Effects of Ultrasonic Vibrations during Quenching on Corrosion of 35crmov Steel in Different Environments

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Abstract. The effects of ultrasonic vibrations during quenching on the corrosion resistance of 35CrMoV steel in acidic, neutral and alkaline mediums with the same Cl⁻ concentration were investigated by electrochemical and immersion tests. The microstructure and corrosion surfaces of specimens were obtained by scanning electron microscope (SEM). The SEM results show that the microstructure of the ultrasonic-aided quenching (USQ) specimen is small martensite, and no residual ferrite compared to the un-ultrasonic-aided quenching (UUSQ) specimen. And the corrosion cracks are lighter and less than that of the UUSQ specimen. It was also found that in the immersion and electrochemical impedance spectroscopy (EIS) tests, the corrosion resistance of the specimens decreased with the decrease of the pH value of mediums, and the corrosion resistance of 35CrMoV steel can be significantly improved by USQ.

1. Introduction

The factors that affect metal corrosion are mainly include external factors and internal factors. The external factors mainly consist of the composition, temperature and PH value of corrosion medium and the force condition of the steel; the internal factors mainly refer to the chemical composition, microstructural, crystal shape and surface structure of the steel. 35CrMoV steel (Chinese standard) is a typical medium carbon steel [1], which is widely used in engineering machinery due to its high static strength, high fatigue limit, and good creep strength, but at the same time, the corrosion of steel is also a matter of value. The corrosion behavior of steel has been studied by many researchers [2-8]. Wang luying et al. found that the compounds containing Cl⁻ and SO4²⁻ can accelerate the corrosion rate of steel [9, 10]. Otani et al. investigated that Zn²⁺ and Al³⁺ could resist corrosion of steel in fresh water to a certain extent [11, 12]. Sol-ji song et al. investigated that the corrosion resistance of steel in seawater environment can be improved by magnesium ions [13].

A large number of chlorides (Cl₂, NaOCl, Ca (OCl)₂ etc.) are widely used in sewage treatment, bleaching and washing clothes [14, 15]. The chlorides can be dissociated into Cl⁻ and OCl⁻ in aqueous solution, which will adversely affect the corrosion of exposed metal equipment. Usually, the penetration of Cl⁻ in solution will destroy the oxide film of the steel. Figure 1 (a) and (b) shows mechanism of Cl⁻ immersion and thinning into the oxide films [16]. After the destruction of the oxide film, the corrosion
process begins with the coupling of electrochemical reactions [17-21]. Figure 1(c) shows the accelerated corrosion of steel by Cl\(^-\).

![Figure 1. Schematic representation of corrosion mechanism.](image)

For this reason, the effects of USQ on corrosion of 35CrMoV steel in different mediums should be studied in the aqueous solution containing Cl\(^-\).

In this experiment, the effects of USQ on the corrosion behavior of 35CrMoV steel in acidic, neutral and alkaline solutions that contains 10 mmol/L Cl\(^-\) were investigated by EIS, immersion test, surface observation and SEM analysis.

2. Experimental

2.1. Specimens

35CrMoV steel blocks (10 × 10 mm in size, 15 mm in thickness) were used as the test specimens. Table 1 shows the chemical composition of steel. Specimens were heated to 850°C and maintained for 0.5h, then cooled by water with and without ultrasonic vibration (Figure 2). The methods for preparing specimens for electrochemical test is shown in Figure 3. Before the microstructure analysis and immersion tests, the tested surfaces of specimens were grounded from #180 to #1500 particle size by SiC sandpapers, and finally were polished by 1μm diamond paste. For the electrochemical measurements, wires were welded on the surfaces of specimens to make an electrical contact. All specimens were impregnated with epoxy resin (Synthetic Resin, New Century Dental Ltd., China), and the exposed surfaces of molded specimens were also grounded and polished, too. All the specimens were ultrasonically cleaned with alcohol (KQ3200DV, Shumei, China) and dried with hot air. The specimens were stored in a sealed bag to avoid contamination and humidity.
Figure 2. Schematic diagram of quenching.

