

Article

Effect of Tempering Time on the Microstructure and Properties of Martensitic Stainless Steel

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Abstract: Martensitic stainless steels (MSSs) have been widely used in the manufacture of turbine blades, surgical instruments, and cutting tools because of their hardness and corrosion resistance. The MSSs are usually tempered at a temperature no higher than 250 °C after quenching to avoid the decline in the hardness, strength, and corrosion resistance of the steels. However, some short-time thermal shocks are inevitable in processes like welding, water grinding, laser marking, etc., in the manufacturing of kitchen knives, all of which may have negative effects on the mechanical properties and corrosion resistance. The effects of these short-time thermal shocks have rarely been studied. In this paper, the martensitic stainless steel 5Cr15MoV (X50CrMoV15 is European Standards) was selected to be tempered at the sensitization temperatures (480 to 600 °C) for a series of times (0.5 to 128 min) after quenching, and the microstructures, hardness, and corrosion resistance of the steel after tempering were investigated. It was shown that the variation in hardness and corrosion resistance of the 5Cr15MoV steel could be divided into four stages over time during tempering at the sensitization temperatures. The hardness of steel was found to increase at first and then decrease with time; accordingly, good corrosion resistance was retained in the initial few minutes of tempering, which then deteriorated fast. The variation in hardness and corrosion resistance of the 5Cr15MoV steel is related to the diffusion of C and Cr atoms at different tempering temperatures. The mechanism of the mechanical properties and corrosion resistance variation caused by the diffusion of C and Cr atoms during tempering at the sensitization temperatures was also discussed.



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Keywords: martensitic stainless steel; tempering time; hardness; corrosion resistance

1. Introduction

Martensitic stainless steels (MSSs) have been widely used in the manufacture of turbine blades, surgical instruments, molds, cutting tools, etc., due to their high strength, hardness, good wear resistance, and corrosion resistance [1–3]. Among them, 5Cr15MoV martensitic stainless steel contains about 15% Cr and 0.5% C, which achieves an optimal balance of hardness and good corrosion resistance. At the same time, the addition of Mo and V in this material further improves the corrosion and wear resistance of the steel. Therefore, this steel has been chosen for the production of kitchen knives [4–6]. Currently, more than 10 million kitchen knives are made from 5Cr15MoV each year worldwide. Heat treatment has a significant effect on the mechanical and corrosion properties of martensitic stainless steels [7,8]. In practical applications, almost all MSSs are heat-treated by quenching and tempering to improve hardness, strength, and corrosion resistance. In general, MSSs are tempered at no higher than 250 °C to avoid a decline in the hardness, strength, and corrosion resistance of the steels [9,10]. Corrosion resistance is a primary characteristic of martensitic stainless steel, and the impact of heat treatment, particularly tempering treatment, on the corrosion resistance of martensitic stainless steel has been an attractive topic for investigation and study [11–14].

During the tempering process, as the tempering temperature is raised and the tempering time increases, the martensite obtained by quenching continuously decomposes. At the same time, carbides precipitate at the martensite and martensite grain boundaries [15–18]. The type, quantity, size, and distribution of the precipitated carbides during the tempering process are crucial to the performance of MSSs [19]. It has been demonstrated that Cr-enriched $M_{23}C_6$ carbides mainly precipitate during tempering in martensitic stainless steels, and these $M_{23}C_6$ carbides have an important influence on the corrosion behavior of MSSs in corrosive environments [20,21]. Cr can be oxidized to a passivation film on the surface of MSSs in the environment to protect the material from attack by corrosive anions (especially Cl^-) [22–24]. The formation of Cr-rich $M_{23}C_6$ precipitation phases also results in a decrease in the Cr content in the vicinity of the precipitation phase, and creates Cr-depleted regions with weak passivation film protection [8,25–27]. In general, the breakdown and dissolution of passivation films prefer to occur at some active locations of the steel surface, such as inclusions, precipitates, and areas with weak passivation films [28,29]. The dissolution of the weak passivation film prioritizes the Cr-depleted regions for corrosion attack, accelerating the corrosion of the steel matrix and promoting the formation of pitting corrosion [20,30]. Therefore, the region around the $M_{23}C_6$ precipitation phase is usually considered the nucleation site of pitting corrosion [31,32].

Babutzka et al. [33] demonstrated that the optimum heat treatment for X50CrMoV15 martensitic stainless steel is when it is austenitized for a sufficiently long time (at least 10 min) between 1050 and 1100 °C, followed by water quenching at a high cooling rate ($>100\text{ K s}^{-1}$). Tempering below 300 °C prevents the precipitation of large amounts of carbides throughout the metal matrix. It is worth pointing out that different studies in recent years have shown almost the same results: at tempering temperatures around 550 °C, Cr-rich carbide precipitation in martensitic stainless steels is maximized and the alloys have the worst corrosion resistance; 400 to 600 °C is considered as the tempering sensitization temperature for martensitic stainless steel [17,20,33–37]. In addition to the study of the effect of tempering temperature on the corrosion resistance of martensitic stainless steels, the effect of tempering time has also been studied. Feng et al. [35] found a significant decrease in the pitting resistance when the Cr-13 type MSSs were tempered within a time window of 2–24 h, while the passivation of MSSs was restored when the steel was tempered for 48 h or longer.

It is generally believed that the microstructure and properties of martensitic stainless steel have been stabilized after quenching and tempering; therefore, almost all the current research focuses on the effect of the temperature and time for tempering on the properties of martensitic stainless steel. However, after quenching and tempering, 5Cr15MoV for knife production still requires a series of processes such as welding, water grinding, laser marking, etc., and during these processes, the work pieces are heated locally to a high temperature (up to 1000 °C) for a short period of time (from a few seconds to a few minutes). The characteristic of the mentioned processes is the involvement of a high density of heat flux in short periods, leading to localized temperature rise surpassing the critical tempering temperature (approximately 250 °C) of the steel. In recent years, kitchen knives made of 5Cr15MoV suffered broken knives, early pitting, and other failures [38], which are related to these thermal shocks. Bijan et al. have studied the welding process of AISI420 martensitic stainless steel turbine blades after quenching and tempering. They found that when the turbine blade was reheated at 300 to 1100 °C for 2 min after heat treatment, the mechanical properties and the corrosion of AISI420 resistance deteriorated; in particular, after $700\text{ °C} \times 2\text{ min}$ reheating, its tensile strength, impact work, hardness, and corrosion resistance became the worst [39].

Considering the welding, water grinding, and laser marking process in knife manufacturing is unavoidable; thus, an in-depth understanding of the above procedures in the steel and the effects of the reheating process on the microstructure and mechanical properties can provide guidance for the production and avoid the early failure. In this study, 5Cr15MoV martensitic stainless steel was used, and the effects of tempering time

(0.5 to 128 min) on the microstructure and properties were investigated at sensitization temperatures (480 to 600 °C). The variations in the microstructures and compositions during the tempering process were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy spectrometry (EDS). The properties of steel after different tempering treatments were evaluated through hardness measurement and electrochemical testing.

2. Experimental Procedure

2.1. Materials and Heat Treatments

The martensitic stainless steel 5Cr15MoV (X50CrMoV15 is European Standards) was commercially purchased in the form of a cold rolled steel sheet with a thickness of 2 mm. The chemical composition was analyzed using X-ray fluorescence spectroscopy and is given in Table 1.

Table 1. The chemical composition of 5Cr15MoV martensitic stainless steel (wt.%).

Steel	C	Cr	Mn	P	Mo	Si	V	S	Fe
5Cr15MoV	0.53	14.3	0.5	0.03	0.48	0.52	0.12	-	Bal.

Prior to conducting the experiments, the plates were cut using wire cutting into 80 mm × 15 mm × 2 mm strip samples for subsequent heat treatment. The samples were heat-treated in a resistance furnace with a heated volume of 0.03 m³. All the samples used in this study were first austenitized at 1050 °C for 15 min and then quenched in oil to room temperature (around 25 °C). The quenched samples were then tempered at varied temperatures (480, 520, 560, and 600 °C) for a series of times (0.5, 1, 2, 4, 8, 16, 32, 64, and 128 min), respectively, and then the samples were air-cooled to the ambient temperature. The variation in tempering parameters after the scheduled quenching treatment is shown in Table 2, we conducted three replicates of the experiment, resulting in a total of 111 samples in this group. In the later section, the samples are labeled according to the tempering time; i.e., S480-0.5 indicates that the samples were quenched at 1050 °C (as all samples in the first step) and then tempered at 480 °C for 0.5 min. After the heat treatment, all the samples were mechanically wet-grinded with silicon carbide paper to remove the oxidized and decarburized layer at the surface.

Table 2. Variation in tempering parameters after predefined quenching treatment.

