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An investigation of pitting initiation mechanism of 1Cr12Ni2W1Mo1V steel after induction hardening

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Pitting potential of the 1Cr12Ni2W1Mo1V steel specimens, which is hardened and tempered at different temperatures, was measured under different corrosion environments and different stress levels. Test results showed that the external stresses have great influence on the pitting initiation of the 1Cr12Ni2W1Mo1V steel besides the material processing, microstructure and corrosion environments. Pitting potentials increase with decreasing of the concentration of chloride ion and have a linear relationship with log C_{Cl^-}. Under a certain concentration of chloride ion, the effects of pH on the induction-hardening specimens after low temperature tempering are negligible, while the effect of pH on the high temperature tempered specimen is relatively great. Pitting potentials decrease dramatically with the increasing of the stress when the stress is lower than 50 MPa; pitting potentials decrease little with the increasing of the stress in the region of 50–400 MPa; pitting potentials tend to be stable when the stress is higher than 400 MPa. Based on the test results, a mathematical expression of passive film cracking coincides with the experimental results. Heat treatment have great effects on the corrosion resistance of 1Cr12Ni2W1Mo1V steel. © *2000 Kluwer Academic Publishers*

1. Introduction

1Cr12Ni2W1Mo1V steel which is used for the steam turbine last stage blades, not only suffers complex stresses, but also suffers corrosion, especially pitting corrosion which is due to corrosive deposits condescend in the blade surface from the impurities of the steam in the working environment. 1Cr12Ni2W1Mo1V steel inclines to the pitting corrosion. Studies [1, 2] show that stress corrosion and corrosion fatigue cracks mostly initiate in the pitting corrosion points, which result in the failure of the blades. So, investigation of behaviors and mechanism of pit initiation is important to increase lifetime of blades and improve heat-treatment processing of the blades steel. Corrosion resistance of metal materials have great relation with their surface passive films [3]. Recent studies of pit initiation try to explain the pit initiation phenomena in ideal metal surfaces (no physical defects such as inclusions, heterogeneity of composition, etc). These theories believe that the initiation of pitting corrosion is due to Cl^- of corrosive environment penetrates and migrates through the passive films, and upon reaching the metal/film interface, results in film breakdown. However, the materials used mostly have defects, defects, corrosion environments and stresses have great effects on the formation of passive film and the breakdown of the film. Therefore, during the study of mechanism of pitting corrosion initiation, the materials, heat-treatment processing, corrosive environment and stress should all be considered, the actual mechanism of pitting corrosion initiation can be reached.

2. Experimental setup

The electrochemical method was used to measure the pitting tendency of materials. This theory divides the corrosion process into oxidization and reduction, and assumes that all oxidization rates are equal to all reduction rates on the corrosion surfaces. The dynamic potential method uses two main characteristic potentials: pitting potential E_b and passive potential E_p to measure the pitting tendency of materials. The typical polarization curve of stainless steel in Cl^- solution is shown

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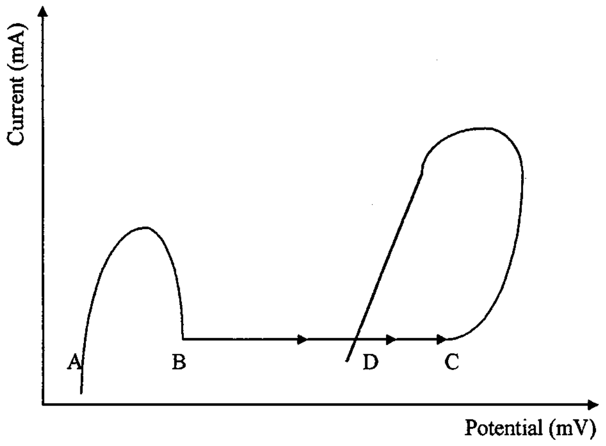


Figure 1 The typical anodic polarization curve of stainless steel in Cl^- solution.

in Fig. 1. In Fig. 1, anodic polarization starts from the corrosion potential A, the metal is at active dissolution process, current increases rapidly with the increase of the potential. When potential reaches point B, passive film forms on the metal surface, current decreases and reaches a certain value and keeps unchangeable with the increase of potential. When potential increases to point C, current starts to increase. This point means the partials of the passive film, and the potential at the point is the pitting potential E_{b}. With the increase of potential, current will continue to increase. Then reverse the scanning direction, current decreases with the decrease of the potential and reaches point D which is the passive potential E_{p}.

