Elimination and Control of $\delta$ Ferrite in M50NiL Bearing Steel

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In this study, the effects of the annealing temperature and holding time on the $\delta$ ferrite content in M50NiL bearing steel are evaluated. The results indicate that when the temperature increases from 900 °C to 1200 °C, the $\delta$ ferrite content increases as a result of the increase in the Cr equivalent in the matrix, which decreases the stability of austenite and promotes the transformation of $\gamma \rightarrow \delta$. At 1300 °C, the $\delta$ ferrite content sharply increases because the austenite transforms into $\delta$ ferrite in large quantities when heated to the $\gamma + \delta$ phase region. When the steel is annealed at 1200 °C, the content of $\delta$ ferrite first decreases and then increases with increasing holding time (0.5–50 h). Meanwhile, the $\delta$ ferrite content reaches the lowest value of 3.5% after 30 h of annealing. The decrease in the $\delta$ ferrite content is attributed to the increase in the Ni equivalent in $\delta$ ferrite, which promotes the transformation from $\delta$ ferrite to austenite. The increase in the $\delta$ ferrite content is attributed to the diffusion of Mo and V ferrite-forming elements into grains, resulting in the nucleation of a large amount of $\delta$ ferrite.

1. Introduction

M50NiL bearing steel is widely used in the aerospace field because of its strength and plasticity matching, high-temperature resistance, and good fatigue performance [1, 2]. The few available studies on M50NiL steel have mainly focused on carburizing, nitriding, and thermal deformation processes [3–10]. In recent years, with the advances in iron and steel metallurgy and progress of social science and technology, numerous alloying elements have been introduced into iron and steel materials to develop new steel grades [11–14]. Owing to the segregation of alloying elements, a large amount of high-temperature ferrite ($\delta$ ferrite) is formed in the ingots [15]. The microstructure and properties of $\delta$ ferrite and the steel matrix differ as follows. In terms of microstructure, $\delta$ ferrite is usually distributed at the grain boundaries. Because of the segregation of ferrite elements such as Cr and Mo, brittle carbides are easily formed on the boundary between the $\delta$ ferrite and matrix [16]. In terms of properties, the strength, hardness, and shear deformation resistance of $\delta$ ferrite are lower than those of the martensitic matrix [17]. The considerable differences in microstructure and properties between $\delta$ ferrite and the steel matrix result in a significant deterioration of the mechanical properties of the steel [18]. Moreover, $\delta$ ferrite is difficult to eliminate, posing several challenges in the research and development of iron and steel materials.

Researchers have extensively studied the generation mechanism, influencing factors, and elimination measures of $\delta$ ferrite. In terms of the mechanism, it is generally agreed that the $\delta$ ferrite in the ingot mainly forms due to the relatively high chromium equivalent and nickel equivalent ratio ($Cr_{eq}/Ni_{eq}$) and nonequilibrium segregation in the material. Here, rapid cooling of the ingot generates $\delta$ ferrite residue [19–21]. Li et al. [22] studied the effect of the annealing process on the dissolution behavior of $\delta$ ferrite in 301 L stainless steel billets and indicated that the diffusion of Cr and Ni mainly controls the decrease in the $\delta$ ferrite content. By annealing at 1300 °C for 60 min, the $\delta$ ferrite content could be reduced to 0.69%. Li et al. [23] studied the
effect of the cooling rate on the δ ferrite content in 316H stainless steel through high-temperature laser confocal microscopy. Their results indicated that lowering the cooling rate led to a reduction in the δ ferrite content. In general, the content of δ ferrite is mainly affected by the segregation of ferrite-forming elements such as Mo and V. The greater the degree of segregation of ferrite-forming elements in the matrix, the higher the content of δ ferrite and vice versa.

Furthermore, the diffusion and distribution of ferrite-forming elements in the matrix are affected by heat treatment. By adjusting the heat treatment parameters, such as the annealing temperature, holding time, and cooling rate, the content of ferrite-forming elements in the austenite matrix can be reduced and the transformation of austenite to δ ferrite can be inhibited. Thus, the content of δ ferrite can be controlled. In addition, the content of austenite-forming elements in δ ferrite should be considered because a high content of these elements in δ ferrite promotes the transformation of δ ferrite to austenite, thereby reducing the δ ferrite content.

