Effect of Post-weld Heat Treatment on the Microstructure and Corrosion Resistance of Deposited Metal of a High-Chromium Nickel-Based Alloy

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Abstract The evolution of Cr_{23}C_6 carbides in the deposited metal (DM) of a high-chromium nickel-based alloy was investigated after the post-weld heat treatment (PWHT) at 650, 750, 850, and 950 °C, respectively. With the increase in temperature, the morphology of the Cr_{23}C_6 carbides at the grain boundaries was transformed from the continuous lamellar-like to the semi-continuous rod-like and then to the discontinuous granular. Besides, the needle-like Cr_{23}C_6 carbides precipitated from γ matrix after PWHT at 850 °C. The coarsening kinetics of the needle-like Cr_{23}C_6 carbides obeyed the Lifshitz–Slyozov–Wagner law with the growth speed of $4.93 \mu\text{m}^3/\text{h}$ in length and $5.56 \times 10^{-3} \mu\text{m}^3/\text{h}$ in width. Moreover, the ratio of the carbide length to width increased rapidly at first and then flattened as the holding time increased to 850 °C. The results of electrochemical corrosion experiment indicated that the needled-like Cr_{23}C_6 carbides impaired the corrosion resistance of DM due to the formation of chromium depletion around the carbides.

KEY WORDS: Post-weld heat treatment; Carbide precipitation; Morphology evolution; Electrochemical behavior

1 Introduction

Ni–Cr–Fe solid-solution-strengthened Ni-based alloys have wide applications prospect in nuclear power industry [1–3]. Before Filler metal 52 was developed, Filler metal 82 and 182 were the widely used consumables for nuclear

power fabrication and repair [4]. However, the application of Filler metal 82 and 182 in nuclear power industry showed that they were susceptible to primary water stress corrosion cracking (SCC) after several years [1]. In order to improve SCC resistance, the filler metals with high chromium, such as Filler metal 52, have been developed [2, 4, 5]. Unfortunately, based on practical production data and experiments results, these high-chromium nickel-based alloys were susceptible to hot cracking during welding [6, 7]. The precipitates in the alloys, especially the carbides containing abundant alloying elements, had a complex effect on crack resistance depending on the precipitates characteristics and application environment [8–10]. Therefore, it was necessary to investigate the evolution of carbides in the high-chromium nickel-based alloy.

MC and $M_{23}C_6$ were the common carbide types in nickel-based alloys during welding or the subsequent post-weld heat treatment (PWHT). The MC -type carbide (M denoted Nb or Ti) exhibiting a face-centered cubic crystal structure typically formed at the end of solidification by eutectic-type

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reactions with γ matrix. The MC carbide could be replaced by $M_{23}C_6$ carbide featuring a complex cubic crystal structure in some superior superalloys with much higher operating temperatures and longer service lifetimes [11]. The $M_{23}C_6$ carbide phase precipitated during aging heat treatment or in service in the temperature ranging from 650 to 1080 °C [12]. In most cases, the M in $M_{23}C_6$ was mainly on behalf of Cr, and sometimes part of chromium atoms in $M_{23}C_6$ would be replaced by molybdenum atoms. The formation of $M_{23}C_6$ carbides would consume a large number of Cr and Mo atoms. Consequently, the corrosion resistance surrounding $M_{23}C_6$ carbides would decrease owing to the depletion of Mo and Cr at that local region [13, 14].

According to the investigation of Angeliu and Was [15], $M_{23}C_6$ carbide formed on the grain boundaries in alloy 690 with the morphologies of continuous, semi-continuous, or discontinuous. The discontinuous $M_{23}C_6$ carbides in long strips stretched into the grains. The $M_{23}C_6$ carbide also showed a needle-like morphology in nickel-based alloy 690 under the certain heat-treated condition [16]. Wang *et al.* [17] reported that nano-scaled $M_{23}C_6$ carbide precipitated during high-temperature creep and distributed in the γ matrix channels at intragranular regions.

