Microstructure and mechanical properties of TLP-bonded 9CrMoCoB heat-resistant steel with Ni–Cr–B interlayer

Yingjun Jiao, Guangmin Sheng, Xue Li, Yuntao Zhang and Xinjian Yuan
College of Materials Science and Engineering, Chongqing University, No. 174, Shazheng Street, Shapingba District, Chongqing 400044, People’s Republic of China
E-mail: gmssheng@cqu.edu.cn
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Abstract
9CrMoCoB heat-resistant steel was transient liquid phase (TLP) bonded by using a Ni–Cr–B amorphous filler metal. Results indicated that the TLP-bonded joint was composed of three feature regions, and the precipitates in the diffusion affected zone (DAZ) were M$_{23}$(C,B)$_6$-type carboborides and M$_{23}$B$_2$-type borides with different morphologies and locations. Fine granular Fe$_2$Mo-type Laves phases and MX-type carbides that existed in the original base metal were found in the grain. The carboborides and borides in the DAZ that grew with the increase in bonding time and temperature were reduced or completely dissolved after post weld heat treatment (PWHT). The joints without PWHT showed high strength and low elongation due to the high hardness and high hardenability of the matrix. The initiation of cracks occurred on borides in the athermal solidification zone and carboborides in the Ni-DAZ and passed through in the bonded seam, resulting in the reduction in the tensile strength of the bonded joints. The hardness of the joints was obviously reduced, and their toughness was obviously improved after PWHT. The highest tensile strength reached to 744 MPa when the TLP joints were bonded at 1150 °C for 30 min, which was comparable with the original base metal.

1. Introduction

With the development of global economy, especially the rapid growth of industry in emerging economies, environmental pollution and energy crisis have attracted increasing attention [1]. In this context, ultrasupercritical fossil power plants have been widely studied and applied, and the utilization efficiency of coal has been greatly improved by improving steam parameters [2–4]. In modern steam power plants, 9%–12% Cr heat-resistant steels are widely applied to valves, vane carriers, inlet pipes, and other components due to their excellent high-temperature mechanical properties at 600 °C [5–11]. However, an increase in steam parameters necessitates the application of new heat-resistant steel because traditional heat-resistant steels are unsuitable for the more severe service conditions. Recently, a new 9CrMoCoB martensitic steel was developed for 620 °C ultrasupercritical fossil power plant [12, 13]. Its high creep strength benefits from the addition of cobalt and boron, which can restrain the formation of δ-ferrite and restrict the coarsening of chromium carbide, respectively.

In spite of the performance improvement of matrix, the premature failure of welded joints seriously reduces the service life of the components, which were mainly joined by gas tungsten arc welding [9–11, 14–16]. In some advanced 9%Cr heat-resistant steels, the fracture life of the weld is approximately 20% of that of the base metal [15]. The typical joint welded by these fusion welding methods consists of heat affected zone (HAZ), welded metal (WM), and base metal (BM) due to the welding heat input [9, 11, 14]. In most cases, type IV cracks are generated in the fine-grained HAZ after long-term service at elevated temperature due to the metallurgical changes caused by welding thermal cycle. Therefore, the creep performance of HAZ in these steel welded joints is lower than that of BM and WM, resulting in the fracture location of joints usually located in the HAZ [9–11].
The formation process of type IV cracks includes the initiation, propagation, and combination of creep cavities to form microcracks, and then the microcracks gradually expand to form macrocracks, leading to the intergranular fracture of weldments \cite{11, 16}. Many researchers have been plagued by this problem in the past decade, and have conducted many studies to clarify the main cause of type IV cracking, which has not been effectively solved.

Transient liquid phase (TLP) bonding has the advantages of diffusion welding and brazing technologies \cite{17, 18}, and has been successfully applied to join the same \cite{19–24} or dissimilar metals \cite{25, 26}. The melting temperature of filler metal is lower than that of the matrix due to the addition of elements, such as B, P, and Si. The filler melts quickly when the bonding temperature exceeds the melting point of the filler. Eutectic reaction at the interface leads to the melting of the matrix and the widening of the liquid filler. With the massive diffusion of B, P, and Si atoms in the liquid filler to the matrix, the melting point at the interface increases. Isothermal solidification starts when the liquidus reaches the holding temperature \cite{23–25}. When isothermal solidification is completed, a joint with comparable mechanical properties to the matrix is obtained \cite{21, 22}. Compared with the high temperature of traditional fusion welding methods, the holding temperature of TLP bonding is low and uniform, which can effectively avoid the generation of HAZ. On the basis of the above characteristics, TLP bonding is a potential technique to join martensitic heat-resistant steel components. However, this advanced method is rarely used.