Quenching	Tempering Temperature (°C)	Tempering Time (min)
1050 °C for 15 min followed by oil-quenching	480	0.5, 1, 2, 4, 8, 16, 32, 64, 128
	520	0.5, 1, 2, 4, 8, 16, 32, 64, 128
	560	0.5, 1, 2, 4, 8, 16, 32, 64, 128
	600	0.5, 1, 2, 4, 8, 16, 32, 64, 128

2.2. Microstructure and Composition Analysis

The heat-treated samples were cut from the strip samples using a cutting machine to obtain samples measuring 10 mm × 10 mm × 2 mm. The samples were then hot-mounted using an XQ-2B metallographic mounting machine. Subsequently, they were sequentially ground with sandpaper of grit sizes 240, 400, 600, 800, 1000, and 1500, respectively. Following this, polishing was performed on the samples using 2.5 µm diamond polishing paste. The samples were thoroughly rinsed with deionized water and alcohol in succession and finally placed in a drying dish. In order to evaluate the effect of different heat treatments on the carbide distribution in the microstructure of steels, the samples were etched with a corrosion solution configured with 5 g FeCl₃ + 10 mL HCl + 85 mL deionized water at room temperature (25 °C) for 5~10 s. The microstructure of the samples was observed using a CLARA GMH scanning electron microscope (Tescan, Brno, Czech Republic). Meanwhile,

the compositions of the precipitated phases in different heat-treated samples were analyzed using the UlitmMax65 energy spectrometer (Oxford Instruments, Abingdon, Oxfordshire, UK) to measure 5 different points for the composition of each place, and an average value was calculated.

A Talos F200X transmission electron microscope (Thermo Scientific, Hillsboro, OR, USA) equipped with an energy spectrometer was used to observe the samples at different tempering temperatures. The morphology of the lath martensite as well as the size, morphology, and type of the precipitated phases were analyzed. The energy spectrometer was used to analyze the Cr elemental content both in the carbides and the surrounding matrix. The prepared samples were first ground into discs of about 0.05 mm in thickness and 3 mm in diameter. The voltage was set to 18 V and then electropolished at $-30\text{ }^{\circ}\text{C}$ with a solution configured with 5 mL of perchloric acid and 95 mL of alcohol using a twin-jet electropolisher.

2.3. Hardness Measurement

The hardness of different heat-treated samples was determined by using an HR-150A Rockwell hardness tester (Mega Instruments, Kunshan, China). The testing procedure involved utilizing a diamond cone penetrator with a vertex angle of 120 degrees, and applying a load of 590 N for a duration of 6 s, and 5 different points were selected on each sample for hardness measurement.

2.4. Electrochemical Measurements

The tempered samples were cut into square samples with size of $10\text{ mm} \times 10\text{ mm}$. After removing the surface oxide layer, copper wires were vertically soldered onto the backside of the test surface using soldering tin. Cold mounting was performed using epoxy resin to insulate the wire connections and prevent contact with the test solution. Prior to testing, the test surface was polished using sandpaper with a grit size of 1500. Subsequently, it was polished with $2.5\text{ }\mu\text{m}$ diamond polishing paste to achieve a smooth and bright surface. After rinsing with ethanol, the samples were dried. Electrochemical testing was conducted using a CHI660E electrochemical workstation. A saturated calomel electrode served as the reference electrode, while a graphite electrode was used as the auxiliary electrode. The 5Cr15MoV MSS samples served as the working electrode. The three-electrode system was immersed into the 5 wt.% NaCl solution at room temperature. At the initialization step, the system was stabilized for 60 min at open-circuit potential, and a potentiodynamic polarization curve of the sample was obtained at a scan rate of 0.33 mV/s . At least three replicates of the experiment were performed for each sample.

This study utilized the Tafel extrapolation method for determining the corrosion rate based on the Potentiodynamic polarization curve. As illustrated in Figure 1, tangent lines were respectively drawn on the anodic and cathodic polarization curves. Subsequently, a line parallel to the X-axis was drawn through the minimum point of the corrosion current density (I_{corr}), where these three lines intersected at point S. By reading the longitudinal coordinates of point S, the self-corrosion potential (E_{corr}) of the specimen was obtained, while the transverse coordinates of point S provided the corrosion current density of the specimen. Moreover, in the case of passivation, the potential at which the corrosion current density starts to increase rapidly on the anodic polarization curve is referred to as the pitting potential (E_{pit}).

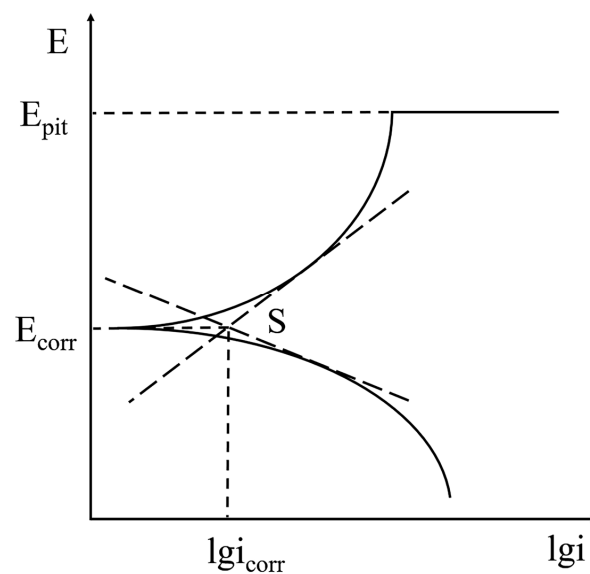


Figure 1. Schematic diagram of the Tafel extrapolation method.

3. Results and Discussion

3.1. Effect of Tempering Temperature

Figure 2 shows the SEM images of 5Cr15MoV steel after quenching and subsequent tempering at different temperatures for 8 min. From Figure 2, it can be observed that the microstructure of 5Cr15MoV samples after heat treatments mainly consists of martensite, residual austenite, and uniformly distributed granular/spherical carbides. The martensite in 5Cr15MoV after quenching is mainly lath martensite. There are also a large number of undissolved granular carbides between the lath martensite during austenitization at 1050 °C for 8 min. The diameter range of the undissolved carbides is mainly 0.5 to 1 µm (Figure 2a). These carbides could also be observed in the subsequent tempered samples (Figure 2b–e).

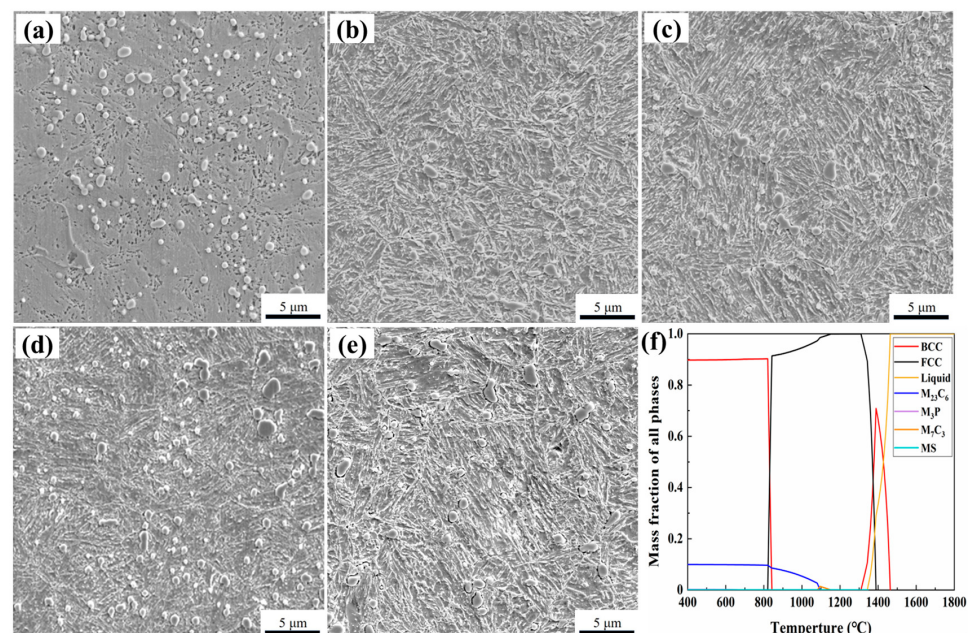


Figure 2. The SEM morphology of 5Cr15MoV: quenched at 1050 °C (a), then tempered at (b) 480 °C, (c) 520 °C, (d) 560 °C, and (e) 600 °C for 8 min, and the transformation trend of the phases in the 5Cr15MoV MSS calculated thermodynamically by Thermo-calc software (2023 Institute stand-alone version) (f).

To confirm the types of carbide during the heat treatment process of 5Cr15MoV MSS, qualitative analysis was conducted using thermodynamic calculations. Figure 2f shows the thermodynamic calculation results of the equilibrium phase diagram of 5Cr15MoV MSS using the TCFE7 database. In the range of 400–600 °C, the 5Cr15MoV MSS is mainly composed of martensite and $M_{23}C_6$ carbides.

The precipitated phases during the heat treatment of 5Cr15MoV MSS were investigated using TEM. By SAED analysis on the carbides in Figure 3a,d, their SAED patterns were obtained and the diffraction spots were calibrated, respectively. Based on the measurement results, it can be confirmed that the carbides in both the quenched and tempered samples are $M_{23}C_6$ carbides (Figure 3c,f). The quenched samples show a distinct lath martensite structure with lath widths of about 200–500 nm (Figure 3a), and a small number of carbides with sizes below 200 nm are distributed as granular/globular particles in the martensite laths and lath interfaces. Meanwhile, in the bright-field image of transmission electron microscopy, a large number of darker streaks can be observed, which indicate clusters of dislocations in the microstructure [17,35], and the higher density of dislocations in the martensitic microstructure leads to the result of higher martensite hardness [40,41]. The highest dislocation density was found in the quenched samples, and the dislocation density decreased after tempering. In contrast, the number of nanoscale carbides increased significantly after tempering. It has been proven that these nanoscale precipitated carbides are also the $M_{23}C_6$ structure, in the literature [42].