It is known that the morphology and distribution of carbides had a crucial effect on the property of nickel-based alloys [15, 18], but the evolution mechanism of carbides in high-Cr nickel-based alloys is still not clear. This study investigated the $Cr_{23}C_6$ carbide evolution in the deposited metal (DM) of a high-Cr nickel-based alloy at different PWHT temperatures. And the evolution mechanism was expounded in detail. The effect of $Cr_{23}C_6$ carbides on the corrosion resistance of the alloy was revealed by electrochemical experiment and scanning electron microscopy (SEM).

2 Materials and Methods

The DM was prepared by GTA (gas tungsten arc) overlay welding layer with the high-chromium nickel-based alloy filler wire on the clean surface of Q235 steel plate, using a current of 115 A DC and a voltage of 13.5 V. The inter-pass temperature was controlled at 100 °C or less, and a welding speed of 25 mm/min was maintained. The as-welded DM was peeled off from the Q235 steel and divided into eight samples that were transversely oriented in the welding direction. One of the samples (I) was selected as the as-welded sample. Four samples (II, III, IV, and V) were heated to 650, 750, 850, and 950 °C, respectively, and then hold for 4 h. The other three samples (VI, VII, and VIII) were heated at 850 °C for 2, 6, and 8 h, respectively. And the samples (II–VIII) undergoing the PWHT were cooled in a furnace. All samples were polished using

standard metallographic techniques and then etched with mixed acid (hydrochloric acid/nitric acid/acetic acid = 1:1:1). The microstructure was examined and analyzed by optical microscope (OM, OLYMPUS GX51), scanning electron microscopy (SEM, JEOL JSM-6360LV), and transmission electron microscopy (TEM, PHILIPS CM200). SEM and TEM were equipped with an ultra-thin window Oxford energy-dispersive spectrometer (EDS). With the aid of EDS in SEM, the chemical composition of the DM in this study was obtained (wt%): 30.32Cr, 3.93Mo, 2.81Nb, 0.25Al, 0.4Ti, 0.05Cu, 8.06Fe, 0.31Si, 0.21Mn, 0.02C, and margin Ni. Using TEM, selected-area electron diffraction (SAED) analysis of the precipitates, which were prepared from the DM, was performed. Using a voltage of 75 V, the thin foils were produced by twinjet polishing with 3% perchloric acid and 97% ethanol at temperatures that ranged from −25 to −29 °C.

All of the electrochemical experiments were performed with a standard three-electrode cell. The DM, platinum sheet with a 10-cm² surface areas, and saturated calomel electrode (SCE) were used as working, counter, and reference electrodes, respectively. The electrolyte consists of 1.0 wt% H₂SO₄ and 40 wt% CH₃COOH. The test temperature was (25 ± 1) °C. Working electrodes were immersed in solution. Experiments were repeated at least three times. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curve were measured by Autolab electrochemical analyzer device. The EIS measurements were taken in a frequency range from 100 kHz to 0.01 Hz by applying 0.01 V amplitude to the system. After that, the potentiodynamic polarization curves were measured at 0.01 V/s scan rate.

3 Results and Analysis

3.1 Microstructural Evolution in DM

Figure 1 shows the morphology of precipitated phase in the as-welded DM. According to our previous study [19], the white blocky particle was TiC, and the island-like constituent was γ /Laves eutectic structure.

Figure 2 shows the SEM and TEM analysis results of the precipitates at the grain boundaries in the DM after PWHT at 650 °C. Figure 2a shows that there were continuously lamellar-like phases precipitated at some grain boundaries. However, the TEM observation shows that the lamellar-like precipitate was composed of many particles that compactly arranged in a row and grew along a certain orientation, as shown in Fig. 2b. The EDS spectrum (Fig. 2c) and SAED pattern (Fig. 2b) of the phase indicated that the lamellar-like phase was the $Cr_{23}C_6$ carbide, in which some Cr atoms were replaced by Mo atoms. The

Fig. 1 SEM image of γ /Laves eutectic structure and TiC in the welded DM

lamellar-like Cr_{23}C_6 carbide had a face-centered cubic crystal structure with a lattice parameter of 1.065 nm. Moreover, the carbide was coherent with the γ matrix following the orientation relationship of $(2\bar{2}4)_{\text{Cr}_{23}\text{C}_6} // (\bar{1}\bar{1}\bar{1})_{\gamma}$.