TLP bonding of 9CrMoCoB martensitic heat-resistant steel with Ni–Cr–B filler was conducted in this study. The influences of bonding parameters on joint microstructure evolution and mechanical properties were

![Figure 1. Applied heat treatments for the TLP joints bonded (a) at 1150 °C for different times and (b) for 30 min at different temperatures.](image)

**Table 1. Compositions of the 9CrMoCoB heat-resistant steel and MBF-80 filler metal (wt%).**

| Alloy   | Fe  | Cr  | Mo  | Co  | Mn  | C   | Ni  | Nb  | N   | V   | B   |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Steel   | Bal.| 9.3 | 1.42| 1.00| 0.80| 0.11| 0.10| 0.06| 0.005| 0.20| 0.006|
| MBF-80  | —   | 15.2| —   | —   | —   | —   | Bal.| —   | —   | —   | 3.74|

\cite{14, 15}.
investigated. Post weld heat treatment (PWHT) was conducted to obtain a more uniform joint and improve the comprehensive mechanical properties of the sample.

2. Experimental procedure

The 9CrMoCoB heat-resistant steel with the standard heat treatment condition was used as the matrix in the present study. Commercial Ni-based amorphous MBF-80 was used as the filler metal, and its melting

Figure 2. Microstructure of the joint TLP bonded at 1150 °C/5 min.

Figure 3. High magnification details of each spot marked in figure 2: (a) precipitates in the B-DAZ, (b) precipitates in the Ni-DAZ, (c) blocky precipitates in the grain, (d) ASZ and ISZ.
temperature ranges from 1040 °C to 1065 °C. The chemical compositions of the parent material and filler are listed in table 1. Cylinders with a size of Φ 14 × 35 mm were cut from the parent material through electrodischarge machining as the matrix. The surfaces of samples were polished by using 1000-grade SiC paper and ultrasonically cleaned in alcohol for 20 min. The Ni–Cr–B filler was placed between the cleaned surfaces. The TLP bonding was conducted at 1150 °C for 5, 15, 30, and 60 min and at 1090, 1120, 1150, and 1180 °C for 30 min. The vacuum of WZC-40 vacuum furnace is approximately 1 × 10⁻³ Pa. PWHT was conducted at the following conditions of (1) 1100 °C/90 min and then cooled in air; (2) 750 °C/120 min and then cooled in air. All the thermal cycles applied to the TLP joints are depicted in figure 1.

The joints were perpendicularly sectioned to the bonding seam. The surfaces were chemically etched in a reagent of 1 g CuSO₄ + 20 ml HCl + 20 ml C₂H₄O + 20 ml H₂O after polishing. Microstructural examination and component analysis of the joints were studied through field emission scanning electron microscopy (SEM) with energy dispersive spectrometer (EDS). The precipitates in the diffusion affected zone (DAZ) were analyzed through transmission electron microscopy (TEM, FEI Tecnai G2 F20). The hardness across the joint was tested on a micro Vickers hardness tester (MH-5L) with a 100 g indentation load and 10 s holding time. Tensile tests were conducted on a universal test machine with a constant speed of 0.5 mm min⁻¹. The fracture surfaces and longitudinal section of the fractured samples were observed through SEM. The constitution of second phases on the fracture surfaces was studied by x-ray diffraction (XRD). Three TLP–bonded specimens at the same parameter were used to reduce the effect of measurement errors.