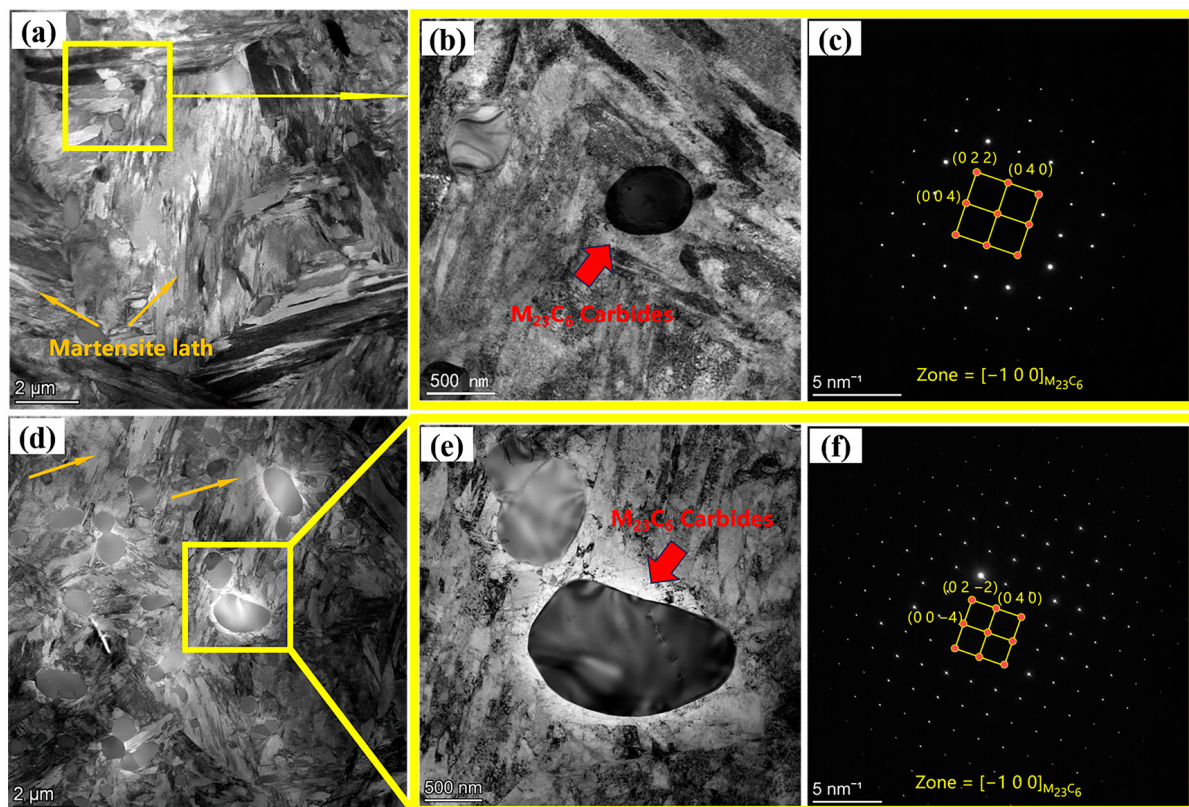


Figure 3. The TEM images of the quenched sample: (a) bright field image, (b) enlarged image of $M_{23}C_6$ carbide of 500 nm size selected by the yellow box in (a), (c) SAED pattern of $M_{23}C_6$ carbide, and TEM images of the 560 °C sample: (d) bright field image, (e) enlarged image of $M_{23}C_6$ carbide of 2 μm size selected by the yellow box in (d), (f) SAED pattern of $M_{23}C_6$ carbide.

The hardness of the samples after quenching and tempering for 8 min is shown in Figure 4. The hardness of the 5Cr15MoV MSS after quenching is 58.3 HRC. The hardness decreases with the increase in tempering temperature after tempering. When tempered at 560 °C for 8 min, the hardness of the sample decreases to 54.0 HRC. The reason for

the decrease in hardness is due to the continuous dissolution of C atoms from martensite during the tempering process, as well as the recovery of matrix atoms through diffusion, which reduces the density of dislocations [40,41,43].

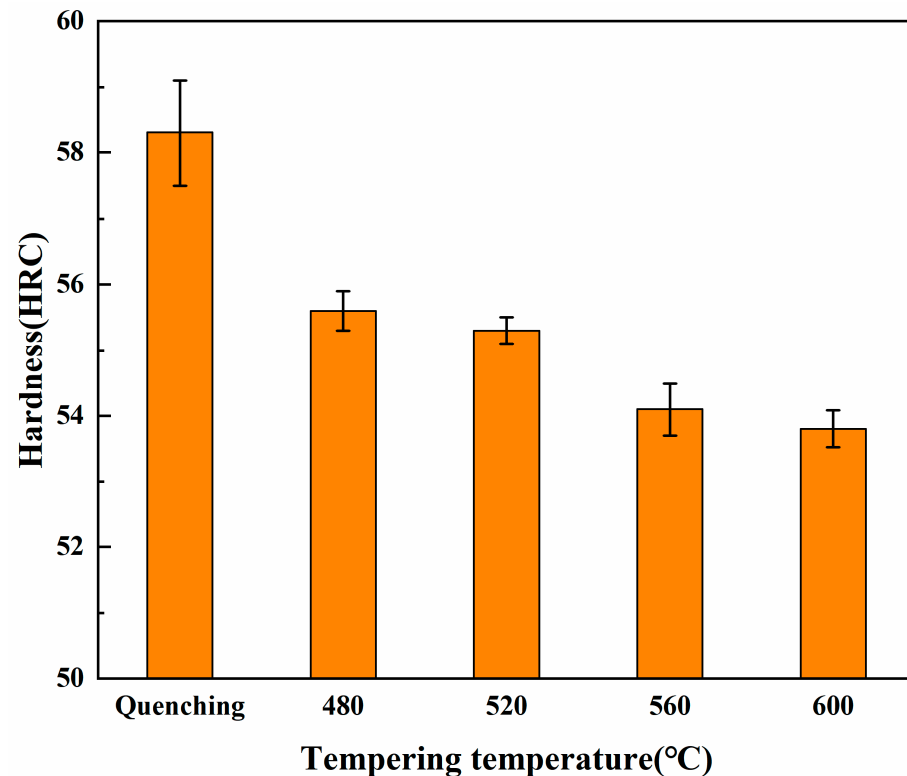


Figure 4. The hardness of 5Cr15MoV samples after quenching and tempering for 8 min at different tempering temperatures.

3.2. Effect of Tempering Time

The SEM results of the samples tempered for 0.5, 1, 2, 8, and 64 min at different tempering temperatures are shown in Figure 5. It is observed that the microstructures of S480-0.5 and S520-0.5 are similar to the quenched microstructure, martensite lath with well-defined grain boundaries is clearly observed in both Figure 5a,b, and a few fine carbides are found. However, when tempering to higher temperatures, such as 560 or 600 °C, the diffusion rate of atoms such as C, Fe, and Cr accelerates. At the same time, the martensite laths decompose continuously, and the fine carbides precipitate rapidly and distribute uniformly over the matrix. Although the martensite laths still exist at different tempering temperatures (e.g., Figure 5e), the martensite grain boundaries become ambiguous as the tempering process progresses, which indicates that the decomposition of the martensite is a continuous process during tempering. It is interesting to note that the microstructure of samples at different tempering temperatures undergoes a rapid change within a short tempering time. The starting time for significant changes in the microstructure varies at different tempering temperatures according to Figure 5. The significant changes in the microstructure in samples tempered at 480 and 520 °C occur at approximately 2 min of tempering (Figure 5i,j). A significant dissolution of the martensite and growth of the precipitated carbides occurs. As the tempering continues, the size of carbide precipitates grows (Figure 5q,r). Similar changes in the microstructure when tempering can also be observed in other literature [31,44]. In contrast, for the 5Cr15MoV samples tempered at 560 and 600 °C, a shorter time is required for a significant change in the microstructure (less than 1 min) (Figure 5g,h).