Figure 3. Specimen preparation for electrochemical measurement: (a) longitudinal section; (b) bottom surface.

Table 1. Chemical composition of 35CrMoV steel (mass %).

| Element | C  | Si  | Mn  | Cr  | Mo  | V  | S   | P   | Fe  |
|---------|----|-----|-----|-----|-----|----|-----|-----|-----|
|         | 0.34 | 0.25 | 0.58 | 1.09 | 0.23 | 0.13 | 0.08 | 0.026 | Bal. |

2.2. Corrosion solutions
Three different solutions, H$_2$SO$_4$ sol (PH=1), NaCl sol (PH=7), and NaOH sol (PH=13) were used as corrosion mediums. The concentration of Cl$^-$ in each solution was adjusted to 10 mmol/L with NaCl. Water used in this study was ordinary tap water and all the chemicals were special analytical grade. The pH of the solutions before immersion and electrochemical tests were measured with a pH meter (VZ8685BZ, AZ Instrument, and China).

2.3. Microstructure analysis
The specimens were immersed in a nitric acid etching solution (2 mL of 70% nitric acid and 48 mL of absolute alcohol) for 10-15 seconds, ultrasonically cleaned with ethyl alcohol and dried with a dryer. The microstructure of the specimens were observed by the SEM (EVO MA10, ZEISS, and Germany). If the microstructure does not show complete, we usually immerse the specimens again in the nital etchant for 10-15 seconds until the microstructures are clearly shown.

2.4. Immersion tests
Specimens were immersed in solutions for 259.2 ks (3 d) at room temperature. The test beakers were open to the air during immersion tests. The quality of the specimens was determined by a microbalance (HZ-104135S, HUAZHI, USA) before and after immersion tests.

2.5. Electrochemical tests
The electrochemical tests were investigated using a traditional three-electrode workation (Chi660e, Chenhua, China). The saturated calomel (Ag/AgCl saturated with KCl) electrode and the platinum sheet were used as a reference electrode and a auxiliary electrode, respectively. The Open-circuit potential (OCP) was measured for 1h, and the potentiodynamic was measured in the cathodic and anodic direction.
with a scanning speed of 5 mV/s. Cathodic and anodic scans were performed separately to obtain the respective electrochemical properties of 35CrMoV steel immersed in solutions having different PH. The EIS measurements were conducted at the open circuit potential, with a frequency range of 100K Hz to 0.1 Hz, an amplitude of 10 mV, and a sampling rate of 12 points per decade. All data in electrochemical measurements can be repeated.

2.6. Surface observations and analysis
Surface topography is an important indicator of the corrosion behavior of the specimens. Therefore, before and after the immersion experiment, the experimental process was photographed with a camera (Nikon D80-DSLR) and the corrosion surface of specimens were observed by SEM. Prior to the analysis, the specimens were ultrasonically washed with ethanol and dried with a dryer.

3. Results and Discussion

3.1. Microstructure
Figure 4 shows the microstructure of 35CrMoV steel. The UUSQ specimen is larger martensite with a small mount of residual ferrite, while the USQ specimen is all small martensite. This is because the quenching medium must have a larger cooling rate in the range of temperature (below 300 °C) where the martensitic transformation occurs. When the ultrasonic vibrations (UV) were added, the range of nucleate boiling can be widened, the hot vapor film on the surface of the specimen was ruptured earlier due to its cavitation and acoustic flow effect. Therefore, there was no residual ferrite of the USQ specimen compared to the UUSQ specimen.

Figure 4. Microstructure of 35CrMoV: (a) un-ultrasonic-aided; (b) ultrasonic-aided.

