE mode, and phase identification was performed using a Rigaku 2500 X-ray diffractometer (XRD).

3 Results and Discussion

3.1 Casting Porosity Microstructure of HK40 Alloy Castings

Figure 1 [Figure 1: see original paper] OM image of typical casting porosity microstructure in HK40 alloy castings. It can be seen that porosity holes of varying degrees exist both at the outer wall and inside the castings. Measurements show that the porosity at the outer wall only exists within 200 mm from the surface. This type of porosity can be removed by subsequent shot peening and leveling processes without significantly affecting casting quality; therefore, no further investigation was conducted on this type in the present work. The porosity holes inside the castings mainly form in regions with relatively coarse

equiaxed dendrites, as indicated by the arrows in Figure 1. These coarse dendrites bridge at the porosity holes, forming a “dendrite bridging” phenomenon, with holes primarily forming in the regions between bridging dendrites. The coarser the bridging dendrites, the larger the size of the porosity holes formed.

Figure 2 [Figure 2: see original paper] SEM images of casting porosity microstructure inside HK40 alloy castings. As indicated by the arrows in Figure 2a, two different morphologies of porosity holes, designated as Type A and Type B, exist at the mid-thickness position of the casting wall. Type A holes are distributed interdendritically. As shown in Figure 2b, they have rough hole walls formed by exposed dendrites, exhibit concave contours, and their shapes are consistent with the boundary morphologies of the dendrites, showing typical microporosity characteristics. EDS analysis revealed that a certain amount of cellular or dendritic carbides are also distributed at the edges of the hole walls of Type A porosity. The size of Type A porosity holes ranges from 10 to 100 μm . Type B porosity holes are distributed in the interdendritic eutectic structure, as shown in Figure 2c, with irregular shapes and sizes ranging from 3 to 10 μm .

3.2 As-Cast Microstructure of HK40 Alloy Ingots with Different B Contents

Figure 3 [Figure 3: see original paper] Longitudinal OM images of cast ingots in HK40 (a), HK40-0.1B (b) and HK40-0.4B (c) alloys. All three alloy ingots have fine equiaxed grain structures at the surface layer, a columnar grain structure perpendicular to the ingot surface in the subsurface layer with similar grain sizes in the columnar grain region, and coarse equiaxed grain structures in the center. Figure 3a shows that the B-free alloy ingot exhibits a very strong columnar grain growth tendency, with a large region of transversely grown columnar grains that form a butt-joint phenomenon near the axis. The central equiaxed grain region is located in the middle-lower part of the ingot and has a relatively small volume. The length of the central shrinkage porosity band in the ingot is approximately 49 mm, the central shrinkage porosity ratio (the ratio of the central shrinkage porosity band length to the total ingot length) is about 63%, and the shrinkage porosity band is 29 mm from the bottom of the ingot. After adding 0.1% B, the equiaxed grain region of the ingot becomes wider, the length of the central shrinkage porosity band is reduced to 44 mm, the central shrinkage porosity ratio decreases to 58%, and the shrinkage porosity band is 31 mm from the bottom of the ingot, as shown in Figure 3b. When the B addition amount is 0.4%, the equiaxed grain region of the ingot further widens, the length of the central shrinkage porosity band is only 25 mm, the central shrinkage porosity ratio is merely 32%, and the shrinkage porosity band is 52 mm from the bottom of the ingot, as shown in Figure 3c. It is evident that the addition of trace B increases the proportion of the equiaxed grain region in HK40 alloy ingots, which can enhance feeding efficiency, narrow and shift upward the central shrinkage porosity band in the ingot, thus significantly improving the central shrinkage porosity and increasing the usable yield of the

ingot.

Figure 4 [Figure 4: see original paper] OM images of HK40 (a), HK40-0.1B (b) and HK40-0.4B (c) alloys. All three as-cast alloys grow in a dendritic morphology, with eutectic structures distributed in the interdendritic regions and grain boundaries. With increasing B content, the average dendrite spacing significantly decreases, dendrites become gradually refined, and the eutectic content gradually increases. Statistical results show that the average dendrite spacings of HK40, HK40-0.1B, and HK40-0.4B alloys are 63, 42, and 32 μm , respectively, and the volume fractions of eutectic are approximately 4.3%, 9.2%, and 16.1%, respectively.