Based on these strategies for regulating the δ ferrite content, this study aimed to explore the effects of the annealing temperature and holding time on the δ ferrite content in M50NiL bearing steel through experiments and Thermo-Calc thermodynamic simulations. The findings are expected to provide a basis for optimizing the annealing process before the forging of cast billets.

2. Experimental Materials and Procedures

2.1. Materials. M50NiL steel cast by a vacuum consumable arc remelting process was used in the experiments. The M50NiL steel composition was determined using inductively coupled plasma atomic emission spectrometer (ICP-AES, IRIS Intrepid II XSP) and a carbon sulfur analyzer (ELTRA CS-800). The results presented in Table 1 are consistent with the nominal designed values.

2.2. Design of Annealing Process. The temperature range of the γ– and γ + δ phase regions was simulated using Thermo-Calc thermodynamic software (Database: TCFE10: Steels/Fe-Alloys v10.1) (Figure 1). When the temperature was lower than 878°C, the body-centered cubic (BCC) phase was ferrite. With decreasing temperature, the ferrite content gradually increased and the austenite (FCC_A1) content gradually decreased. The temperature range of 878–1227°C was the γ-phase region, and annealing in this temperature range was conducive to the elimination of δ ferrite. When the temperature increased above 1227°C, the austenite gradually changed to δ ferrite, resulting in a gradual increase in the δ ferrite content; the peak value was reached at 1414°C.

Based on the above analysis, the influence of the annealing temperature was explored at 900, 1000, 1100, and 1200°C for 0.5 h and compared to that at 1300°C for 0.5 h. Furthermore, the effect of the holding time (0.5, 5, 10, 30, and 50 h) was investigated at 1200°C. Cube-shaped samples with side lengths of 20 mm were used for annealing. The annealing process was as follows. First, the samples were heated at room temperature in a resistance furnace at a rate of 20°C min⁻¹ and then insulated at a specific temperature. After the insulation was complete, the samples were naturally cooled in the furnace.

2.3. Microstructural Characterization. After polishing, the sample was etched with a 4 vol. % nitric acid solution, and the microstructure of the sample was observed using a metallurgical microscope (Axio Observer 3 materials). The carbides, δ ferrite, and martensite matrix were observed using scanning electron microscopy (SEM, Phenom Particle X) and analyzed using electron probe microanalysis (EPMA, JXA-iHP200F). The hardness of δ ferrite was measured using a microhardness tester (Qness Q30+) according to GB/T 4340.1-2009, with a load of 25 g and a retention time of 15 s. The test was performed five times at different locations, and the average value was calculated. The δ ferrite content (expressed as an area fraction) was obtained by calculating the area percentage of δ ferrite in five metallographic photographs (100×). The Ni equivalent in δ ferrite and the Cr equivalent in the matrix were estimated using equations (1) and (2), respectively [24]. As the C content is difficult to accurately detect, the Ni equivalent consisted of the measured Ni and Mn contents. In addition, the Gibbs free energies of carbide formation were calculated using FactSage 8.0 software (selected databases: FacatPS, FStel, FTSalt, and FTimsic).

\[ \text{Ni}_{\text{eq}} = (30 \text{C} + \text{Ni}) + 0.5\text{Mn}, \]  
\[ \text{Cr}_{\text{eq}} = (\text{Cr} + 1.5\text{Mo}) + (2\text{Si} + 5\text{V}). \]  

3. Results and Discussion

3.1. Microstructural Analysis of the M50NiL Ingot. The microstructural characteristics of the M50NiL ingot are shown in Figure 2. As observed from the metallographic diagram in Figure 2(a), large amounts of δ ferrite are distributed along the grain boundaries. The statistical results indicate that the area fraction of δ ferrite in the ingot is 8.75%. The microhardness tests show an average hardness of 356 HV for δ ferrite and a relatively high hardness of 465 HV for the matrix. In the SEM image of Figure 2(b), the matrix is lath martensite with a small amount of inclusion and strip carbides in δ ferrite. The backscattered electron image at higher multiples is shown in Figure 3, where white- and black-strip carbides are found in δ ferrite. Thus, the as-cast microstructure of M50NiL steel was as follows: the matrix was lath martensite, δ ferrite was distributed along the grain boundaries, and there were black- and white-strip carbides in δ ferrite.