3.2. Immersion tests
Figure 5(a) shows the specimens at the beginning of immersion and Figure 5(b) shows the specimens after immersion for 259.2 ks (3 d) in solutions. In Figure 5(b), there are many brown corrosion products on the surface of specimen in the neutral NaCl sol, regardless of whether UV is added during quenching. We can see that the specimens in the H2SO4 sol have been black, but the specimens in the NaOH sol have not changed much. Figure 5(c) shows the surface images of specimens after immersion in different solutions after ultrasonic cleaning. We can see that the amounts of corrosion traces of the USQ specimen are obviously weakened compared with the UUSQ specimen. This is due to the reduction reaction of the oxygen in the cathode (Eq. 1).
\[ O_2 + 2H_2O + 4e^- = 4OH^- \] (1)

The \(H^+\) in \(H_2SO_4\) sol will consume the \(OH^-\) and promote the corrosion process, while the \(OH^-\) in \(NaOH\) sol will hinder the reduction reaction of the oxygen in the cathode, which is unfavorable to the corrosion process.

The corrosion weightlessness was calculated by measuring the quality of specimens before and after immersion for 259.2 ks (3 d) in different mediums. Figure 6 shows the corrosion weightlessness associated with the PH of solutions. As the PH of the mediums increase, the corrosion weightlessness gradually decreases. And the corrosion loss of the UUSQ specimen is greater than that of the USQ specimen. Thus, the results of immersion corrosion tests indicate that the corrosion resistance of the specimen’s decreases as the PH value of the mediums decreases, and USQ has a good inhibition effect on the corrosion of 35CrMoV steel in aqueous solution containing \(Cl^-\).

**Figure 5.** Appearance of specimens after immersion in the solutions (a) at starting time, (b) at immersion for 259.2 ks (3 d), and (c) surface images of specimens after immersion.

**Figure 6.** Corrosion weightlessness as a function of PH, X.
3.3. Electrochemical tests

3.3.1. Open-circuit potential (OCP) and potentiodynamic polarization. The OCP of specimens measured in the solutions of different PH gradually reach a stable value (The change of potential is less than 2mv/s) after around 3600 s of immersion (Figure 7 (a)). Only slight difference can be noticed between UUSQ specimen and USQ specimen in the same solution, and the OCP of the USQ specimen is always higher than that of the UUSQ specimen. Figure 6 (b) shows the OCP at 1 s and at 3600 s as a function of X. The UUSQ specimen in acid solution shows the highest average potential, and the USQ specimen in alkaline solution shows the lowest average potential compared to the other specimens in other corrosion mediums.

Figure 8 (a, b) shows the cathodic polarization curves and anodic polarization curves, respectively. As can be seen from Figure 8 (a) and (b), the specimens in acid solution shows the highest current density compared with other solutions, and the USQ specimen always has lower current density than the UUSQ specimen in the same solution.

![Figure 7](image-url) (a) Open-circuit potential during the immersion tests in different solutions and (b) corrosion potential of specimen during immersion at 1 s and at 3000 s.

![Figure 8](image-url) (a) Cathodic and (b) anodic polarization curves of specimen immersed in the different solutions

3.3.2. Electrochemical impedance spectroscopy (EIS). Figure 9 shows the Nyquist plots of the specimens immersed in solutions for 1 h. Among three experimental solutions, the size of capacitive arc increases with the increase of PH of the solution, and the magnitude of Nyquist plot of the USQ specimen in the same solution is larger compared to the UUSQ specimen. The magnitude of Nyquist plots
represents the corrosion resistance of the specimens, and they are positively correlated [22, 23]. Therefore, the specimen has the largest corrosion rate in acidic medium and the smallest corrosion rate in alkaline medium. And the corrosion resistance of 35CrMoV steel can be significantly improved by USQ.