Figure 5 [Figure 5: see original paper] XRD spectra of the extract phases in as-cast HK40 and HK40-0.4B alloys. In the extracted phases of B-free HK40 alloy as-cast structure, aside from a small amount of γ matrix, the secondary phases are mainly M7C3 carbides, whereas the carbides in HK40-0.4B as-cast alloy are M23C6 carbides, which also contain a certain amount of M2B borides.

Figure 6 [Figure 6: see original paper] SEM-BSE images in interdendritic regions in the cast HK40 (a), HK40-0.1B (b) and HK40-0.4B (c) alloys. By comparing Figures 6a and b, it can be seen that the addition of 0.1% B coarsens the skeleton-like carbide eutectic in the interdendritic regions, while a very small amount of needle-like black contrast phases are distributed around the carbides. When the B addition amount is 0.4%, the gray-contrast carbides in HK40 alloy are distributed in a network pattern, and the number of needle-like black contrast phases significantly increases, as shown in Figure 6c.

Figure 7 [Figure 7: see original paper] SEM images of the precipitated phases in interdendritic regions of the HK40 (a) and HK40-0.4B (b) alloys after phase extraction. Combined with the XRD results in Figure 5, it is indicated that the interdendritic regions of B-free HK40 as-cast alloy consist of M7C3 carbides growing in dendritic or cellular morphologies, whereas the interdendritic carbides in HK40-0.4B as-cast alloy transform into lamellar M23C6 carbides, with rod-like M2B borides also present.

3.3 Microstructure of HK40 Alloys with Different B Contents After Isothermal Melting and Quenching

Figure 8 [Figure 8: see original paper] OM images of quenched microstructures in HK40 (a, c, e) and HK40-0.4B (b, d, f) alloys after heated for 15 min at 1210 $^{\circ}\text{C}$ (a, b), 1250 $^{\circ}\text{C}$ (c, d) and 1290 $^{\circ}\text{C}$ (e, f). Figure 8a shows that after holding at 1210 $^{\circ}\text{C}$ for 15 min, the skeleton-like carbides in HK40 alloy disappear, and a large number of fine granular carbides precipitate around the residual skeleton-like carbides, which may be due to the transformation of M7C3 carbides to M23C6 carbides during holding at high temperature[12,13]. Under these temperature conditions, HK40-0.4B alloy experiences not only partial redissolution of carbides but also a very small amount of initial melting, as shown in Figure 8b. Based on the XRD results in Figure 5 and the morphologies of the

precipitated phases in Figure 7, it can be inferred that the substance undergoing initial melting at this temperature should be rod-like M₂B borides. It is evident that the initial melting temperature of M₂B borides is lower than that of M₂₃C₆ carbides. Figures 8c and d show the quenched microstructures of HK40 and HK40-0.4B as-cast alloys after holding at 1250 °C for 15 min. It can be seen that the carbides in HK40 as-cast alloy largely redissolve, a large number of fine granular M₂₃C₆ carbides precipitate around the undissolved skeleton-like M₇C₃ carbides, and a small amount of initial melting occurs. In HK40-0.4B alloy, a large amount of liquid appears, with various liquid pools between secondary dendrites being isolated from each other, while liquid pools between primary dendrites or on grain boundaries remain interconnected through capillary channels. This liquid is mainly caused by the complete melting of low-melting-point M₂B borides, which dissolves M₂₃C₆ carbides into the initially melted liquid pools. Additionally, since M₂B borides are preferentially distributed on grain boundaries, the melt pools formed on grain boundaries are more continuous. Figures 8e and f show the microstructures of the two alloys after quenching following holding at 1290 °C for 15 min. It can be seen that after holding at 1290 °C for 15 min, both HK40 and HK40-0.4B as-cast alloys have a certain amount of liquid phase in the interdendritic regions or grain boundaries. The liquid phase content in HK40 alloy is small and the capillaries are not interconnected, whereas the liquid phase content in HK40-0.4B alloy is large and the capillaries are in an interconnected state.