The material used in study is partial induction hardening 1Cr12Ni2W1Mo1V steel tempered at 540°C, 350°C, 250°C respectively. The measured area of samples shown in Fig. 2a is 0.25 cm^2, the other areas are sealed with epoxy, although there are crevice corrosion on the interface of the sample and the epoxy, the measured areas were not found. And the measured surfaces are all polished with 5# metallographic sand paper before the experiment. The experiment of the effect of chloride ions on pitting potentials is performed in sodium chloride solution, and the concentration of the solution is from 0.0001 mol/L to 4.473 mol/L and pH value is 7. The experiment of the effect of pH values on pitting potentials is performed in sodium chloride solution, and concentration of the solution is 4.473 mol/L that has different pH values. The pH values were controlled by adding HCl and NaOH solution and measured by standard pH meter. Before experimenting, every solution was deoxidized by argon for an hour. The anodic-polarization curves which were used to measure the pitting potentials, were measured by dynamic potential method, assistant electrode is Pt, and reference electrode is 232 type saturation calomel electrode, scanning speed is 10–15 mV/min. The sample used in measuring the effect of stress on the pitting potentials is shown in Fig. 2b, there is 40 mm length of partial induction hardening region in the middle of the sample, measured regions are induction hardening region and its transitional region, and measured area is 0.3 cm^2, the other areas are sealed with epoxy. The experiment is performed in sodium chloride solution, and the concentration of the solution is 4.373 mol/L, pH values is 7. The experiment is performed in atmosphere. The stresses are loaded through self-made equipment shown in Fig. 3. The stresses used in the experiments are 0, 49 MPa, 98 MPa, 196 MPa, 294 MPa, 392 MPa, 490 MPa and 588 MPa respectively. The pitting potentials

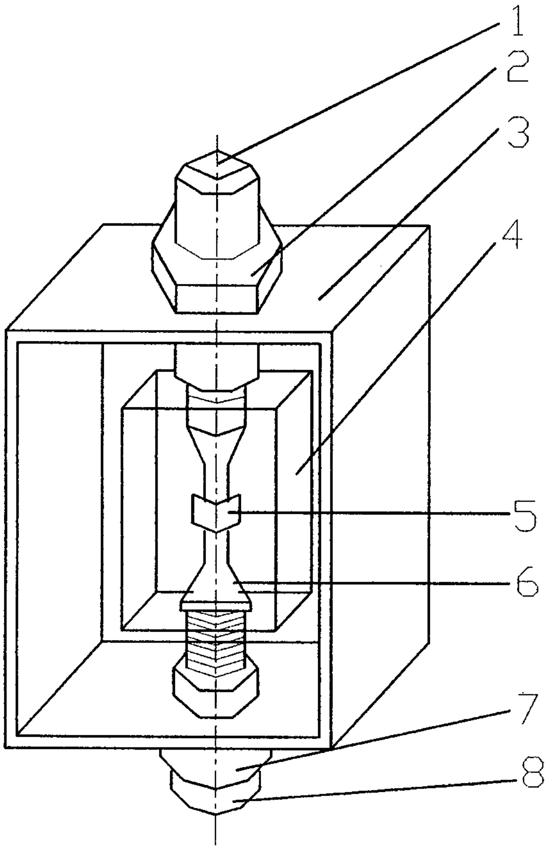
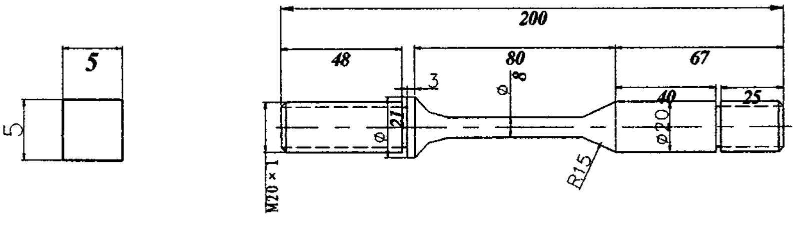


Figure 3 Schematic of experimental setup: 1, Bolt; 2, Nut; 3, Load base; 4, Corrosion chamber; 5, Pt electrode; 6, Specimen; 7, Sphere seal; and 8, Sphere support.