3. Results

3.1. Microstructure characteristics of 9CrMoCoB joint
The typical microstructure of the joint TLP bonded at 1150 °C/5 min is displayed in figure 2. The bond region consists of three parts: the DAZ, the isothermal solidification zone (ISZ), and the athermal solidification zone (ASZ).
Figure 3 displays the high magnification details of different areas of the joint marked in figure 2. The chemical composition of selected spots was measured through EDS to confirm the precipitated phases with different shapes and determine the interdiffusion regularity of elements in the TLP-bonded joint. The results are listed in table 2. Figure 4 shows the EDS elemental distribution maps of the joint. The DAZ is divided into two parts by comparing figures 3(a) and (b). For the convenience of discussion, we define the two regions as B-DAZ and Ni-DAZ, respectively. The matrix in the B-DAZ is lath martensite, where blocky and long strip precipitated phases were formed at the grain boundaries, and blocky precipitated phases were formed within the grains. A long strip area with a width of approximately 10 μm without lath martensite was formed in the Ni-DAZ near the S/L interface, and dense blocky and short rod precipitated phases were formed in this area. In accordance with the chemical compositions of spots A and C, the matrix composition in B-DAZ was similar to that of the parent metal, and the Ni content in the Ni-DAZ matrix increased significantly. This condition indicates that only the boron atoms diffuse in the B-DAZ, and the nickel atoms in the liquid phase diffuse only a short distance into the matrix. The chemical compositions of spots B and D reveal that these precipitates at the grain boundary and in the Ni-DAZ are Fe–Cr–Mn rich carboborides. Figure 3(c) shows the blocky precipitates in the grain. The EDS result reveals that the composition of spot E is close to that of spots B and D, suggesting the presence of Fe–Cr–Mn rich carboborides. The blocky precipitate of spot F exhibits a composition of Fe 38.9, Mo 53.2, Cr 6.9, Co 0.6, and Mn 0.4 at%, which is Fe–Mo–Cr rich boride. This finding is consistent with the EDS results of the
selected area scan in figure 4, which indicate that two types of precipitated phase are formed in the grain. Figure 3(d) shows the microstructure of ASZ and ISZ. In accordance with the chemical compositions of spots G and H, the ASZ and ISZ are Cr–Mn–Mo rich boride and Fe–Cr rich Ni-based solid solution, respectively.

TEM analysis was conducted to identify the structure of the precipitated phase in DAZ. The TEM micrographs of the precipitated phases at the grain boundary and in Ni-DAZ are displayed in figures 5(a), (b). The electron diffraction patterns (EDPs) shown in figures 5(c), (d) confirmed that these Fe–Cr–Mn-enriched phases are cubic M23(C,B)6-type carboborides with lattice parameters of $a = 1.06$ nm. Figure 6(a) shows the blocky phases precipitated in the grain. The EDPs in figures 6(b)–(c) indicate that these blocky precipitates are cubic M23(C,B)6-type carboborides and tetragonal M3B2-type borides. The lattice parameters $a$ and $c$ of M3B2 were measured to be 0.58 and 0.31 nm, respectively. Figure 7(a) shows the TEM image of fine precipitated phases, which are difficult to be analyzed through SEM. In accordance with the EDP results in figure 7(b)–(d), these granular precipitates are identified as M3B2, Fe2Mo-type Laves phase, and MX-type carbide. The crystal structure and lattice parameters of the granular M3B2-type borides are similar to those of blocky M3B2-type borides. As shown in figure 7(a), Laves phase mainly precipitated on the lath boundaries, and M3B2-type borides and MX-type carbides were dispersed within the grain.

3.2. Effect of bonding time and temperature on joint microstructure

The effect of bonding time on joint microstructure was studied to obtain a fully ISZ in the center of the joint. Figure 8 displays the SEM micrographs of joints bonded at 1150 °C for various times of 5, 15, 30, and 60 min. As shown in figure 8(a), continuous single-phase Cr–Mn–Mo-enriched borides were formed in the bonded seam of the joint bonded at 1150 °C/5 min. As presented in figure 8(b), the discontinuous Cr–Mn–Mo-enriched borides in the center of the joint demonstrated that 15 min is still insufficient to obtain a complete ISZ. With the further diffusion of nickel and boron atoms to the matrix, the width of Ni-DAZ increased obviously, and the size of precipitates in the B-DAZ and Ni-DAZ became coarser. Isothermal solidification was fully completed in the
center of the joint at 1150 °C when the holding time was extended to 30 and 60 min, as shown in figures 8(c)–(d), where the ASZ disappeared, and only the ISZ existed. Similarly, in the DAZ, the width of Ni-DAZ and the size of precipitates further increased with time.