When the PWHT temperature increased to 750 °C, Fig. 3 shows that the morphology of Cr_{23}C_6 carbides at the grain boundaries presented as the semi-continuous rod-like shape. The Cr_{23}C_6 carbides became thicker than that at 650 °C.

The SEM and TEM analysis of the precipitates in the DM after PWHT at 850 °C is shown in Fig. 4. When the temperature increased to 850 °C, Fig. 4a and b shows that the Cr_{23}C_6 carbides at grain boundaries were granular. And some granular Cr_{23}C_6 carbides precipitated in the grain interior nearby the grain boundaries with the average size of 0.5 μm . Besides, a large number of needle-like phases precipitated from the γ matrix of DM and segmented the γ matrix into many fragments. The TEM analysis revealed that the needle-like phase had a face-centered cubic crystal structure (Fig. 4c). And from EDS results, it can be obtained that the phase mainly contained 78.17 wt% Cr, 10.07 wt% Ni, and 6.49 wt% Mo. Hence, it can be

Fig. 3 SEM image of the Cr_{23}C_6 carbide and γ /Laves eutectic structure at the grain boundary

concluded that the needle-like phase was Cr_{23}C_6 carbide, and Cr atoms were partially replaced by Mo atoms. The SAED pattern in Fig. 4c shows a certain orientation relationship between the needle-like Cr_{23}C_6 carbide with γ matrix: $(151)_{\text{Cr}_{23}\text{C}_6} // (111)_{\gamma}$, and the electron diffraction zone axis was $[1\bar{1}\bar{1}]$. Figure 4c shows that there were three favorable orientations for the needle-like Cr_{23}C_6 carbides, and these orientations crossed each other at 120° in the space. These favorable orientations were further found to be the three close-packed directions of γ phase- $\langle 110 \rangle$ direction, along which Cr_{23}C_6 carbides needed the minimum energy to precipitate from the γ matrix.

Figure 5 shows the SEM images of the DM after PWHT at 950 °C. There were still a lot of granular Cr_{23}C_6 carbides and part of those linked together at the grain boundaries (Fig. 5a, b). Figure 5a shows that the needle-like Cr_{23}C_6 carbides substantially disappeared in the dendrite arms, only a few in the interdendritic regions. The size of needle-like Cr_{23}C_6 in the width and length increased significantly compared with that at 850 °C. The advantageous precipitation orientations of the carbides still crossed a 120° in the space (Fig. 5c). Moreover, the γ /Laves eutectic structure completely disappeared after PWHT at 950 °C.

Fig. 2 Analysis of the lamellar-like Cr_{23}C_6 carbides at the grain boundary in the DM after PWHT at 650 °C: **a** SEM image, **b** TEM image and SAED pattern, **c** EDS spectrum

Fig. 4 SEM and TEM analysis of the precipitates in the DM after PWHT at 850 °C: **a** granular Cr_{23}C_6 carbides at the grain boundary, **b** magnification of the region in the red frame of **a**, **c** TEM image and SAED pattern of the needle-like Cr_{23}C_6 carbides

Fig. 5 SEM images of the microstructure in the DM after PWHT at 950 °C: **a** precipitates distribution, **b** granular Cr_{23}C_6 carbides at the grain boundary, **c** needle-like Cr_{23}C_6 carbides in the interdendritic region

3.2 Electrochemical Corrosion Behavior

Figure 6 shows the typical Nyquist plots and potentiodynamic polarization curves of the DM in the electrochemical corrosion. The Nyquist plots were all composed of a capacitive loop with one small radius of circular arc at high frequency and a large semicircle that did not end at low frequency for all immersion times. As illustrated in Fig. 6a, the capacitive loop radius of the curve, which was formed in the electrochemical corrosion test for the DM after PWHT at 850 °C, was significantly smaller than that at 650

and 750 °C. The result suggested that the DM after PWHT at 850 °C had the smaller surface charge transfer resistance, which indicated that the corrosion resistance of the DM after PWHT at 850 °C was poorer compared with that at 650 and 750 °C. Figure 6b shows the potentiodynamic polarization curves. The cathodic branches can be extrapolated back to the corrosion potential E_c to give the corrosion current density i_c [20, 21]. E_c and i_c of the DM after PWHT at the three different temperatures were almost equal: $E_c = -0.25$ V, $i_c = 4.79 \times 10^{-7}$ A mm⁻². Table 1 shows the values of breakdown potential (E_p) and passive