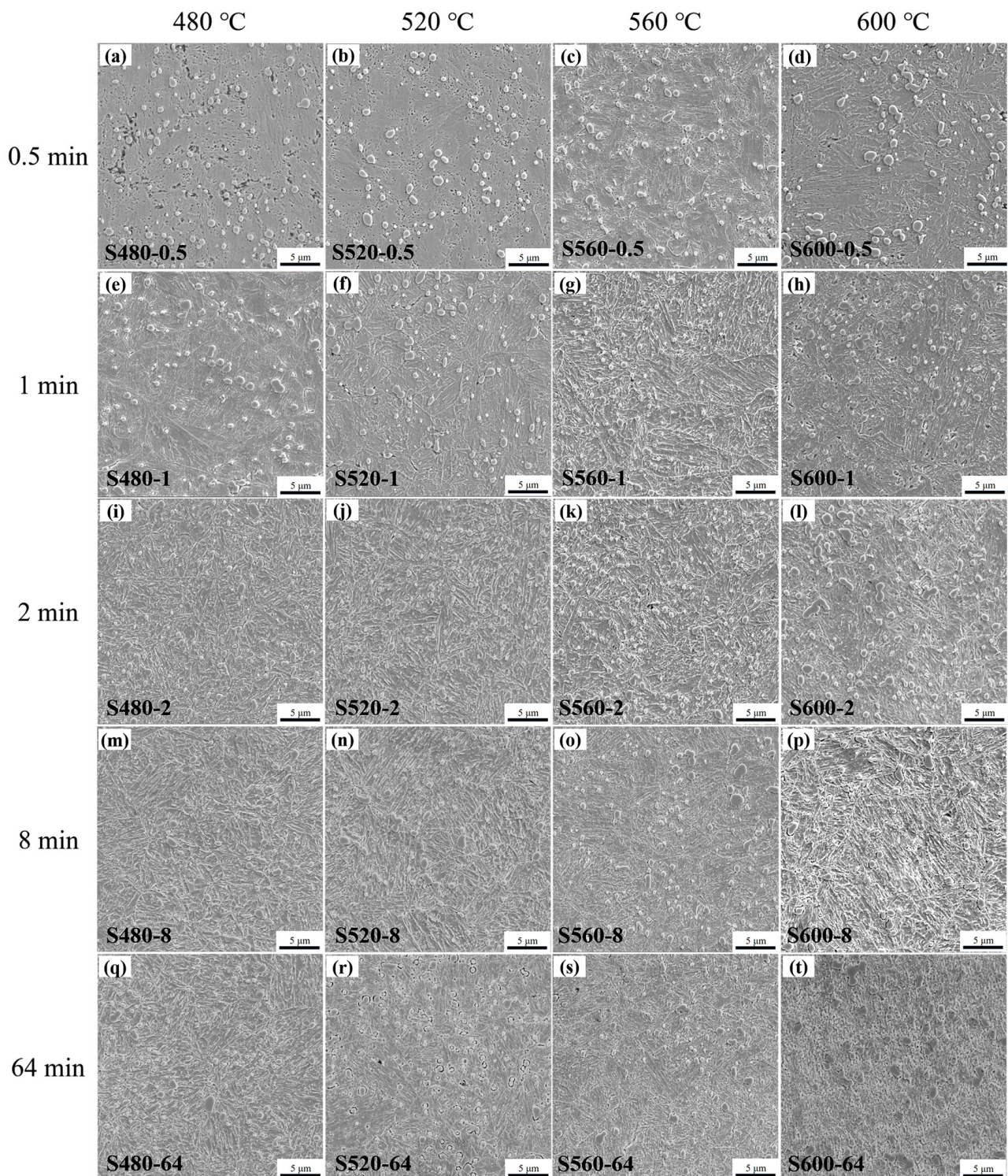


Figure 5. SEM micrographs of the samples: tempered at 480 °C for 0.5 min (a), 1 min (e), 2 min (i), 8 min (m), and 64 min (q); at 520 °C for 0.5 min (b), 1 min (f), 2 min (j), 8 min (n), and 64 min (r); at 560 °C for 0.5 min (c), 1 min (g), 2 min (k), 8 min (o), and 64 min (s); at 600 °C for 0.5 min (d), 1 min (h), 2 min (l), 8 min (p), and 64 min (t).

The hardness of the 5Cr15MoV samples at different tempering temperatures and tempering times is illustrated in Figure 6. It can be clearly observed from Figure 6 that with the increase in tempering time, the hardness change during the tempering process is roughly composed of four stages. The first stage corresponds to a short period of tempering

up to 0.5 min. The hardness of the samples tempered at 480 and 520 °C increased to 60.6 and 60.2 HRC, respectively. However, the samples tempered at 560 and 600 °C do not exhibit any increase in hardness. The reason is that when tempering for 0.5 min, as interstitial atoms, the C atoms easily precipitate from the martensite, and then segregate in the matrix, resulting in an additional solid solution strengthening, and an increase in sample hardness. While the tempering temperature increased to 560 °C or 600 °C, the speeds of the C atoms are further accelerated, and the carbides are formed within 0.5 min. Although the newly formed carbides can partially compensate for the decrease in hardness, the reduction in C content within the martensite leads to a decrease in hardness that exceeds the influence of the newly formed carbides, resulting in a slight reduction in hardness for the samples tempered at 560 °C and 600 °C.

In the second stage, the hardness decreases rapidly when the samples are tempered roughly from 0.5 to 2 min, as shown in Figure 6. The hardness of all the samples decreases by more than 3 HRC in 2 min regardless of the tempering temperature. The decrease in the hardness during the second stage is related to the continuous precipitation of the carbides and the continuous reduction in carbon content in the martensite.

The third stage corresponds to a slowly decreasing trend in the hardness of the samples during tempering from 2 to 16 min. At this stage, the decomposition of the martensite slows down, while the carbides increase slightly. The formation of the carbides depends not only on the mobility of C atoms but also on the mobility of the matrix atoms. However, the diffusion rates of other atoms are generally slower compared to carbon atoms. Consequently, the quantity of carbides continues to slightly increase during tempering from 2 to 16 min. These newly formed carbides can partially compensate for the decrease in hardness, so the decline in hardness of the samples slows down.

The fourth stage is a steady decline in hardness when tempering for more than 16 min. The content of C in the martensite is close to equilibrium, the carbides begin to grow, and the hardness of the samples steadily declines. It is noteworthy that the final hardness after tempering is closely related to temperature. The hardness after tempering is not only related to the dissolution of the C atoms but also to the recovery and recrystallization of the martensite. Tempered to 560 °C and 600 °C, the diffusion ability of the matrix atoms, such as Cr and Fe, increases exponentially, and the martensite undergoes recovery and recrystallization. This is shown in Figure 5, where the boundaries of the martensite have become blurred.

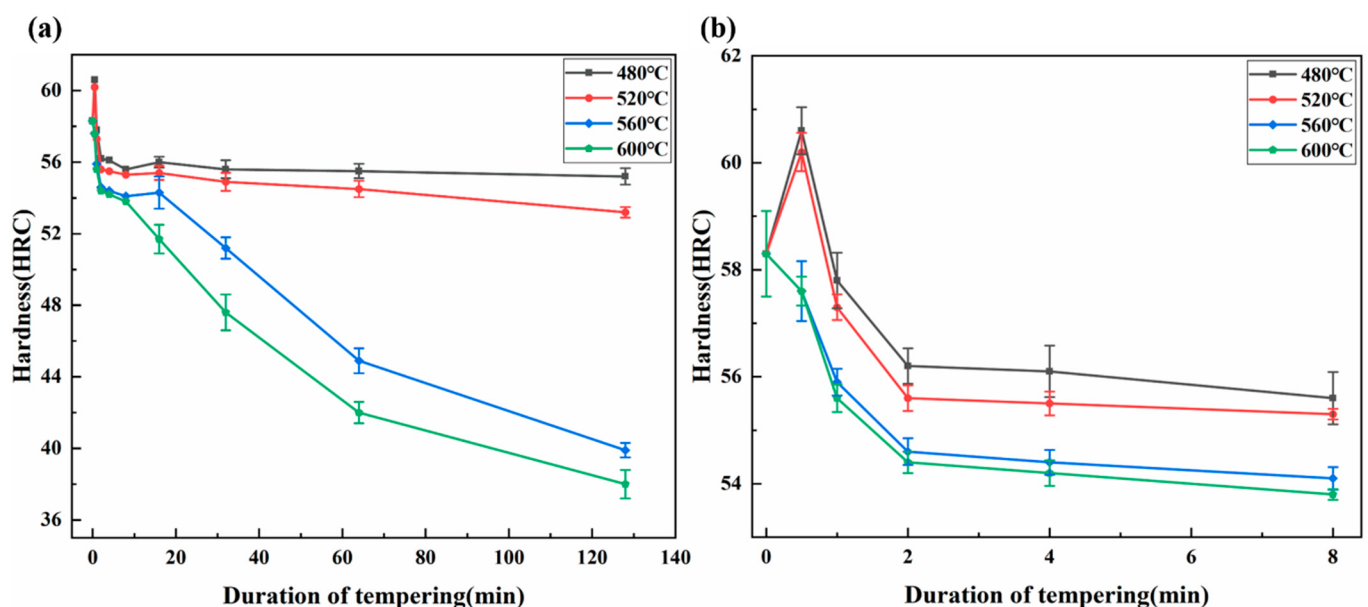


Figure 6. Hardness of the 5Cr15MoV samples with different tempering temperatures and times (a), local magnification of the hardness of the samples tempered within 8 min (b).

3.3. Electrochemical Properties

The potentiodynamic polarization curves of samples with different tempering temperatures in 5 wt.% NaCl solution after tempering for 0.5, 1, 2, 16, and 64 min are shown in Figure 7. The electrochemical results obtained from the potentiodynamic polarization tests are listed in Table 3. The corrosion current density of the quenched sample is very low, about 1.86×10^{-8} A/cm², and the self-corrosion potential, pitting potential, and passivation zone width ($E_{\text{pit}} - E_{\text{corr}}$) are as high as -0.168 , 0.129 , and 0.297 V_{SCE} (all potentials are relative to a saturated calomel electrode), respectively. Therefore, the quenched sample has the best corrosion resistance in this experiment.