Figure 9 displays the SEM micrographs of joints bonded for 30 min at varying temperatures from 1090 °C to 1180 °C. As shown in figures 9(a)–(b), a few discontinuous Cr–Mn–Mo-enriched borides were found in the joint seams bonded at 1090 °C and 1120 °C for 30 min, indicating that the holding time at the two temperatures was insufficient to obtain a complete ISZ. In the DAZ, the range of precipitates and the diffusion distance of Ni atoms expanded with the increase in temperature. In other words, the width of B-DZA and Ni-DAZ increased. As discussed above, a complete ISZ was obtained in the center of the joint when the temperature rose to 1150 °C, as shown in figure 9(c). The width of Ni-DAZ and the size of precipitates were further increased. As shown in figure 9(d) continuous precipitations were formed at the Ni-DAZ and grain boundary when bonding at 1180 °C. The width of the Ni-DAZ expanded sharply, especially at the grain boundary. Although isothermal solidification was fully completed, these continuous precipitates in Ni-DAZ seriously reduced the mechanical properties of the joint, which will be discussed later.

3.3. Effect of PWHT on joint microstructure
The microstructure and composition of the joint are uneven, and the matrix has high hardness and high tendency of hardenability after the TLP bonding process because many large-size carborbides or borides are found in the DAZ and ASZ. PWHT should be conducted to optimize the microstructure of the joint and improve its comprehensive mechanical properties. Referring to the work of Yan et al [27, 28], the PWHT parameter was selected as follows: (1) normalized at 1100 °C for 90 min and then cooled in air; (2) Tempered at 750 °C for 120 min and then cooled in air.

In accordance with the above results, the microstructures of joints bonded at some parameters are similar. Four TLP-bonded joints after PWHT with typical microstructures (1150 °C/5 min, 1090 °C/30 min, 1150 °C/30 min, and 1180 °C/30 min) were chosen to be analyzed, as shown in figure 10. As illustrated in figure 11, the
elemental line profiles across the joints (1150 °C/5 min and 1150 °C/30 min) before and after PWHT were measured through EDS. The microstructure and composition of the joints became homogenous after PWHT. The diffusion distance of nickel into base metal became farther, and more elements in the matrix diffused into the ISZ than before PWHT, as shown in figures 11(c)–(d). In the B-DAZ, the original blocky and long strip
carboborides at the grain boundary and in the grain dissolved and replaced by granular precipitates. As shown in figure 10(a)–(c), these granular precipitates formed some irregular closed rings, where their size is close to or slightly larger than that of the previous carboborides before PWHT. This condition is because atomic segregation occurred at the positions of the original carboborides after they were dissolved, and these atoms did not have sufficient time to diffuse to other positions of the matrix and precipitated again in the form of granular carboborides. As shown in figure 10(a)–(c), the quantity and size of blocky and rod carboborides in the Ni-DAZ decreased significantly. However, the continuous carboborides in the joint bonded at 1180 °C/30 min still existed after PWHT, as shown in figure 10(d). Similarly, although the size of the ASZ in the center of the bonded seam reduced after PWHT, completely eliminating it is difficult under the selected PWHT conditions.

3.4. Effect of PWHT on joint mechanical properties

The hardness tests were conducted across the joints (1150 °C/5 min and 1150 °C/30 min) before and after PWHT due to the similar phase compositions of the joints, as shown in figure 12. In accordance with the black curves, the hardness of different regions across the joints before PWHT varied greatly. The hardness of the DAZ and base metal improved significantly after the TLP bonding process (the initial average hardness of base metal is 252 HV). The continuous borides in the center line (i.e., ASZ) and Ni-based solid solution (i.e., ISZ) presented the maximum and minimum hardness, respectively. The hardness of B-DAZ was higher than that of the matrix due to the precipitations in this region. The hardness of Ni-DAZ was lower than that of B-DAZ because no martensitic transformation was found due to the nickel diffusion in this region. However, the hardness of this area was still higher than that of the original matrix due to the formation of a large number of carboborides. The red curves displayed the varieties of hardness across the joints after PWHT. The hardness became more homogeneous. The hardness of BM returned to the initial state before bonding. The existence of fine granular precipitations caused the hardness of B-DAZ to be slightly higher than that of BM. The decrease in hardness of
the Ni-DAZ was due to the partial dissolution of carboborides. However, the hardness of the ASZ and ISZ changed slightly after PWHT.