To analyze the distribution of ferrite- and austenite-forming elements, EPMA surface scanning was conducted and the results are presented in Figure 3. The strip carbides mainly contain ferrite-forming elements such as Mo and V. Moreover, the white-strip carbides contain more Mo, whereas the black carbides contain more V. Considering the composition of the δ ferrite and matrix phases, the Ni and V contents in δ ferrite are lower than those in the martensite.
matrix, while the C, Cr, and Mo contents are similar in the two phases. For the abnormally low V content in δ ferrite, a large amount of VC in δ ferrite should be considered.

3.2. Effect of Annealing Temperature on the δ Ferrite Content. Figure S1 shows metallographic images of the samples after annealing at different temperatures. The δ ferrite is mainly distributed in long strips, and a small amount exists in the form of particles. Statistical analysis showed that after annealing at 900°C, 1000°C, 1100°C, and 1200°C for 0.5 h, the δ ferrite contents were 4.2%, 7.5%, 8.1%, and 8.3%, respectively (Figure 4). Thus, all δ ferrite contents were less than 8.75%, indicating that annealing in the austenite temperature range can indeed promote the transformation of δ ferrite to austenite. Moreover, as evident in Figure 4, the δ ferrite content slightly increases with increasing annealing temperature. For comparison, a δ ferrite content of 21.3% was determined after annealing at 1300°C for 0.5 h, which is significantly higher than that obtained at the previous annealing temperature. In this case, heating to the γ + δ phase region (Figure 1) led to the transformation of a large amount of austenite into δ ferrite.

The changes of Ni equivalent in δ ferrite and Cr equivalent in matrix under different annealing temperatures were tested, and the results are shown in Figure 5. As observed in Figure 5(a), after the sample was annealed at 900°C,
the Ni equivalent in the δ ferrite was similar to that in the as-cast samples, whereas it was higher after annealing at 1000–1200°C (Figure 5(a)). The increase of Ni content reduced the stability of δ ferrite and promoted the transformation of δ → γ. Therefore, the δ ferrite content decreased after annealing at 1000–1200°C compared with the as-cast condition. The reason for obtaining the lowest δ ferrite content after annealing at 900°C (Figure 4) should be evaluated. A study [25] has shown that at the initial stage, the δ → γ transformation is controlled by the phase transition driving force, which is higher at low temperatures and lower at high temperatures. The gradual phase transition is determined by the diffusion of alloying elements. In this experiment, the heating rate was fast (up to 20°C min⁻¹), and the effect of the heating process was not considered. Therefore, at 900°C for 0.5 h, the phase transition driving force was high, and more δ ferrite was converted into γ, whereas at 1000–1200°C, the phase transition driving force was weak, and the content of transformed δ ferrite was lower.
As observed from Figure 5(a), when annealed at 1000–1200°C for 0.5 h, the Ni equivalents of the samples are similar, indicating no significant difference in the $\delta \rightarrow \gamma$ transformation driven by Ni and Mn diffusion. At this time, the $\delta$ ferrite content in the sample is less affected by the Ni equivalent and is likely primarily affected by the Cr equivalent in the matrix. With increasing annealing temperature, the Cr equivalent in the matrix shows a tendency of increasing first and then decreasing, and reaches its peak at 1100°C (Figure 5(b)). When the annealing temperature is 900°C, the Cr equivalent in the matrix is similar to that in the as-cast state. At this time, the Mo content in the steel matrix is significantly lower (Table S1). When the temperature is increased from 900°C to 1100°C, the Cr equivalent in the matrix shows an upward tendency, mainly because the molybdenum carbide located on the boundary of $\delta$ ferrite gradually dissolves (white phase in Figure S2) and diffuses into the austenite matrix. Table S1 also shows that the content of Mo in the matrix increases with increasing temperature in the range of 900–1100°C. The increase in the Cr equivalent in the matrix promotes the transformation of $\gamma \rightarrow \delta$; thus, the $\delta$ ferrite content increases with increasing annealing temperature. At 1200°C, the Cr equivalent in the matrix was still high, as well as, the $\delta$ ferrite content.