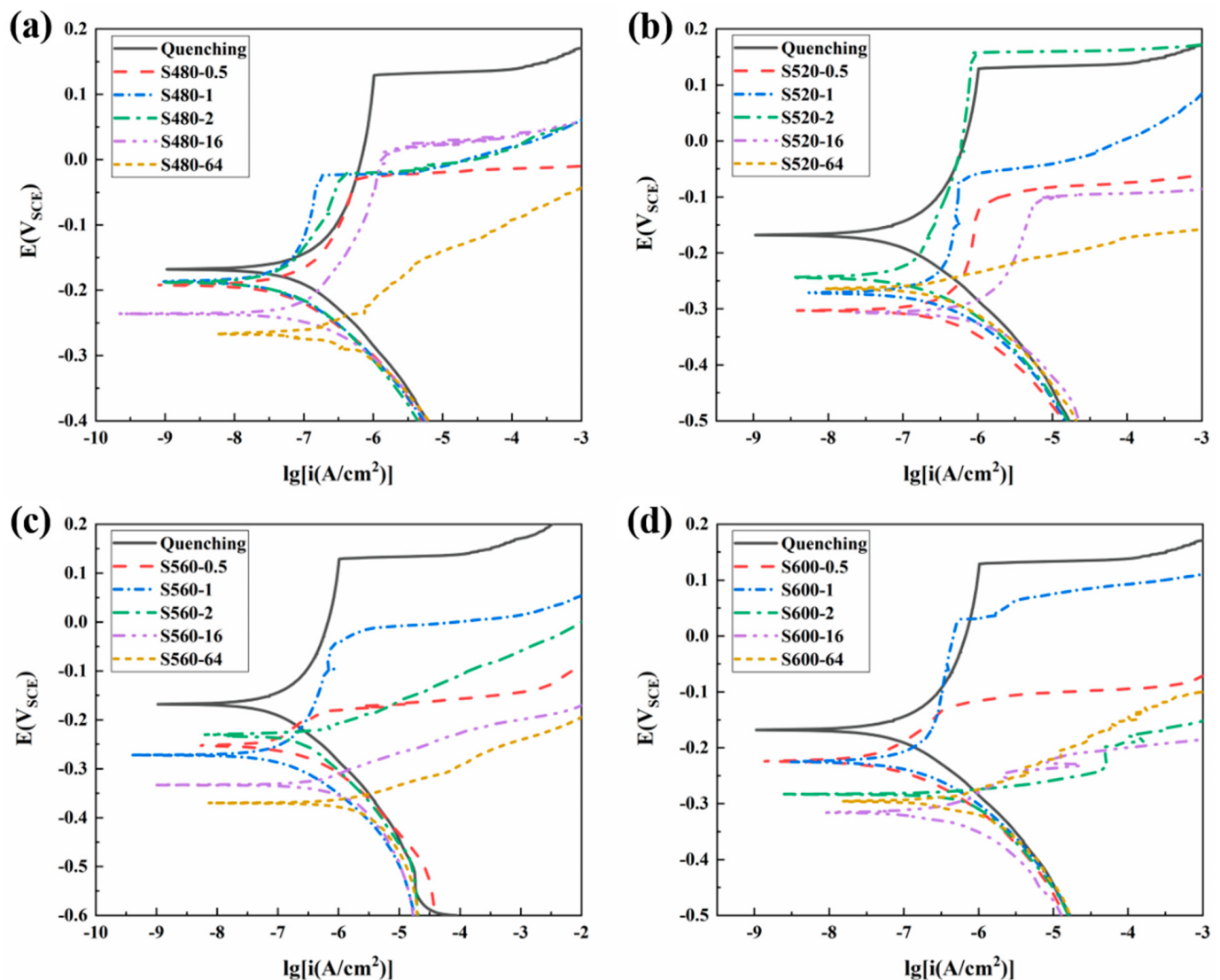


Figure 7. (a–d) Potentiodynamic polarization curves of the 5Cr15MoV samples in 5 wt.% NaCl solution with different tempering temperatures and times.

The notable variation observed in the potentiodynamic polarization curves is that, in the case of extremely short quenching and tempering for less than 1 min, all samples undergo passivation in 5 wt.% NaCl solution. However, with an increase in tempering time, the passivation phenomenon disappeared in the samples.

It is worth noting that similar changes were observed in almost all samples tempered at different temperatures. Specifically, the I_{corr} decreased initially and then increased with increasing tempering time. Conversely, E_{corr} , E_{pit} , and $E_{\text{pit}} - E_{\text{corr}}$ increased initially and then decreased with the increase in the tempering time. These data clearly demonstrate that the corrosion resistance does not exhibit a linear relationship with tempering time within extremely short timeframes. Furthermore, the samples tempered at 480 °C show a slight recovery of corrosion resistance until about 16 min. As the tempering temperature increases, the tempering time for slight recovery of corrosion resistance at 520, 560, and 600 °C is at about 2, 1, and 1 min, respectively. It indicates that the increase in tempering temperature shortens the tempering time required for corrosion resistance recovery. Simultaneously, tempered at 480 °C, the corrosion resistance of the samples rapidly deteriorates at approximately 64 min of tempering. For tempering at 520, 560, and 600 °C, the sharp decline in corrosion resistance occurs at 16, 2, and 2 min, respectively. The reason is that the diffusion coefficient of Cr atoms increases exponentially with the tempering temperature, which is about $1.5 \times 10^{-21} \text{ m}^2/\text{s}$ at 520 °C, and increases to about $1.04 \times 10^{-20} \text{ m}^2/\text{s}$ at 560 °C [45], showing a significant increase in diffusion ability.

Table 3. Electrochemical results obtained from potentiodynamic polarization tests on the 5Cr15MoV samples. I_{corr} : corrosion current density, E_{corr} : self-corrosion potential, E_{pit} : pitting potential, $E_{\text{pit}} - E_{\text{corr}}$: passivation zone width.

Heat Treatment	I_{corr} (10^{-7} A/cm^2)	E_{corr} (V _{SCE})	E_{pit} (V _{SCE})	$E_{\text{pit}} - E_{\text{corr}}$ (V _{SCE})
Quenching	0.186 ± 0.047	-0.168 ± 0.021	0.129 ± 0.043	0.297 ± 0.064
S480-0.5	0.199 ± 0.088	-0.192 ± 0.026	-0.027 ± 0.025	0.165 ± 0.051
S480-1	0.182 ± 0.075	-0.186 ± 0.03	-0.024 ± 0.05	0.162 ± 0.08
S480-2	0.158 ± 0.101	-0.188 ± 0.061	-0.021 ± 0.039	0.167 ± 0.108
S480-16	0.251 ± 0.084	-0.236 ± 0.054	0.011 ± 0.049	0.247 ± 0.103
S480-64	1.55 ± 0.34	-0.267 ± 0.079		
S520-0.5	0.631 ± 0.099	-0.303 ± 0.034	-0.125 ± 0.017	0.178 ± 0.051
S520-1	0.49 ± 0.073	-0.271 ± 0.023	-0.072 ± 0.065	0.199 ± 0.094
S520-2	0.468 ± 0.092	-0.244 ± 0.034	0.157 ± 0.087	0.401 ± 0.121
S520-16	2.69 ± 0.337	-0.307 ± 0.051	-0.106 ± 0.038	0.201 ± 0.089
S520-64	3.16 ± 0.541	-0.204 ± 0.047		
S560-0.5	0.955 ± 0.152	-0.252 ± 0.019	-0.202 ± 0.104	0.05 ± 0.123
S560-1	0.562 ± 0.107	-0.272 ± 0.037	-0.047 ± 0.073	0.225 ± 0.11
S560-2	1.51 ± 0.687	-0.230 ± 0.076		
S560-16	3.47 ± 1.203	-0.333 ± 0.068		
S560-64	6.92 ± 2.759	-0.370 ± 0.103		
S600-0.5	0.417 ± 0.114	-0.224 ± 0.046	-0.130 ± 0.082	0.094 ± 0.128
S600-1	0.489 ± 0.078	-0.225 ± 0.041	-0.031 ± 0.034	0.194 ± 0.075
S600-2	1.74 ± 0.23	-0.283 ± 0.065	-0.197 ± 0.078	0.086 ± 0.143
S600-16	3.98 ± 0.854	-0.315 ± 0.114		
S600-64	5.37 ± 1.397	-0.296 ± 0.093		

In addition, the corrosion resistance deteriorates and then improves with the increasing temperature at the same tempering time. After tempering at 560 °C for 64 min, the sample exhibited the highest I_{corr} of approximately $6.92 \times 10^{-7} \text{ A/cm}^2$, which is more than one order of magnitude higher than the I_{corr} of the quenched sample. Additionally, the E_{corr} is the lowest at approximately $-0.370 \text{ V}_{\text{SCE}}$, and passivation does not take place, so S560-64 exhibited the worst corrosion resistance. Compared with the tempering at 560 °C, the corrosion resistance was improved when the temperature was increased to 600 °C, where not only is the I_{corr} lower and the E_{corr} and E_{pit} higher, but also the passivation occurs when tempering at 600 °C for 2 min, while no passivation occurs at 560 °C. This indicates that the corrosion resistance of tempering at 600 °C is better than tempering at 560 °C; i.e., the corrosion resistance is worst when tempering at 560 °C.