The mechanical properties of joints were studied by tensile tests at room temperature. Figures 13(a), (b) illustrate the stress–strain curves of four types of tensile specimens with typical morphologies before and after PWHT.

Table 3. Chemical compositions of spots A–G in figure 14 (at%).

| Spots | Fe  | Ni  | Cr  | Mn  | Mo  | Co  | Phases                   |
|-------|-----|-----|-----|-----|-----|-----|--------------------------|
| A     | 5.3 | 5.2 | 77.3| 8.5 | 3.5 | 0.2 | Borides in ASZ           |
| B     | 29.3| 56.7|12.6 | 0.5 | 0.4 | 0.5 | Ni-based solid solution  |
| C     | 5.8 | 5.9 | 75.4| 9.0 | 3.8 | 0.1 | Borides in ASZ           |
| D     | 26.7| 58.8|13.5 | 0.3 | 0.4 | 0.3 | Ni-based solid solution  |
| E     | 67.2| 1.2 |21.5 | 6.9 | 2.1 | 1.1 | Carboborides             |
| F     | 66.7| 1.5 |22.3 | 5.8 | 2.9 | 0.8 | Carboborides             |
| G     | 80.1| 9.5 | 7.6 | 0.6 | 0.8 | 1.4 | α-Fe                     |

Figure 14. SEM micrographs of fracture surfaces and longitudinal section of the fractured samples. (a)–(b) 1150 °C/5 min, (c)–(d) 1090 °C/30 min, (e)–(f) 1150 °C/30 min, and (g)–(h) 1180 °C/30 min (black arrow: ASZ; white arrow: ISZ; red arrow: dimple).

Figure 15. XRD patterns taken from the fracture surfaces of the TLP joints bonded at 1150 °C/5 min (sample 1) and 1180 °C/30 min (sample 2).
PWHT, respectively. The inset maps are the images of the fractured specimens. As shown in figure 13(a), these samples without PWHT fractured regularly along the bonding seam of the joint and showed high strength and low elongation due to the high hardness and high hardenability of the base metal. Figure 14 shows the SEM micrographs of fracture surfaces and longitudinal section of the fractured samples. The tensile strength of the joint bonded at 1150 °C/5 min reached 704 MPa, but its elongation was only 2.2%. As shown in figure 14(a), small and smooth planes, cracks, and quasi-cleavage facets existed at the fracture surface, indicating that it is a typical brittle fracture. As shown in figure 14(b), the fracture path passed through the ASZ (black arrows) and ISZ (white arrows). The chemical composition of each phases was measured by EDS to further confirm the reaction phases on the fracture surfaces of the TLP joints. The results are listed in table 3. XRD analysis of the fracture surfaces of the joints bonded at 1150 °C/5 min and 1180 °C/30 min was conducted. The results are shown in figure 15. In accordance with the EDS results in table 3, the phases marked A and B were Cr–Mn–Mo-enriched borides and Fe–Cr-enriched Ni-based solid solution, respectively. Ni-based solid solution and M23B6-type borides were observed in the XRD spectrum, which was consistent with the EDS results. Cracks initiated on these hard and brittle borides, and propagated rapidly along the bonded seam during the tensile process. The tensile strength of the joint bonded at 1090 °C/30 min with discontinuous ASZ in the center increased to 768 MPa, but its elongation was still only 2.5%. The SEM images of fracture surface and longitudinal section of the fractured sample are illustrated in figures 14(c), (d). A large area full of dimples is found on the fracture surface in addition to the small and smooth planes, cracks, and quasi-cleavage facets. Granular precipitates can be observed in mostly every dimple. The EDS results of spot E indicate that these granular precipitates are Fe–Cr–Mn-enriched carboborides. The fracture path is rugged partially through the ASZ and ISZ, and partially distributed along the interface between the ISZ and Ni-DAZ. The fracture at the interface between ISZ and Ni-DAZ is full of dimples (red arrows). The fracture surface exhibited brittle fracture and ductile fracture characteristics because the cracks originated on the borides in ASZ and the carboborides in Ni-DAZ at the same time. The joint bonded at 1150 °C/30 min with fully ISZ exhibited the highest strength of 924 MPa and elongation of 3.18%. As shown in figures 14(e), (f), dimples dominate the fracture surface, indicating the ductile fracture features. The fracture path is mainly distributed along the interface of ISZ and Ni-DAZ. However, the stress–strain curve and macro fracture morphology of the fractured sample exhibit the brittle fracture features due to the early failure of the joint caused by crack initiation on carboborides. When the joint was bonded at 1180 °C/30 min, the fracture surface is occupied by quasi-cleavage planes and tearing edges.
as shown in figure 14(g), which is a brittle fracture feature. The chemical compositions of spot F indicate that this joint is Fe–Cr–Mn enriched carboborides. Given that the fracture occurred at the interface between the ISZ and Ni-DAZ, α-Fe and Ni-based solid solution were observed in the XRD spectrum in addition to M$_{23}$(C,B)$_h$-type carboborides, as shown in figure 15. The cracks initiated and propagated on these continuous carboborides in the Ni-DAZ, as shown in figure 14(h), seriously reducing the tensile strength of the joint.