Fig. 6 Electrochemical analysis: **a** Nyquist plots, **b** potentiodynamic polarization curves

Table 1 Values of the breakdown potential (E_p) and passive current (i_p) at 650, 750, and 850 °C

Temperature	E_p (V)	i_p (10^{-7} A mm $^{-2}$)
650 °C	0.75	2.75
750 °C	0.75	3.16
850 °C	0.75	3.89

current (i_p) at 650, 750, and 850 °C. It can be concluded that the i_p was largest at 850 °C and also indicated that the corrosion resistance of DM after PWHT at 850 °C was poorer than that at 650 and 750 °C.

4 Discussion

Lifshitz–Slyozov–Wagner (LSW) theory describes the kinetics of precipitate coarsening [22, 23], and can be expressed as

$$\bar{r}^3 - \bar{r}_0^3 = k(t - t_0), \quad k = \frac{8D\gamma S\Omega^2}{9RT}, \quad (1)$$

where r_0 is the average radius of precipitates at the onset of coarsening when $t = t_0$, r is the average radius at time t , k

is the rate constant, D is the solute diffusion coefficient, S is the equilibrium concentration of the element in the particles, γ is the interfacial energy of needle-like Cr_{23}C_6 carbides and matrix, Ω is the atomic volume, R is the gas constant, and T is the heat treatment temperature. However, the LSW theory is only limited to the case of spherical particles.

Speich and Oriani had extended the LSW theory to the case of non-spherical particles in the rod shape with hemispherical caps after modifying the rate constant [24, 25]:

$$l^3 - l_0^3 = K(t - t_0), \quad K = \frac{8D\gamma S\Omega^2}{9RT\beta \ln(2\beta)}, \quad (2)$$

where l is the length of the particles at time t , l_0 is the average length of the particles when $t = t_0$, K is the rate constant, and β is the mean aspect ratio ($\beta = l/2r$) of the major axis (l) to the minor axis ($2r$) of the particles.

When the PWHT temperature increased to 850 °C, Cr_{23}C_6 carbides in needle-like morphology could precipitate from γ matrix (Fig. 4). To further understand the coarsening characteristic of the needle-like Cr_{23}C_6 carbides, the length l and width w of needle-like Cr_{23}C_6 carbides at 850 °C for different holding times were

Fig. 7 Morphology of needle-like Cr_{23}C_6 carbides at 850 °C for different holding times: **a** 2 h, **b** 4 h, **c** 6 h, **d** 8 h

Table 2 Size of the needle-like Cr₂₃C₆ carbides after PWHT at 850 °C in different holding times

<i>t</i> (h)	$\bar{l}$ (μm)	$\bar{l}^3$ (μm ³)	$\bar{w}$ (μm)	$\bar{w}^3$ (10 ⁻³ μm ³)
2	1.66	4.59	0.19	6.44
4	2.36	13.18	0.26	17.78
6	2.83	22.72	0.30	27.27
8	3.25	34.25	0.34	40.35

Fig. 8 Linear relationship between the size ($\bar{l}^3$ and $\bar{w}^3$) of needle-like Cr₂₃C₆ carbides and the holding time *t* at 850 °C in the DM (ρ was the correlation coefficient, and through the analysis of variance, the *F* value can be obtained)

investigated. Figure 7 shows that not only did the number of needle-like Cr₂₃C₆ carbides increase, but also the size both in length and width became larger obviously with prolonging the holding time. The average length $\bar{l}$ and width $\bar{w}$ of the needle-like Cr₂₃C₆ carbides in different holding times are listed in Table 2.