(a) (b)

Figure 2 Corrosion specimens.

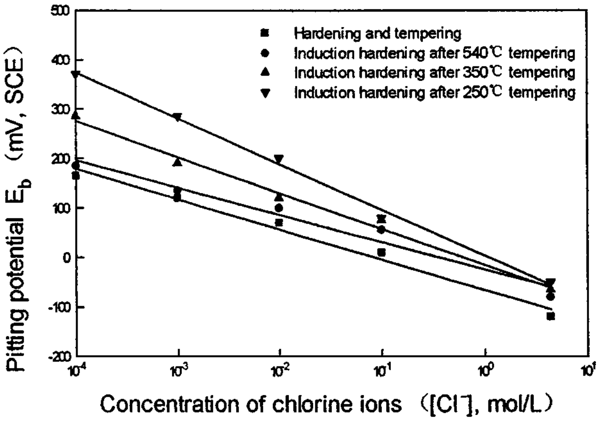


Figure 4 The relationship between pitting potential and the concentration of chloride ions.

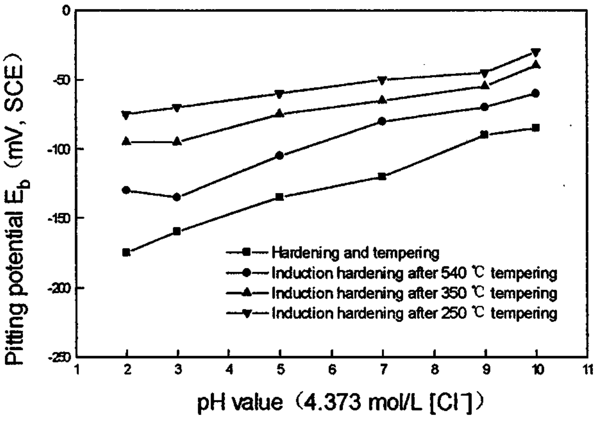


Figure 5 The relationship between pitting potential and pH values.

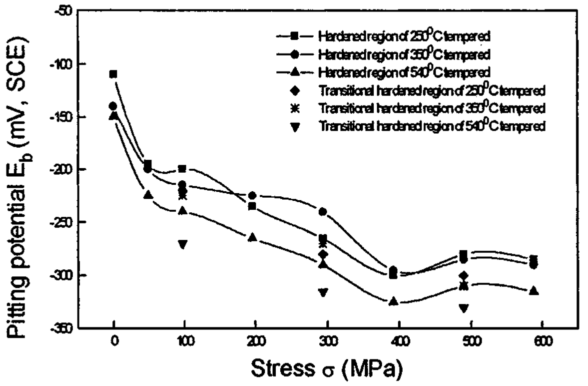


Figure 6 The relationship between the pitting potential and stress (4.373 mol/L Cl^-, pH = 7).

were measured through dynamic potential method measuring anodic-polarization curves. Assistant electrode is Pt, to reduce experimental error, the assistant electrode is arc and is concentrated with the sample so as to maintain the equal distances between assistant electrode and the working surfaces of the samples. Reference electrode is 232 type saturation calomel electrode, scanning speed is 10–15 mV/min. The samples are all polished with 320# metallographic sand paper before the experiment.

3. Results and discussion

Fig. 4 is the relationship between pitting potentials and the concentration of chloride ions. The pitting potentials of four different heat-treatment specimens decrease with the increasing of the concentration of chloride ions, and pitting potential has linear relationship with log C_{cl^-}. The pitting potentials of induction hardening specimens are higher than those of hardening and tempering specimens under the same level of concentration of chloride ions. With the increasing of tempering temperature (from 250°C to 540°C), the pitting potentials of induction hardening specimens decrease gradually under the same level of the concentration of chloride ions. The difference between the pitting potentials of three different induction-hardening specimens decreases gradually with the increasing of the concentration of chloride ions. Compared to induction hardening specimens, the pitting potentials of hardening and tempering specimens is the lowest, but has only a little bit of difference with those of induction hardening specimens after 540°C tempering.