The stress–strain curves shown in figure 13(b) revealed that the tensile strength of the samples after PWHT decreased slightly, whereas the toughness increased significantly. Obvious yield phenomenon was observed, and plastic deformation was produced in the samples. Figure 16 shows the fracture surfaces of the samples bonded at different parameters. The samples bonded at 1150 °C/5 min, 1090 °C/30 min, and 1180 °C/30 min with PWHT fractured along the bonded seam, as shown in figure 13(b). Their fracture morphologies were similar to that of TLP-bonded joints without PWHT, as shown in figures 16(a), (b), and (d). On the basis of the above fracture analysis, the existence of residual borides in the ASZ and carboborides in the Ni-DAZ after PWHT was the reason for premature failure. As shown in figure 16(c), the specimen bonded at 1150 °C/30 min fractured in the base metal, and the fracture morphology was full of dimples. The tensile strength and elongation of 744 MPa and 19.54% indicated that the mechanical properties of the matrix recovered back to the condition before bonding, and the joint equivalent to the mechanical properties of the original base metal was obtained.

4. Discussion

4.1. TLP bonding formation mechanism

In accordance with the above experimental results, the TLP bonding formation mechanism is discussed in this section.

ISZ and ASZ: At the beginning of the TLP bonding, the Ni–Cr–B interlayer melted quickly when the temperature reached the filler melting point (approximately 1050 °C). Eutectic reaction between the filler and the base metal occurred at the interface, resulting in the dissolution of the matrix and the widening of the liquid filler. With the diffusion of B atoms into the base metal and the dissolution of elements in the base metal into the liquid phase, the melting point of liquid filler increased. Fe, Mn, Mo, and other elements were added to the liquid phase due to the dissolution of the matrix and the interdiffusion of atoms. Isothermal solidification began when the liquidus temperature reached the holding temperature. Thus, an Fe–Cr-enriched Ni-based solid solution was formed on the solid/liquid (S/L) interface toward the centerline. However, the residual liquid in the center of the joint was driven by rapid cooling to form Cr–Mn–Mo–B-enriched intermetallic compounds, that is, ASZ, when the bonding time was insufficient to form a fully ISZ. These hard intermetallic compounds seriously affect the mechanical properties of the joint [21]. In the process of TLP bonding, these compounds are usually used to appropriately increase the bonding temperature or prolong the holding time to avoid the formation of ASZ.

DAZ: In the TLP bonding process, the concentration of boron exceeded the maximum solubility of the substrate because the boron diffused into the base metal. Therefore, boron atoms reacted with the atoms in the matrix, inevitably forming borides or carboborides [19, 23]. In accordance with the EDS results in figure 4, boron atoms reacted with Cr, Fe, Mn, and C atoms in the matrix to form M$_{23}$(C,B)$_h$-type carboborides within the two regions. Other researchers [8–10] found that the M$_{23}$(Cr)$_h$-type carbides are distributed mainly at the prior grain boundary and the lath boundary and have a relatively high coarsening rate, which is consistent with the experimental results. When boron atoms diffused into the grain, they reacted with Mo, Fe, and Cr atoms to form M$_3$B$_2$-type borides in addition to forming M$_{23}$(C,B)$_h$-type carboborides. Fine granular Fe$_2$Mo-type Laves phases and MX-type carbides that existed in the original base metal were found in the grain. The Laves phases retarded the recovery of the lath structure by a pinning effect, and the MX-type carbides inhibited the dislocation movement, which can improve the creep fracture strength of the matrix [8, 14]. In accordance with the EDS results of spot C, nickel atoms with an atomic fraction of 11.1% diffused into this region. The diffusion distance of nickel atom is closer than that of boron atom because the size of nickel atom is similar to that of iron atom and larger than that of boron atom, as shown in figure 4. The nickel element increased the stability of the undercooled austenite, and the matrix in this region did not undergo martensitic transformation with the furnace cooling, resulting in the formation of an α-Fe band with a width of approximately 10 μm.