4 Discussion

4.1 Types and Causes of Casting Defects in HK40 Alloys

During solidification, when the liquid in a certain region of the casting becomes completely isolated from the remaining liquid, shrinkage cavities and porosity form in this region because it has no source of feeding during solidification. Based on the degree and temperature range of feeding insufficiency, porosity defects are mainly classified into two forms, Type A and Type B, as shown in Figure 2. According to solidification principles, Type A porosity forms when the residual liquid phase per unit volume is relatively abundant. Due to the disconnection of capillaries, isolated micro liquid pools cannot be fed. Type A porosity causes feeding insufficiency in relatively large regions, forming in the entire region between bridging dendrites with completely no liquid feeding. Type B porosity forms when the residual liquid phase per unit volume is relatively small. During the formation of low-melting-point phases in interdendritic regions, it cannot be fed due to solidification shrinkage. Type B porosity causes feeding insufficiency in smaller regions, forming only in partial regions between adjacent dendrites due to insufficient liquid feeding. The formation temperature of Type B porosity is lower than that of Type A porosity.

Under the same casting conditions, the columnar grain growth tendency of cast-

ings has a close relationship with the formation tendency of casting shrinkage porosity. Gao et al.[14] found that under the same cooling conditions, alloys with stronger columnar grain growth tendencies have smaller feeding expansion angles and are more prone to porosity formation. Under the temperature gradient in the wall thickness direction during casting, if the undercooling required for dendrite growth is small, dendrites grow rapidly in the preferred growth direction, leading to a strong columnar grain growth tendency along the wall thickness direction of the casting. Figure 3a shows that HK40 alloy has an extremely strong columnar grain growth tendency, indicating that dendrites in HK40 alloy have very fast growth rates in the preferred orientation. When the wall thickness of HK40 castings is large or the casting cooling rate is low, the coarse and disordered dendrites located in the central equiaxed grain region of the casting can still grow rapidly in certain orientations, triggering rapid connection of dendrite trunks and the “dendrite bridging” phenomenon, resulting in feeding insufficiency in the regions between connected dendrites and thus producing Type A casting porosity, as shown in Figures 1 and 2a. The combined observations from Figures 4a, 7a, and 8a indicate that HK40 alloy has a low volume fraction of interdendritic eutectic, narrow interdendritic regions, and the eutectic carbides M7C3 in these regions grow in coarse dendritic and cellular morphologies. Therefore, during the late stage of solidification, carbides in the interdendritic regions block the interdendritic feeding channels, causing feeding insufficiency between adjacent dendrites, which is the main cause of Type B casting porosity.

4.2 Effect of B Micro-Alloying on Casting Defects in HK40 Alloys

As a method for casting alloy composition design and optimization, B micro-alloying plays different roles in different alloy systems[15~17]. However, there have been no reports on the effects of B micro-alloying on the casting microstructure and defects of Fe-Cr-Ni based alloys. As shown in Figure 3, under the same casting conditions, the addition of trace B significantly reduces the shrinkage cavity volume in HK40 alloy ingots and shifts the shrinkage porosity band upward, thus enhancing the feeding capacity of HK40 alloy and reducing the tendency for casting shrinkage porosity defects.

This study found that the addition of trace B reduces the columnar grain growth tendency of ingots (Figure 3) while significantly refining dendrites. In particular, the addition of 0.4% B reduces the average dendrite spacing by about half (Figure 4), thereby effectively reducing the occurrence of the “dendrite bridging” phenomenon and decreasing the formation tendency of Type A porosity. Numerous studies[18~21] have shown that B addition can effectively refine the microstructure of casting alloys. There are three main mechanisms for B refinement of microstructure[22~24]: B generates constitutional undercooling at the solidification front, provides nucleation cores for the solidifying phase, and borides pin and inhibit the growth of the solid phase. Constitutional undercooling is mainly generated because solute atoms are rejected into the melt

during alloy solidification, establishing an enriched layer of solute atoms at the solidification front. When constitutional undercooling increases to a certain value, the increased enrichment of solute at the solidification front leads to the precipitation of fine M₂B borides, which become nucleation cores for the solidifying phase under melt undercooling conditions, increasing the nucleation rate. When the B content is small, the additional undercooling generated by B at the alloy solidification front is very small, producing only a minimal amount of borides in the final solidified interdendritic regions (Figure 6b). When the B content increases to 0.4%, a large number of needle-like borides are distributed in the interdendritic regions of the primary phase (Figure 6c). These borides can produce grain boundary pinning, effectively inhibiting dendrite growth and reducing the average dendrite spacing. Therefore, B addition reduces the formation tendency of Type A porosity by refining the dendrites in HK40 alloy (Figure 4).