To summarize, at 900°C, the decrease in $\delta$ ferrite is mainly due to the phase transformation driving force, while at higher temperatures of 1000–1200°C, the Cr equivalent in the matrix increases because molybdenum carbides dissolve, thereby promoting the transformation of $\gamma \rightarrow \delta$. Thus, the $\delta$ ferrite content slightly increases (Figure 4). When the annealing temperature is 900°C, the $\delta$ ferrite content can be effectively reduced, but large amounts of undissolved and unevenly distributed Mo and V carbides remain in the matrix (Figure 6), as indicated by the energy-dispersive X-ray spectroscopy (EDS) point analysis. These unevenly distributed carbides have adverse effects on the mechanical properties of steel. Thus, controlling the $\delta$ ferrite content to an acceptably low level and ensuring high-temperature diffusion annealing can result in a uniform distribution of alloying elements in the matrix. In addition, increasing the annealing temperature can shorten the required holding time, which is beneficial to industrial production. Comprehensively considering these variables, the recommended annealing temperature is 1200°C.

3.3. Effect of Holding Time on the $\delta$ Ferrite Content. A metallographic map of specimens annealed at 1200°C for different holding times is shown in Figure 7. With increases in the holding time, the morphology of $\delta$ ferrite gradually changes from long strips to nearly spherical shape with rounded edges. According to statistical analyses, after the ingot was annealed at 1200°C for 0.5 h, 5 h, 10 h, 30 h, and 50 h, the $\delta$ ferrite contents were 8.3%, 4.4%, 4.0%, 3.5%, and 9.7%, respectively. A trend of first decreasing and then increasing was observed, and the lowest value was reached at 30 h, as shown in Figure 8.

Figure 9 shows the change of Ni equivalent in $\delta$ ferrite and Cr equivalent in the matrix of M50NiL steel after annealing at 1200°C for different holding times. In Figure 9(a), the Ni equivalent in $\delta$ ferrite increases with longer holding times. It can be seen from Table S2 that the content of Ni in $\delta$ ferrite gradually increases with prolonged holding and the content of Mn changes insignificantly. The increase in the Ni equivalent is due to the existence of different Ni contents in the $\delta$ ferrite and matrix in the ingot, which leads to the gradual diffusion of Ni from austenite to $\delta$ ferrite during annealing. In Figure 9(b), the Cr equivalent in the matrix does not considerably change with increasing holding time (detailed elemental changes are shown in Table S2), which may be because of the small difference in the contents of Mo and V carbides distributed along the
Figure 6: SEM image of M50NiL steel annealed at 900°C for 0.5 h: (a) SEM and (b) EDS.

Figure 7: Optical micrographs of M50NiL steel annealed at 1200°C for different holding times: (a) 0.5 h, (b) 5 h, (c) 10 h, (d) 30 h, and (e) 50 h.
boundary of δ ferrite (Figure S3). Therefore, in the range of 0.5–30 h, with the extension of the holding time, the transformation of $\delta \rightarrow \gamma$ is promoted and the content of $\delta$ ferrite gradually decreases because of the higher Ni equivalent in $\delta$ ferrite. When the holding time is less than 30 h, $\delta$ ferrite is mainly distributed along the grain boundaries (Figures 7(a)–7(d)), whereas when the holding time is extended to 50 h, large amounts of $\delta$ ferrite are observed inside the grains (Figure 7(e)). This is because the ferrite-forming elements (Mo and V) diffuse into the grains, promoting the transformation of $\gamma \rightarrow \delta$ and generating $\delta$ ferrite inside the grains. However, Figure 9(b) shows that the Cr equivalent in the matrix does not significantly increase at 50 h, which may be a result of a sufficiently long holding time and sufficient diffusion of ferrite-forming elements at 1200°C. Based on the above analysis, the optimal holding time is 30 h.