The TLP process and the formation of precipitated phases mainly depended on the diffusion of B, and the formation of Ni-DAZ was affected by the diffusion of Ni. The effect of bonding parameters on the microstructure of DAZ can be qualitatively analyzed by using Fick’s first law.

\[
J' = -D(dC/dx)St
\]

where $J'$ is the diffusion quantity of components, $D$ is the diffusion coefficient, $dC/dx$ is the concentration gradient, $S$ is the diffusion area, and $t$ is the diffusion time. The coefficient $D$ can be expressed as
where $D_0$ is the diffusion constant, $Q$ is the activation energy, $R$ is the gas constant, and $T$ is the thermodynamic temperature. On the basis of the results of Hirano and Karlsson et al., boron in austenite, $D_{0B} = 2 \times 10^{-6} \text{ m}^2 \text{s}^{-1}$, $Q_{B} = 110.9 \text{ KJ mol}^{-1}$ [29]; nickel in austenite, $D_{0Ni} = 7.7 \times 10^{-5} \text{ m}^2 \text{s}^{-1}$, $Q_{Ni} = 280 \text{ KJ mol}^{-1}$ [30]. In accordance with equation (2), $D_B$ and $D_{Ni}$ increase exponentially with bonding temperature, as shown in figure 17(a). In accordance with equation (1), the diffusion quantity of B and Ni to the matrix at the same parameter is controlled by the diffusion coefficient $(D)$ and the concentration gradient $(\frac{dC}{dx})$. Although the concentration gradient of nickel is higher than that of boron, the diffusion coefficient of boron is five to eight orders of magnitude higher than that of nickel at different temperatures, as shown in figure 17(a). For example, at 1150 °C (1423 K), $D_{0B}^{1423K} = 1.74 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$, and $D_{0Ni}^{1423K} = 4.35 \times 10^{-15} \text{ m}^2 \text{s}^{-1}$. Therefore, the diffusion amount of boron is higher than that of nickel in the initial stage of isothermal solidification. This finding explains why the width of B-DAZ is larger than that of Ni-DAZ. Figure 17(b) shows the average width of Ni-DAZ in the joints bonded at 1150 °C. With the prolongation of time, diffusion coefficients $(D)$ remain constant, and the concentration gradient $(\frac{dC}{dx})$ decreases, resulting in the decrease in growth rate of the Ni-DAZ width. Figure 17(c) shows the average width of the Ni-DAZ in joints bonded at different temperatures. The increase in temperature has a more obvious influence on the width of Ni-DAZ than the extension of time by comparing figures 17(b) and (c). This condition is because the influence of temperature on the microstructure of DAZ mainly depends on the diffusion coefficient $(D)$, which increases exponentially with temperature. The diffusion coefficient of nickel is greater at the grain boundary than within the grain. This condition explains why the diffusion distance of nickel is farther at the grain boundary than within the grain, as illustrated in figure 9(d).

The existence of hard and brittle intermetallic compound in the ASZ is considered to be the main reason for the premature failure of TLP-bonded joint [21]. Obtaining a joint with complete ISZ is always expected. Therefore, a model based on Fick’s second law was established to calculate the time required to complete the isothermal solidification [31, 32]. In this model, the solute distribution in the matrix can be expressed as follows:

$$D = D_0 \exp \left(-\frac{Q}{RT}\right), \quad (2)$$

Figure 17. (a) Diffusion coefficient of B and Ni in austenite at different temperatures, (b) Average width of the Ni-DAZ of joints bonded at 1150 °C, (c) Average width of the Ni-DAZ of joints bonded for 30 min.
\[ C_{(x,t)} = C_m + \frac{1}{2}(C_0 - C_m) \left\{ \operatorname{erf} \left( \frac{x + w}{(4Dt)^{1/2}} \right) - \operatorname{erf} \left( \frac{x - w}{(4Dt)^{1/2}} \right) \right\}, \] (3)