The kinetic undercooling for crystal nucleation and growth during alloy casting depends on the cooling rate of the casting process and constitutional undercooling. During metal mold casting, the region around the ingot has a high temperature gradient, and the undercooling at the solidification front is mainly determined by solid-liquid undercooling caused by the high cooling rate. Therefore, despite the addition of different B contents, a certain amount of columnar grain region still exists around HK40 ingots (Figure 3). Inside the ingot, due to the low cooling rate, the effect of solid-liquid undercooling decreases, and constitutional undercooling caused by B addition gradually becomes dominant. The larger the B addition amount, the more significant the constitutional undercooling effect, and the smaller the columnar grain region. Constitutional undercooling causes borides formed at the solidification front to inhibit rapid dendrite growth in the preferred direction, thereby transforming the columnar grain region in B-free ingots into an equiaxed grain region and increasing the proportion of the equiaxed grain region in the ingot (Figure 3).

On the other hand, B addition can change the solidification characteristics of interdendritic liquid during solidification, thereby directly affecting the formation tendency of Type B porosity. First, B micro-alloying significantly increases the volume fraction of interdendritic eutectic phases (Figure 4), which widens the feeding channels between adjacent dendrites during the early stages of eutectic carbide nucleation and growth. Second, B micro-alloying can change the precipitation type of interdendritic carbides. The combined observations from Figures 5, 6, and 7 indicate that the addition of 0.4% B suppresses the precipitation of dendritic M₇C₃ carbides at high temperatures, causing lamellar M₂₃C₆ carbides to precipitate at slightly lower temperatures. Therefore, B addition can prevent coarse dendritic or cellular M₇C₃ carbides precipitated in the solid-liquid region from blocking the feeding channels between adjacent dendrites. Meanwhile, the addition of 0.4% B lowers the solidus temperature and carbide dissolution temperature of HK40 alloy, which enables the capillaries and micro liquid pools between adjacent dendrites in B-added alloys to remain connected at lower temperatures during solidification, expanding the temperature range

for feeding.

Two types of carbides, M₂3C₆ and M₇C₃, mainly exist in HK40 alloy, with M₂3C₆ being more stable than M₇C₃[25,26]. After B addition, the carbides in HK40 alloy transform from M₇C₃ to M₂3C₆, which may be due to two reasons. First, as can be seen from Figure 7, fine needle-like borides often appear inside M₂3C₆ carbides. Therefore, during solidification of interdendritic liquid, borides may provide nucleation cores for M₂3C₆ carbides, causing M₂3C₆ carbides to grow along specific directions on the basis of borides, thus forming lamellar M₂3C₆ carbides. The crystallographic orientation relationship between carbides and borides and the related mechanisms need to be determined through further experimental research. Another possibility is that B addition causes alloying elements such as Cr to combine with it to form M₂B borides, reducing the concentration of carbide-forming elements in interdendritic regions and decreasing the nucleation driving force for carbides. This leads to the precipitation of M₂3C₆ carbides, which have a smaller nucleation driving force and are thermodynamically more stable, in the interdendritic regions.

These results demonstrate that B micro-alloying can not only refine dendrites, reduce the occurrence of “dendrite bridging,” and effectively decrease the formation tendency of Type A porosity, but also increase the volume fraction of low-melting-point phases in interdendritic regions, promote the transformation of coarse M₇C₃ carbides into lamellar M₂3C₆ carbides, enhance liquid feeding during the formation of interdendritic low-melting-point phases, and reduce the formation tendency of Type B porosity. Therefore, B micro-alloying can change the solidification characteristics of HK40 alloy and effectively reduce the tendency for casting porosity formation.

5 Conclusions

- (1) Two types of casting porosity defects, Type A and Type B, exist in HK40 alloy castings. Type A porosity forms in the coarse equiaxed grain region inside castings and is mainly caused by insufficient feeding in the regions between bridging dendrites due to rapid dendritic growth and bridging. The formation of Type B porosity is caused by M₇C₃ carbides growing in interdendritic regions that block interdendritic feeding channels.
- (2) B micro-alloying can reduce the strong columnar grain growth tendency in HK40 alloy castings and refine dendrites, thereby reducing the formation of Type A casting porosity defects in HK40 alloy.
- (3) B micro-alloying increases the volume fraction of interdendritic eutectic phases in HK40 alloy, transforms the dendritic M₇C₃ carbides into lamellar M₂3C₆ carbides, prevents carbides from blocking interdendritic feeding channels, and thus reduces the formation tendency of Type B casting porosity defects.

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