SEM-EDS and TEM-EDS were employed to analyze the composition of the samples, in particular, point scanning, line scanning, and area scanning on the heat-treated 5Cr15MoV samples. Figure 8 shows the curves of Cr content in the steel matrix with different heat treatments. The Cr content in the matrix is found to be positively correlated with the corrosion resistance of the samples. Although it demonstrates a decreasing trend of the Cr content with the extension of the tempering time, the Cr content of the samples does not decrease significantly in the initial 0.5~2 min of the tempering treatment. This can be explained by the precipitation of carbides from the matrix during the extremely short tempering time, resulting in the formation of Cr-depleted regions. Subsequently, the diffusion of Cr atoms from some remote regions with respect to the carbides replenishes the Cr content in the Cr-depleted regions, narrowing the width of the Cr-depleted regions [20]. Additionally, at higher temperatures, the diffusion rate of the Cr atoms increases, which is favored to restore the corrosion resistance at 600 °C. Then, the carbides continue to precipitate and grow, and the Cr content slowly decreases and eventually achieves a plateau [46,47].

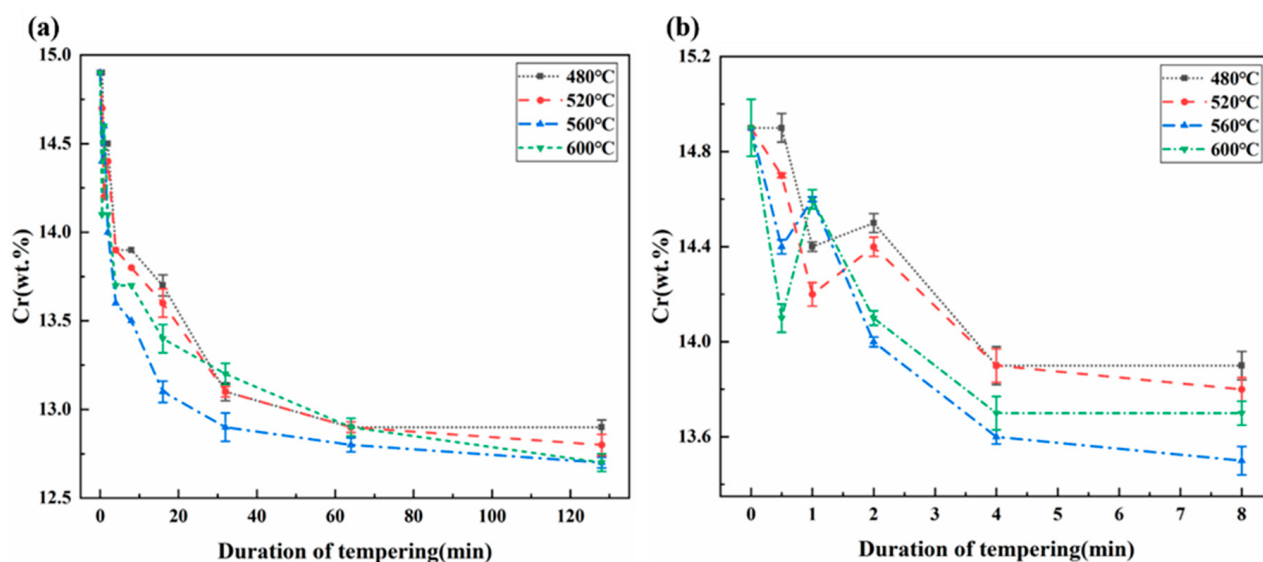


Figure 8. Variation curves of Cr elemental content in 5Cr15MoV matrix with different heat treatments (a), and local magnification of Cr changes within 8 min of tempering (b).

Recently, several research groups have successfully characterized the Cr-depleted regions around $M_{23}C_6$ carbides by TEM-EDS line scanning in 13 wt.% MSSs [34], such as AM355 MSS [48] and 0Cr13 MSS [49], and proved that the Cr content of the Cr-depleted regions and the width of the Cr-depleted regions have a combined effect on the pitting resistance of the MSSs. Figure 9 shows the TEM images of the samples at different tempering temperatures and the elemental distribution around the carbides. The orange dashed line in the figure shows the extent of the TEM-EDS line scanning. A region with the lowest Cr content and a lower Cr/Fe atomic ratio with respect to the matrix was observed at the carbide–matrix interface. This observation suggests the presence of a Cr-depleted region in proximity to the $M_{23}C_6$ carbides. Unlike the tempered samples, the Cr content of the quenched sample decreases slightly from the carbides to the matrix interface and there is no Cr-depleted region. The average widths of the Cr-depleted regions in the samples tempered at 480 °C for 16 min, at 520 °C for 2 min, at 560 °C for 1 min, and at 600 °C for 1 min are 25.5, 37, 48.5, and 40 nm, respectively. The width of the Cr-depleted region increases first and then decreases with the tempering temperatures.

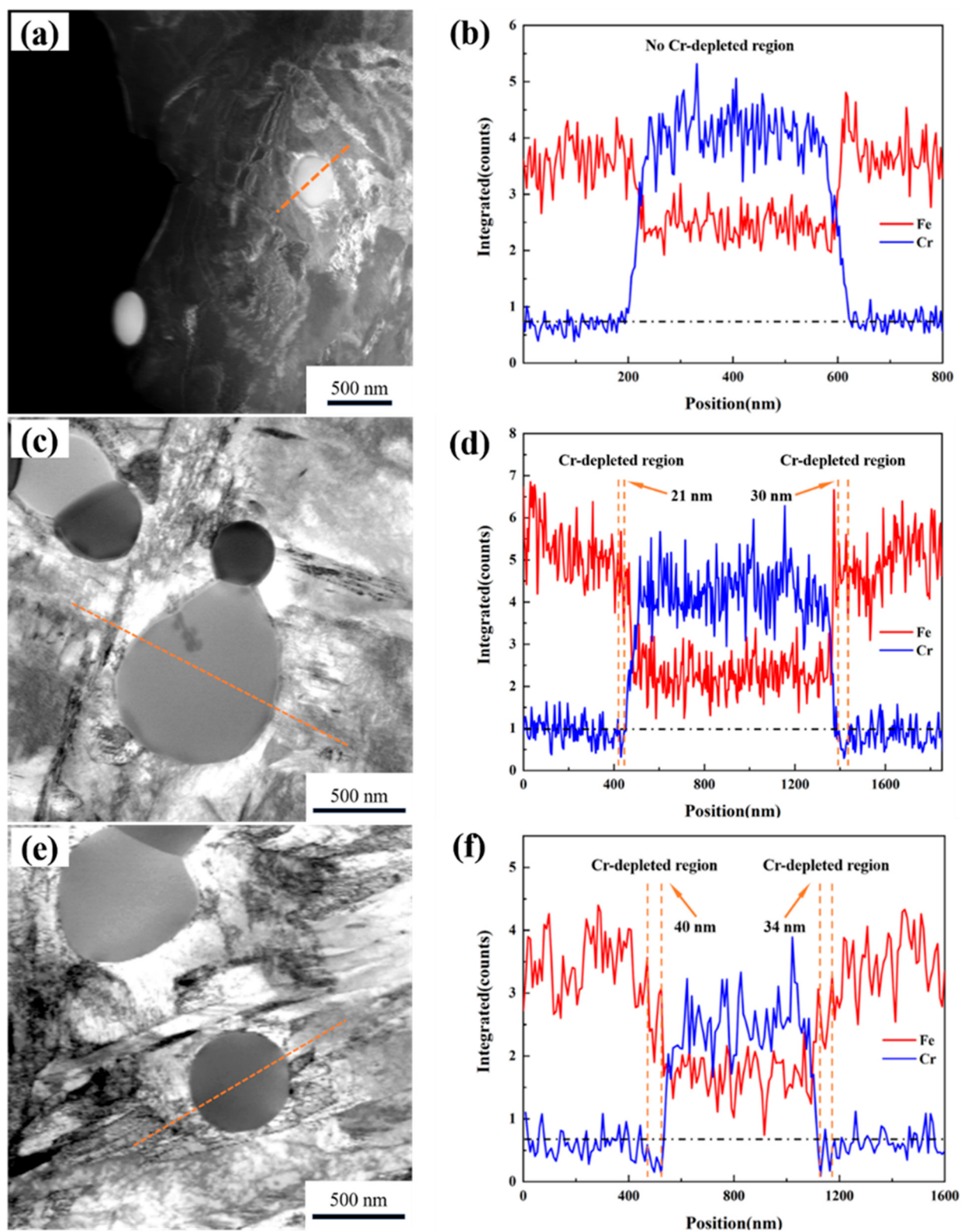


Figure 9. Cont.