According to Table 2, the linear regression equation about *t* and the size ($\bar{l}^3$, $\bar{w}^3$) was fitted by the least square method:

$$\bar{l}^3 - 5.95 = 4.93(t - 2), \quad (3)$$

$$\bar{w}^3 - 4.85 \times 10^{-3} = 5.56 \times 10^{-3}(t - 2), \quad (4)$$

Figure 8 shows that there was a good linear relationship between *t* and the size ($\bar{l}^3$ and $\bar{w}^3$), which implied that the growth of needle-like Cr₂₃C₆ carbides well met the LSW aging theory. Furthermore, Eqs. (3) and (4) revealed that the growth speed of needle-like Cr₂₃C₆ carbides was $K_l = 4.93 \mu\text{m}^3/\text{h}$ and $K_w = 5.56 \times 10^{-3} \mu\text{m}^3/\text{h}$ in DM under PWHT at 850 °C for 2–8 h. Obviously, the growth speed in length of the needle-like Cr₂₃C₆ carbides was much faster than that in width.

Fig. 9 Relationship between α ($\alpha = \bar{l}/\bar{w}$) and the holding time *t*

Figure 9 shows the law that the ratio α of $\bar{l}$ to $\bar{w}$ varied with the holding time. When the holding time was prolonged, α value increased, but the increase rate decreased. When the needle-like Cr₂₃C₆ carbide precipitated coherently with the γ matrix, the final shape of the needle-like Cr₂₃C₆ carbide not only depended on the minimum interfacial energy criterion, but also needed to meet the minimum elastic energy criterion [26, 27]:

$$\alpha = \frac{\gamma_l}{\gamma_w} + \frac{\pi A t}{12 \gamma_w}, \quad (5)$$

where γ_l and γ_w are the interfacial energy between the needle-like Cr₂₃C₆ carbide and the γ matrix in length and width directions, respectively, and *A* is the parameter that related the mismatch degree. Equation (5) shows that the value of α tends to the ratio of γ_l to γ_w when the size of needle-like Cr₂₃C₆ carbide is much small, that is, *A* is close to zero. The elastic strain energy increased with the needle-like Cr₂₃C₆ carbide growth. When the needle-like Cr₂₃C₆ carbides grew to a certain extent, the value of α mainly depended on the elastic strain energy of the carbides, resulting in the constant increase in α value. The increase rate of α reduced when the needle-like Cr₂₃C₆ carbide and γ matrix lost the coherent relationship. The above analysis was consistent with the changing rule (Fig. 9) that the measured α value rapidly increased in the initial stage and then flattened with the increase in holding time.

To further understand the corrosion resistance of the alloy at different PWHT temperatures, the DM was analyzed by SEM after the electrochemical corrosion, as shown in Fig. 10. It can be observed that almost no corrosion occurred on the DM after PWHT at 650 and 750 °C, but the DM after PWHT at 850 °C suffered severe corrosion, especially around the needle-like Cr₂₃C₆ carbides. As the needle-like Cr₂₃C₆ carbides precipitation occurred,

Fig. 10 SEM images of the DM with PWHT at various temperatures for 4 h after the electrochemical corrosion: **a** 650 °C, **b** 750 °C, **c** 850 °C, **d** magnification of the region in the red frame of **c**

Cr atoms would be consumed from the γ matrix nearby needle-like Cr_{23}C_6 carbides. The Cr-depleted zone would be formed around the needle-like Cr_{23}C_6 carbides. The corrosion resistance surrounding the needled-like Cr_{23}C_6 carbides would decrease owing to the Cr depletion at that local region [15].

5 Conclusions

1. The morphology of the Cr_{23}C_6 carbides at the grain boundaries transformed from the continuous lamellar-like to the semi-continuous rod-like and then to the discontinuous granular with the increase in PWHT temperature.
2. The needle-like Cr_{23}C_6 carbides precipitated from γ matrix after PWHT at 850 °C. The growth of the carbide in length and width coincided with the LSW law with the extension of the holding time at 850 °C.
3. According to the result of the electrochemical experiment, the corrosion resistance of DM was poorer after PWHT at 850 °C than that at 650 and 750 °C. Due to the needle-like Cr_{23}C_6 carbides precipitation after PWHT at 850 °C, the Cr-depleted regions around the

carbides formed. The corrosion resistance of DM decreased significantly in those regions.

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