Fig. 5 is the relationship between pitting potentials and pH values. pH values have slight effects on the pitting potentials under the certain concentration of chloride ions (4.373 mol/L Cl^-). The trend is clearer for induction hardening specimens after lower temperature tempering specimens. When pH values equal to 2 or 3, the pitting potentials of induction hardening specimens are nearly the same values, but as for hardening and tempering specimens, pH values have relatively great effects on the pitting potentials.

Fig. 6 is the relationship between pitting potentials and stresses. The pitting potentials of induction hardening transitional regions are lower than those of induction hardening regions. The difference is about 10–30 mV. For the induction hardening specimens after three different temperatures tempering, there are three stages of the pitting potentials with the increasing of stresses: (1) pitting potentials decrease dramatically with the increasing of the stresses when the stress is lower than 50 MPa; (2) pitting potentials decrease gradually with the increasing of the stresses when the stresses are in the region of 50–400 MPa; (3) pitting potentials continue to increase when the stress is higher than 400 MPa, while stresses reach 500 MPa, the pitting potentials tend to be stable, and nearly no change with the increasing of the stresses.

Fig. 4–6 showed that the corrosion resistance of induction-hardening specimens after 250°C tempering is the highest.

4. Discussion

Currently there are four pitting initiation mechanism: (1) competitive ion absorption theory; (2) complex ion formation theory; (3) ion penetration theory; (4) chemico-mechanical theory. Although these theories can account for most of the experimental data qualitatively, no quatitive treatment has developed so far, they are many shortcomings. Macdonald. etc. [4, 5] propose a model to explain pitting initiation as breakdown of passive film formed in metal surface: the growth of a passive film involves transport of both anions (chloride ions) and cations (metal ions) or their respective vacancies. Furthermore, anions diffuse from the film/solution (f/s) interface to the metal/film (m/f) interface and subsequently result in film thickening. On the other hand, cation diffusion, while not excluded, results only in dissolution and not in the growth of the primary passive film. One consequence of the diffusion of metal cation from the m/f to the f/s interfaces is that metal vacancies (or "metal holes") are created at the metal/film interface. These metal "holes" will tend to submerge into the bulk of the metal and hence to "disappear". However, when the cations diffusion rate (i.e. the metal hole production rate) is higher than the rate of "metal hole" submergence into the bulk, the metal holes will start piling up and hence will form a void at the metal/film interface (this is the process of pit initiation). When the void grows to a certain critical size, the passive film suffers local collapse which then marks the end of pit incubation period. Subsequently, the collapse site dissolves much faster than any other place on the surface thereby leading to pit growth. At the same time, mathematical expression for the relation between the pitting potential and the concentration of chloride ions is as following:

$$E_{\mathrm{b}} = \frac{4.606RT}{xF\alpha}\log\frac{J_{\mathrm{m}} - A - B\varepsilon_{\mathrm{p}}}{J^{0}\mu^{-x/2}} - \frac{2.303RT}{\alpha F}\log a^{\mathrm{cl}^{-}} \tag{1}$$

$$J^{0} = xK D_{\mathrm{VM}^{x}}\left[\frac{N_{\mathrm{V}}}{\Omega}\right]^{1+x/2}\exp\left(\frac{-\Delta G_{\mathrm{s}}^{0}}{RT}\right) \tag{2}$$

$$K = \frac{F\varepsilon}{RT} \tag{3}$$

where J_{m} is the rate of submergence of the metal holes into the bulk metal, x is the charge on a cation, ε is the field strength in the film, $D_{\mathrm{VM}^{x}}$ is the diffusivity of the cation vacancy, N_{V} is Avogadro's number, Ω is the molecular volume per cation, $\Delta G_{\mathrm{s}}^{0}$ is the charge in Gibbs energy for the Schottky-pair reaction, α is a constant, F is Faraday's constant, $a_{\mathrm{Cl}^{-}}$ is the activity of chloride ion in solution, ε_{p} is effective strain, μ is the chemical potential, A and B are material constants respectively.