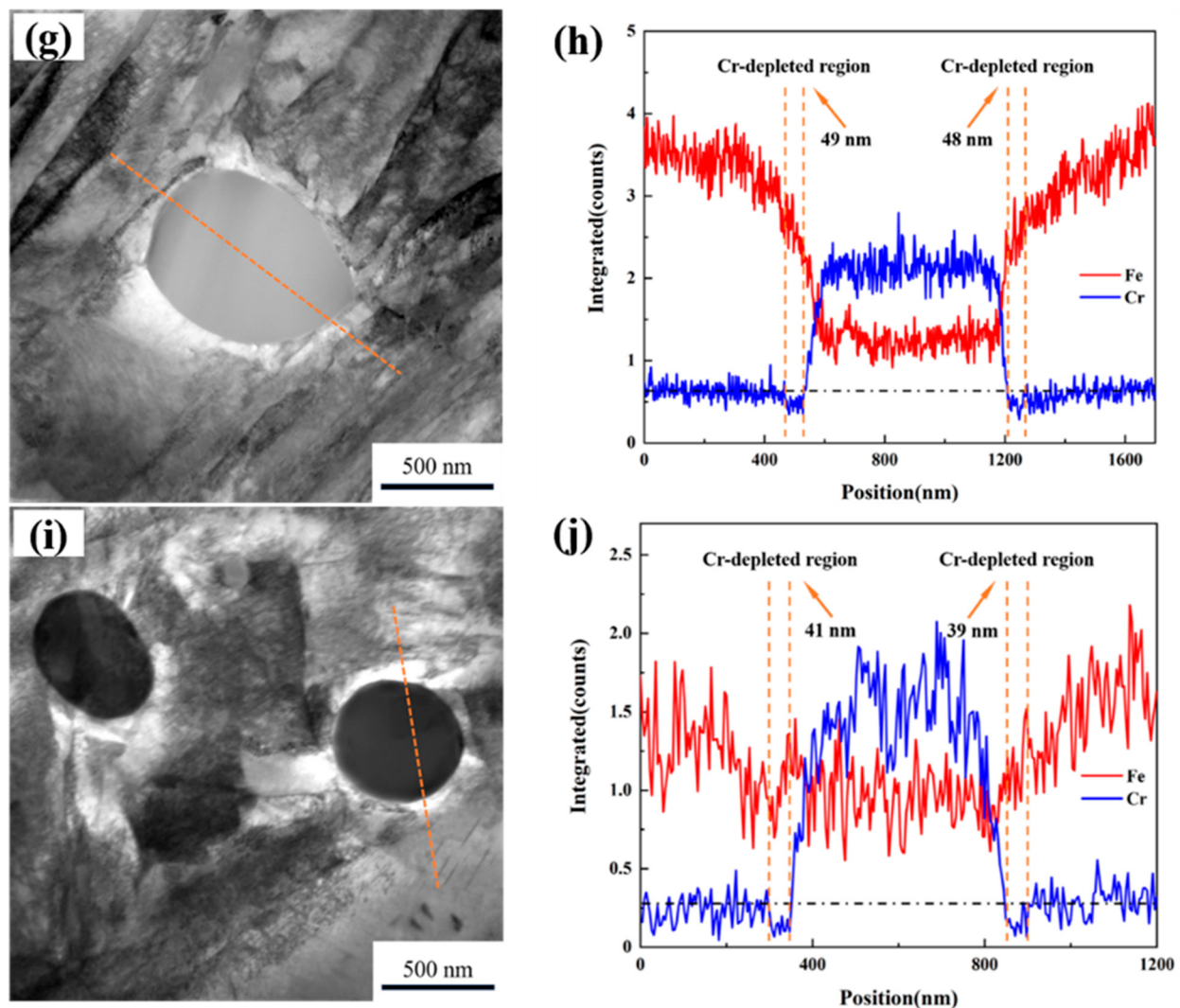


Figure 9. TEM images of the samples with different heat treatments: (a) quenching, (c) tempering at 480 °C × 16 min, (e) 520 °C × 2 min, (g) 560 °C × 1 min, and (i) 600 °C × 1 min; and the elemental distribution of the carbides of the samples with different heat treatments: (b) quenching, (d) tempering at 480 °C × 16 min, (f) 520 °C × 2 min, (h) 560 °C × 1 min, and (j) 600 °C × 1 min.

To further investigate the increase in the Cr content and the Cr-depleted regions, an area scanning experiment was carried out on the sample tempered at 600 °C for 1 min. Figure 10 shows the area scanning and linear scanning results obtained by TEM of the sample tempered at 600 °C for 1 min. From the area scanning results in Figure 10b,c, it can be clearly observed that there are three different carbides in the sample tempered at 600 °C based on the content of Cr, especially Fe, in the carbides. Carbide I, like the carbides in other samples tempered at 480, 520, and 560 °C (Figure 9), has a low Fe content in the carbides, and there are Cr-depleted regions around the carbide (Figure 10d). On the contrary, the Fe content in carbide III is quite high, and there is no Cr-depleted region around the carbide (Figure 10f). In carbide II, the Fe content is basically the same as that of the surrounding matrix, and the Cr-depleted region also does not exist (Figure 10e). The results indicate that when the samples are tempered at 600 °C, the Fe atoms begin to diffuse into the carbides and partially replace the Cr atoms, resulting in relieving the Cr-depleted regions around the carbides. This can partially explain why the corrosion resistance of the samples tempered at 600 °C is improved compared to that of the samples tempered at 560 °C.

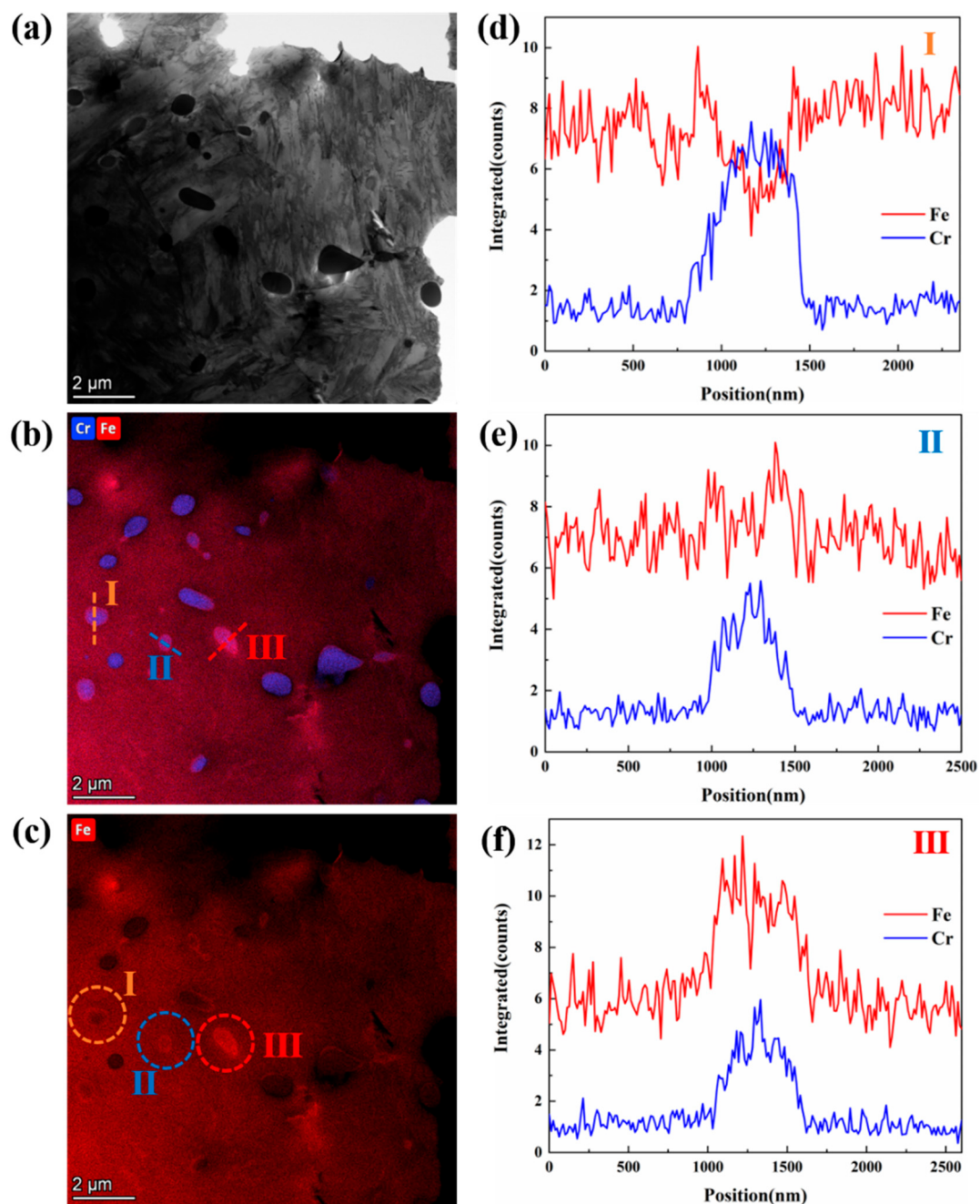


Figure 10. TEM images of the sample tempered at 600 °C for 1 min: (a) Bright-field image, area scanning images of Cr (b), and Fe (c), and line scanning results of carbide I (d), II (e), and III (f) in (b).