where \( C_{(x,t)} \) is the boron concentration as a function of distance \( x \) and time \( t \), \( C_m \) and \( C_0 \) are the concentrations of boron in the original matrix and in the filler, \( x \) denotes the distance from the center of filler, \( w \) is the half thickness of the inserted filler, and \( D \) is the diffusion coefficient of boron in the matrix. Isothermal solidification is completed when the boron concentration at the centerline of the liquid filler \( (C_{(x,t)}, x = 0) \) is reduced to the solid solubility of boron in nickel \( (C_s) \). In this condition, equation (1) can be simplified as follows:

\[ \frac{C_s - C_m}{C_0 - C_m} = \operatorname{erf} \left( \frac{w}{(4Dt)^{1/2}} \right). \] (4)

In this experiment, the thickness of the interlayer \((2w)\) is 30 \( \mu \)m. The concentrations of boron in the original matrix and in the filler \((C_m \text{ and } C_0)\) are 0.03 and 17.12 at\%, respectively. In accordance with the work of O.A. Ojo et al\[33, 34\], the value of \( C_s \) is taken as 0.3 at\%. The diffusion coefficient in the matrix \((D)\) is shown in figure 17(a). In ideal circumstances, the calculated \( t_f \) values at the holding temperatures of 1090 \( ^\circ \)C, 1120 \( ^\circ \)C, 1150 \( ^\circ \)C, and 1180 \( ^\circ \)C are approximately 41, 34, 27, and 23 min, respectively, which are consistent with our experimental results. Therefore, we can reasonably select the bonding temperature and time to obtain joints with uniform microstructure and equivalent mechanical properties to the matrix on the basis of the model calculation results.

5. Conclusion

(1) The TLP-bonded joint at 1150 \( ^\circ \)C/5 min was composed of DAZ, ISZ, and ASZ. The DAZ was divided into two parts: B-DAZ and Ni-DAZ. In the Ni-DAZ, the precipitates were M23(C,B)6-type carboborides. In the B-DAZ, blocky and long strip M23(C,B)6-type carboborides were formed at the grain boundary. Blocky M23(C,B)6-type carboborides and blocky and fine granular M23B2-type borides precipitated within the grain. Fine granular Fe2Mo-type Laves phases and MX-type carbides that existed in the original base metal were found in the grain. The ASZ and ISZ were Cr–Mn–Mo-enriched boride and Fe–Cr-enriched Ni-based solid solution, respectively.

(2) With the increase in bonding time or temperature, the amount of Cr–Mn–Mo rich boride in the ASZ decreased, and a fully ISZ was obtained. The width of Ni-DAZ and the size of precipitates in the DAZ increased gradually. The exponential increase in the diffusion coefficient with temperature led to a more significant effect of increasing temperature on the microstructure of DAZ than the prolonging of time.

(3) The microstructure and composition of the joints became homogenous after PWHT. In the B-DAZ, the original blocky and long strip carboborides at the grain boundary and in the grain dissolved and replaced by granular precipitates. In the Ni-DAZ, the quantity and size of blocky and rod-like carboborides decreased significantly. However, the continuous carboborides in the Ni-DAZ and in the ASZ still existed after PWHT.

(4) The joints without PWHT fractured along the bonded seam and showed high strength and low elongation due to the high hardness and high hardenability of the matrix. The joint bonded at 1150 \( ^\circ \)C/30 min with fully ISZ exhibited the highest strength of 924 MPa and elongation of 3.18\%. The initiation of cracks occurred on the hard borides in the ASZ and carboborides in the Ni-DAZ and passed through in the bonded seam, resulting in the reduction in the tensile strength of the bonded joints.

(5) The hardness of the specimens was obviously reduced, and their toughness was obviously improved after PWHT. The specimen obtained at 1150 \( ^\circ \)C/30 min after PWHT fractured in the base metal. The tensile strength and elongation (744 MPa/19.54\%) of the specimen were comparable with the original base metal.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

ORCID iDs

Guangmin Sheng © https://orcid.org/0000-0002-9552-8531

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