The carbides precipitated in M50NiL steel are also noteworthy. The Gibbs free energies of molybdenum carbide and vanadium carbide formation were calculated using FactSage 8.0 software (Figure S4). Lower Gibbs free energy values correspond to enhanced carbide formation; therefore, the priority of carbide formation is $\text{VC} > \text{Mo}_2\text{C} > \text{MoC}$. Thus, it can be considered that the molybdenum carbide in steel exists in the form of Mo$_2$C. As shown in Figures S4(a) and S4(b), VC is easily formed at low temperatures, while Mo$_2$C is easily formed at high temperatures. A lower carbide precipitation temperature implies that the phase is more difficult to grow. Therefore, VC phases are relatively small and often precipitate in the form of nanoparticles in vanadium micro-alloyed steel for precipitation strengthening [26]. However, after annealing at 900–1200°C, black-strip VC with lengths of 1–5 μm is observed in $\delta$ ferrite (Figure S2).
Feng et al. [27] studied the effect of solute elements on the precipitation behavior of carbonitride in X80 pipeline steel and reported that increasing the content of C or V is conducive to increasing the precipitation temperature of VC. When the contents of C and V are 0.02% and 0.017%, respectively, the precipitation temperature of VC is 695°C. The elemental contents of C and V in M50NiL steel are 0.113% and 1.23%, respectively (Table 1); thus, the precipitation temperature of VC in M50NiL steel should be above 695°C. VC can precipitate at a relatively high temperature, and because of the slow cooling during furnace cooling, there is sufficient time for precipitate growth. In addition, the ferrite-forming element V is easily segregated in δ ferrite; therefore, VC can be precipitated at 900–1200 °C after annealing.

4. Conclusion and Prospects

(1) The optimal annealing process temperature and holding time are 1200°C and 30 h, respectively, resulting in a significant reduction of the δ ferrite content of M50NiL steel and the area percentage of δ ferrite from 8.75% in the initial as-cast state to 3.5%.

(2) When the annealing temperature was increased from 900°C to 1200°C, the content of δ ferrite increased owing to the increase of Cr equivalent in the matrix, which reduced the stability of the austenite matrix and promoted the transformation of γ → δ. When the annealing temperature was 1300°C, the δ ferrite content increased sharply, because this temperature is in the γ + δ phase region, resulting in the formation of a large amount of δ ferrite.

(3) At 1200°C, the decrease of δ ferrite content in the range of 0.5–30 h was a result of the increase of the Ni equivalent in δ ferrite, reducing its stability. When the holding time was 50 h, the increase of δ ferrite content was due to the diffusion of Mo and V ferrite-forming elements into the grains, resulting in a large amount of nucleation of δ ferrite.

Although the aim of this study on the annealing process was to eliminate and control the δ ferrite content in M50NiL steel, δ ferrite could not be completely eliminated. As part of our future work, we intend to study the effect of the cooling rate and smelting method on the δ ferrite content in the ingot and reduce element segregation as much as possible to reduce the δ ferrite content. In addition, the properties of δ ferrite itself and the effect of δ ferrite on the microstructure and properties of steel are not completely clear, requiring additional research.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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Supplementary Materials

Figure S1: metallographic photographs of M50NiL steel after annealing at different temperatures for 0.5 h: (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C, and (e) 1300°C. Figure S2: scanning electron microscopy images of M50NiL steel after annealing at different temperatures for 0.5 h: (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C, and (e) 1300°C. Figure S3: scanning electron microscopy images of M50NiL steel after annealing at 1200°C for different holding times: (a) 0.5 h, (b) 5 h, (c) 10 h, (d) 30 h, and (e) 50 h. Figure S4: Gibbs free energies of carbides formed at different temperatures: (a) VC, (b) Mo2C, and (c) MoC. Table S1: elemental composition (wt. %) in different phases of M50NiL steel after annealing at different temperatures for 0.5 h. Table S2: elemental composition (wt. %) in different phases of M50NiL steel after annealing at 1200°C for different holding times. (Supplementary Materials)

References