4. Mechanism Exploration

Figure 11 illustrates the effect of carbides and the Cr-depleted regions on the pitting corrosion behavior of 5Cr15MoV MSS. The Cr content in the matrix of the quenched sample is the highest because a sufficient amount of Cr was dissolved into the matrix during austenitization, and there is almost no Cr-depleted region in the quenched sample, so the passivation film is very stable and has the best pitting resistance (Figure 11a). When the samples are tempered, they move forward to the first stage of tempering (less than 0.5 min). As an interstitial atom, the diffusion rate of C is much faster than that of the matrix atom Fe and the substitutional atom Cr. For example, when the samples are heated at 560 °C, the diffusion coefficient of C atoms is about $2.6 \times 10^{-12} \text{ m}^2/\text{s}$, and the diffusion coefficient of Cr atoms is about $7 \times 10^{-21} \text{ m}^2/\text{s}$ [45]. In the first stage, the C atoms in martensite segregate

first, while the Cr atoms have not yet begun to diffuse (Figure 11b). The segregation of the C atoms can cause a slight increase in the hardness of the samples, while the corrosion resistance of the samples has basically not changed because the Cr content in the matrix remains unchanged at this time.

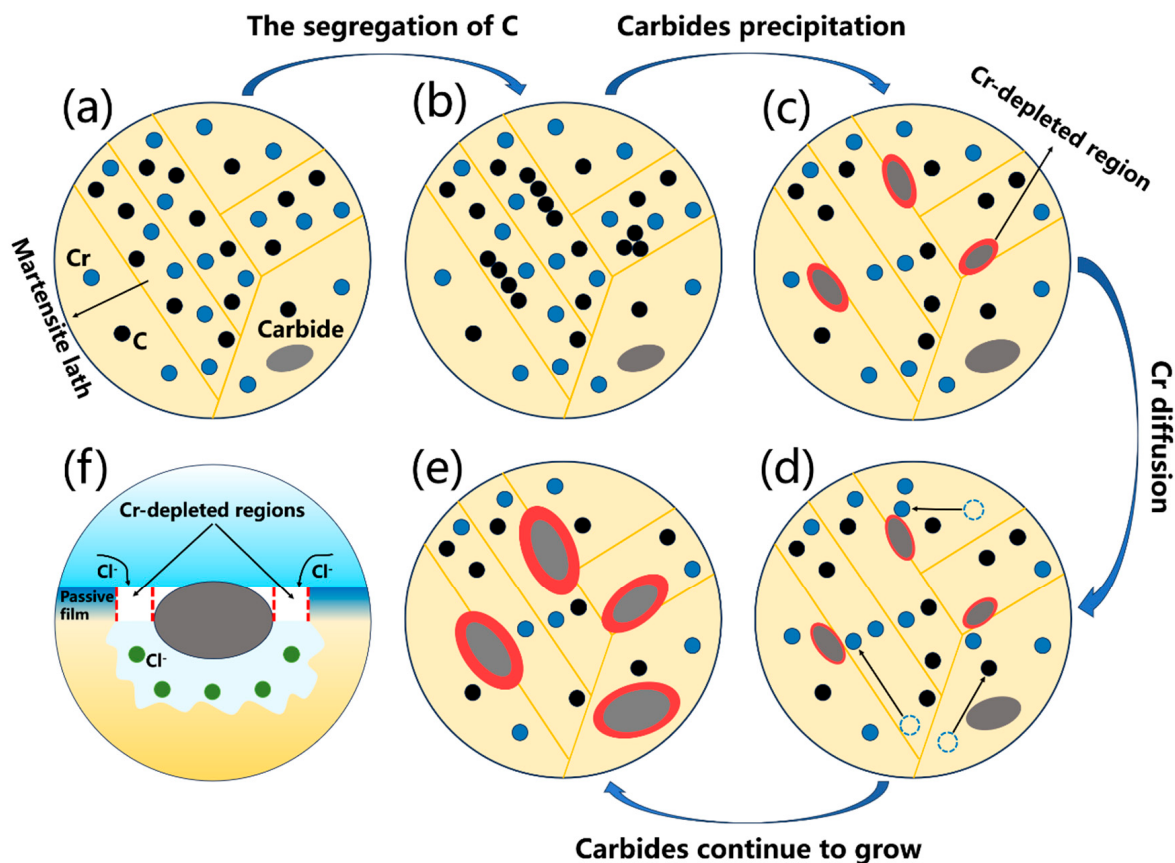


Figure 11. Schematic of the influence of the $M_{23}C_6$ carbides on the pitting behavior of 5Cr15MoV MSS: (a) Schematic of the microstructure after quenching, (b) the segregation of C, (c) carbides precipitation, (d) Cr diffusion, (e) carbides continue to grow, and (f) Schematic of the pitting corrosion.

When the samples are tempered in the second stage, which is 0.5 to 2 min, the carbides begin to precipitate from the martensite (Figure 11c). The precipitation of the carbides causes a rapid decrease in the C content in the martensite, resulting in a rapid decrease in the hardness. Simultaneously, a large number of the Cr atoms enter the carbides from the martensite because the precipitated carbides are rich in Cr. Therefore, the Cr-depleted regions are formed at the boundary between the precipitated carbides and the matrix, leading to a sharp decrease in corrosion resistance.

In the third stage, the samples are tempered from 2 to 16 min. The increase in the amount of the carbides slows down, and the precipitated carbides begin to grow at that time (Figure 11d). Although the growth of the precipitated carbides will continue to consume C and Cr in the martensite, the C and Cr atoms in the martensite will continue to diffuse toward the Cr-depleted regions, i.e., the boundary between the precipitated carbides and the martensite, due to the concentration difference. This leads to the Cr content in the Cr-depleted regions increasing, and the width of the Cr-depleted regions decreasing. This is the reason why the corrosion resistance of the samples tempered from 2 to 16 min is improved.

When the samples are tempered for more than 16 min, the tempering transformation enters the stable stage, i.e., the fourth stage (Figure 11e). At this time, the C and Cr atoms continue to diffuse, and the carbides continue to precipitate and grow. The content of C in

the martensite is close to equilibrium, and the hardness of the samples steadily declines. The supplementation of the Cr atoms into the Cr-depleted regions by the diffusion of the Cr atoms around the carbides cannot keep up with the Cr atoms consumed because of their growth. As a result, the width of the Cr-depleted regions becomes larger and larger, and the corrosion resistance of the samples continues to decrease.

Several studies have indicated that the width of the Cr-depleted regions and the Cr content in the Cr-depleted regions have a significant impact on pitting corrosion [42,49]. The $M_{23}C_6$ carbides are Cr-rich, and the Cr content in the Cr-depleted regions around the $M_{23}C_6$ carbides is greatly reduced. The passivation films formed in the Cr-depleted regions are relatively weak and easily dissolved [26–29]. After the dissolution of the weak passive film, the formation of pit-like nuclei in the Cr-depleted regions (Figure 11f) provides a diffusion pathway for corrosive electrolytes to penetrate toward the matrix, thereby further dissolving the metal around the $M_{23}C_6$ carbides. As a result, the wider the width of the Cr-depleted region is, the faster the pitting corrosion around it occurs.

The influence of tempering temperature on the hardness and corrosion resistance of the samples is mainly reflected in the effects of temperature on the diffusion ability of atoms such as C and Cr. Due to the much higher diffusion coefficient of C atoms compared to that of Cr atoms [45], the hardness of the samples changes earlier than the corrosion resistance when tempered from 480 °C to 600 °C. Meanwhile, the diffusion coefficients of C and Cr atoms increase exponentially with temperature [45], then the hardness and corrosion resistance of the samples tempered at 560 °C or 600 °C change significantly faster than those of the samples tempered at 480 °C or 520 °C. It is worth pointing out that when the samples are tempered at 600 °C, the Fe atoms begin to partially replace the Cr atoms in the carbides. Thus, the corrosion resistance of the samples tempered at 600 °C is improved to a certain extent compared to that of the samples tempered at 560 °C.

5. Conclusions

In summary, the evolution of the microstructure and properties of 5Cr15MoV MSS was investigated after tempering at different tempering temperatures and different times; the main conclusions are the following:

- (1) Overall, when the 5Cr15MoV MSS is tempered from 480 to 600 °C, the hardness and corrosion resistance of the samples decrease with tempering temperature and tempering time. The tempering process can be roughly divided into four stages based on the tempering time. Tempered for no more than 0.5 min, the hardness of the samples slightly increases, and there is no significant change in the corrosion resistance of the samples compared to the quenched sample. When the samples are tempered for 0.5 to 2 min, the carbides begin to precipitate and the hardness and corrosion resistance of the samples rapidly decrease. Tempered from 2 to 16 min, the corrosion resistance of the samples is improved because of the supplement of the Cr atoms in the Cr-depleted regions by diffusion of the Cr atoms from the matrix. In the last stage, the samples are tempered for more than 16 min. The hardness and corrosion resistance of the samples continue to decrease.
- (2) The higher the tempering temperature is, the faster the changes in the hardness and corrosion resistance of the sample occur. The changes in the microstructure and properties of the samples during tempering depend on the influence of temperature on the diffusion coefficient of the atoms such as C and Cr. Tempered at 480 °C, the corrosion resistance of the sample will sharply decrease after tempering for 64 min. The corresponding tempering time for the samples tempered at 560 °C and 600 °C is shortened to 2 min.
- (3) Fe atoms begin to partially replace Cr atoms in the carbides when the samples were tempered at 600 °C in this experiment. The corrosion resistance of the samples tempered at 600 °C is improved to a certain extent compared to that of the samples tempered at 560 °C.

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