From Equation 1, pitting potential decreases with the increasing of the concentration of chloride ion in solution and pitting potential has linear relation with $\log a_{\mathrm{Cl}^{-}}$, which coincides with experimental results in Fig. 4 and the experimental result of Janik-Czachor [6]. pH values have slight effects on pitting potentials, which mainly due to the formation of blocking section in pit so that the pH values in blocking section keep constant [7]. Fig. 6 shows that when stress is lower than 50 MPa, the pitting potentials of three induction hardening specimens decrease dramatically with the increasing of stress, this may be due to the difference of Young's modulus between matrix and oxidate, sulphide and alloy carbide, under the effect of stresses, phase interface formed relative great tensile stress resulting from stress concentration, so as to promote the breakdown of passive film which results in pitting potentials decreasing dramatically. When stress is in the region of 50–400 Mpa, the change of the pitting potentials with the increasing of stress is basically the same for three different induction hardening specimens. With the stresses increasing, interface regions between second phase and matrix will gradually yield, resulting in stress reducing near the interface, so that pitting potential decreases gradually with the increasing of stress in the region of 50–400 MPa. Compared to lower stresses, this effect is relatively slight. When stress is greater than 400 MPa, when phase interface region yield fully, pit still initiates in phase interface, with stress increasing further, the stress has no further effect on pitting potentials.

Under different experimental conditions, the corrosion resistance of induction-hardening specimens after 250°C, 350°C and 540°C tempering is better than that of hardening and tempering specimens and the corrosion resistance of induction-hardening specimens after 250°C tempering is the highest. This may be caused by the different microstructures of the material after different heat-treatment. Studies [8] showed sulphide, oxide and carbide have great effects on the pitting initiation of stainless steel. There are different kinds of carbides due to different tempering temperatures. There are $(\mathrm{Fe,Cr})_{23}\mathrm{C}_{6}$ and $(\mathrm{Fe,Cr})_{7}\mathrm{C}_{3}$ carbides after 540°C tempering, $(\mathrm{Fe,Cr})_{7}\mathrm{C}_{3}$ and $(\mathrm{Fe,Cr})_{3}\mathrm{C}$ carbides after 350°C tempering, and $(\mathrm{Fe,Cr})_{3}\mathrm{C}$ carbides after 250°C tempering. Compared to $(\mathrm{Fe,Cr})_{7}\mathrm{C}_{3}$ and $(\mathrm{Fe,Cr})_{3}\mathrm{C}$ carbides, the precipitation of $(\mathrm{Fe,Cr})_{23}\mathrm{C}_{6}$ carbides decreases chromium in the matrix around the carbide and worsens the corrosion properties of 1Cr12Ni2W1Mo1V steel.

5. Conclusions

(1) The pitting potentials decrease with the increasing of the concentration of chloride ions, and have linear relationship with $\log \mathrm{C}_{\mathrm{Cl}^{-}}$;

(2) Under a certain concentration of chloride ion, the effects of pH on the induction-hardening specimens after low temperature tempering are negligible, while the effect of pH on the high temperature tempered specimen is relatively great;

(3) For the induction hardening specimens after three different temperatures tempering, there are three stages of the pitting potentials with the increasing of stresses: (1) pitting potentials decrease dramatically with the increasing of the stresses when the stress is lower than 50 MPa; (2) pitting potentials decrease gradually with the increasing of the stresses when the stresses are in the region of 50–400 MPa; (3) pitting potentials continue to increase when the stress is higher than 400 MPa, while stresses reach 500 MPa, the pitting potentials tend to be stable, and nearly no change with the increasing of the stresses;

(4) Based on the experimental analysis, the pitting potential mathematics expression coincides with the experimental data;

(5) The corrosion resistance of induction hardening specimens after 250°C tempering is the highest, and the heat-treatment have great effects on the pitting corrosion resistance of 1Cr12Ni2W1Mo1V steel.

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