Figure 9(d) shows the equivalent circuit model. All spectra can be well represented by the equivalent circuits. This model includes solution resistance ($R_{\text{sol}}$), charge-transfer resistance ($R_{\text{ct}}$), reference electrode (RE), working electrode (WE) and constant phase element (CPE), Q. The impedance can be expressed by an equation containing of $R_{\text{sol}}$, $R_{\text{ct}}$ and CPE parameters $n$ and $Q$ (2):

$$Z = R_{\text{sol}} + \frac{R_{\text{ct}}}{1 + (j\omega)^n Q R_{\text{ct}}}$$

Where $\omega = 2\pi f$, $f$ is the frequency in units of Hz. The value $n$ of the CPE parameter varies between 0 and 1. When $n = 1$, the CPE appears as a pure capacitor, and when $n = 0$, the CPE appears as a pure resistor. The fitting results are shown in Table 2. The larger the $R_{\text{ct}}$, the better corrosion resistance of the 35CrMoV steel in solution. This means that USQ can form a denser protective layer on the surface of the specimen, which increases the ion and charge transport resistance, delays the destruction process of the passivation film, and reduces the corrosion rate of steel. $Q$ represents the structure of solution/metal interface and the defect area in the oxide film of the metal [24]. So, the smaller $Q$ indicates that the USQ can reduce the defect of the oxide film on 35CrMoV steel. Therefore, the of EIS tests results show that the corrosion rate of the 35CrMoV steel decreases with the increase of PH of solutions, the corrosion resistance of the specimens can be significantly improved by the USQ.

**Figure 9.** Nyquist EIS spectra of 35CrMoV steel after immersion for 1 h and the equivalent circuit fitted with the experimental EIS data.
Table 2. Fitting parameters calculated by an equivalent circuit

| Elements     | PH  | 1         | 7         | 13        |
|--------------|-----|-----------|-----------|-----------|
| $R_{sol}$ ($\Omega \cdot \text{cm}^2$) | 27.46/30.03 | 277.3/270 | 24.87/25.48 |
| $Q$ ($\text{S} \cdot \text{sn cm}^{-2}$) | $3.53 \times 10^{-4}/3.30 \times 10^{-4}$ | $3.14 \times 10^{-4}/2.83 \times 10^{-4}$ | $4.47 \times 10^{-5}/3.71 \times 10^{-5}$ |
| $n$          | 0.91/0.91 | 0.63/0.67 | 0.85/0.90  |
| $R_{ct}$ ($\Omega \cdot \text{cm}^2$) | 26.91/33.38 | 2911/3175 | 6.60$\times 10^5$/1.76$\times 10^5$ |

Note: The denominator represents the fitted parameters of the UUSQ sample, and the numerator represents the fitted parameters of the USQ sample.

3.4. Surface observations and analysis

Figure 10 shows the SEM images of specimens and completely different surface morphology are observed for different specimens in different solutions. The results of immersion corrosion tests show that the corrosion rates of the specimens after immersion for 259.2 ks (3 d) are different in different solution. Obvious corrosion cracks can be observed clearly in H$_2$SO$_4$$_4$$_4$ and NaCl$_4$$_4$$_4$, and the obvious corrosion pits can be observed on the specimens’ surface in H$_2$SO$_4$$_4$$_4$, while there are no obvious changes on the surface of the specimens in NaOH$_4$$_4$. Additionally, the corrosion of the UUSQ specimen is more serious compared with the USQ specimen in the same solution. For example, the corrosion cracks of the USQ specimen were narrower, shallower, and sparse than that of the UUSQ specimen (Figure 10(a, d) (b, e)). This is because the ferrite grains are more susceptible to corrosion [25]. The results suggest that the corrosion rate increases with the decrease of PH of the solution, and ultrasonic vibration has a good corrosion inhibition effect on 35CrMoV steel in the 10 mmol/L Cl$^-$ aqueous solution. These results correspond with the electrochemical tests.

![Figure 10](image_url)
4. Conclusion
The effects of USQ on corrosion of 35CrMoV steel corrosion in different solutions were studied by SEM and EIS.
1) Ultrasonic waves can improve the quenching intensity of the quenching medium, thereby refining the martensite and reducing the residual ferrite in the 35CrMoV steel.
2) In acidic, neutral and alkaline medium with the same Cl\(^-\) concentration, the corrosion resistance of 35CrMoV steel decreases as the PH value of the mediums decreases.
3) Ultrasonic-aided quenching (USQ) can significantly improve the corrosion resistance of 35CrMoV steel compared to the un-ultrasonic-aided quenching (UUSQ) specimen.

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