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Healing of hydrogen-attacked cracks in split specimens with recovering heat treatment in vacuum

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Abstract: The healing mechanism of hydrogen-attacked cracks in low carbon steel and Cr-Mo steel and its influencing factors during the healing process were studied by recovering heat treatment of split specimens in vacuum. The result showed that crack pacing turns much smaller under the condition of pure heating, especially for crack tips. The healing effect is well related to the length of cracks with the shorter in priority. By the primary mechanism of thermal diffusion, iron and carbon atoms must diffuse at the high speed in steel to realize that plasticity deformation energy exceeds and overcomes surface tensile force energy. In addition, phase transformation and stress-stain relationship also have positive effects on the process.

Key words: hydrogen-attack; crack; healing; heat treatment

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1 Introduction

Some work has been doing about the mechanism of crack healing [1-6], however, it has not found any report in crack healing caused by hydrogen-attack. This paper is based on the experiment using recovering heat treatment of split specimens in vacuum environment, so as to study the crack healing process in 20G steel and Cr-Mo steel to different degrees. The emphasis probes into original inner crack conglutination in materials, discusses the positive action of phase transformation during the course of heat treatment, and investigates the influence of alloy elements (especially Cr and Mo) on the healing process. The figures of the same area within the same specimen before and after the heat treatment can be observed originally and some contrasts can be made by this means, which is of great importance to the research of crack healing mechanism. But former inner cracks are turned into surface ones after split, so there is no methane which exists in the hydrogen-attack cracks.

2 Experimental

Materials for this experiment are 20G steel, 15CrMo steel and 2.25Cr1Mo steel. The chemical composition (mass fraction, %) of 20g steel is: C, 0.21; Si, 0.15; Mn, 0.40; S, 0.035; P, 0.032. The chemical composition (mass fraction, %) of 15CrMo steel is: C, 0.14; Si, 0.27; Cr, 0.95; Mo, 0.48; Mn, 0.55; S, 0.031; P, 0.035. The chemical ingredients (mass fraction, %) of 2.25Cr1Mo steel are as follows: C, 0.17; Si, 0.34; Cr, 2.25; Mo, 0.90; Mn, 0.54; Ni, 0.13; S, 0.03; P, 0.03. Hydrogen-attacked cracks available within the specimens were gotten in the way by which materials were put into vessels where there existed different temperatures, pressures and time (All hydrogen-attack conditions were above each corresponding Nelson Curves). Exposed in the environment with a hydrogen pressure of 18 MPa and kept for 480 h (20 d), 20G steel was heated to these temperature respectively: 300, 350, 480°C; while another 20G specimen was heated to 400°C for 240 h (10 d) with the same hydrogen pressure. 15CrMo steel was heated to 300°C for 240 h (10 d) with a hydrogen pressure of 18MPa, and 2.25Cr1Mo steel was heated to 450°C for 480 h (20 d) with a hydrogen pressure of 18 MPa.

First, specimens with hydrogen-attacked cracks were split, furbished, polished, eroded and marked. Then took them to the optics microscope and SEM so as to observe their beginning appearances before heat

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treatment. After that they were encased and heated in quartz tubes which have vacuums of 1.33×10^{-2}-1.33×10^{-3} Pa. 20G steel was kept at 650°C and 1000°C for 30 min and 120 min respectively before taken out for cooling down. 15CrMo steel and 2.25Cr1Mo steel were cooled down after being heated up and kept at 600°C for 30 min and 360 min. Finally optics microscope and SEM were used to look into the same area around marks done before, some contrasts were made with the beginning figures of cracks that were not heated, the experiment results were analyzed and discussed.

3 Results and discussion

Under experimental conditions above, all specimens experience hydrogen-attack, with methane bubbles or cracks formed along grain boundaries. The structural characteristics of hydrogen-attacked 20G steel are listed as **table 1**. Within carbon steel, a lot of holes, tiny cracks appear along the weak parts like stratum organism or chain fillings, as shown in **figure 1** (a) and **figure 2** (a). In 15CrMo steel cavities appear regularly along grain boundaries, few of which are within crystals, and slight cracks are found somewhere along grain boundaries, as shown in **figure 3** (a). In 2.25Cr1Mo steel cavities are extremely few, for hydrogen-attacked cracks are found under such conditions, as shown in **figure 4** (a). Cracks of the same specimen are distributed randomly, with partially different sizes, shapes, quantities, and depths. Crack statuses are different according to different degrees of hydrogen-attack.

Table 1 Structural features of 20G steel after hydrogen-attack

Hydrogen-attack condition	Hydrogen-attack grade	Microcosmic structural features			
		Pearlite / %	Pearlite appearance	Cracks along grain boundaries	Degree of de-carbonization
T=300°C P=18 MPa t=28800 min	Slight de-carbonization and slight cracks along grain boundaries	>15	Globosity, some in short slice	Tiny bubbles, with continuous tiny cracks along grain boundaries	About 10%
T=350°C P=18 MPa t=28800 min	Clear de-carbonization and slight cracks along grain boundaries	About 10-15	Globosity, some in short slice, tiny piece of ferrite emerges within pearlite	Tiny bubbles, with continuous tiny cracks along grain boundaries	About 25%
T=400°C P=18 MPa t=28800 min	Relatively serious de-carbonization and cracks along grain boundaries	About 10	Basically globosity, part completely de-carbonized into ferrite	Tiny bubbles, relatively serious cracks along grain boundaries	About 50%
T=480°C P=18 MPa t=28800 min	Serious de-carbonization and cracks along grain boundaries	About 5	Globosity or spots, island-like ferrite emerges on the pearlite	Tiny bubble, serious cracks along grain boundaries	About 60%

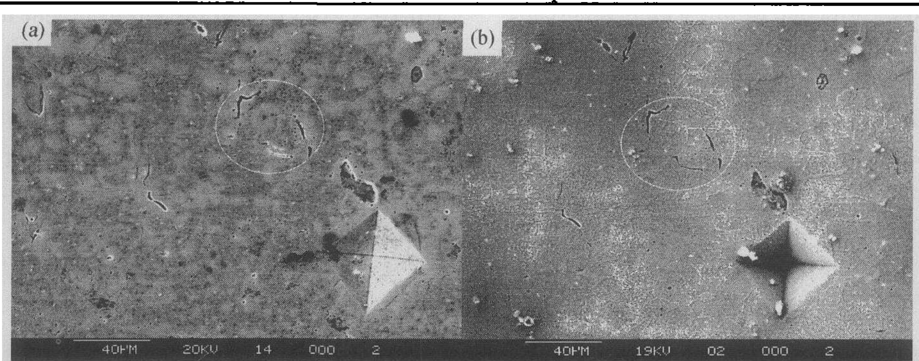

Figure 1 Healing comparison of hydrogen-attacked cracks in 20G steel: (a) cracks appearance after hydrogen-attack, 450°C, 18MPa, 480 h; (b) the same cracks after heat treatment in vacuum environment, 650°C, 30 min.

Figure 1(a) is the inner structure and crack appearances of 20G steel after hydrogen-attack under conditions shown as follows: 20G steel is heated to 300°C for 28800 min with a hydrogen pressure of 18 MPa.

Figure 1(b) is the same place of the same specimen observed at the original place after it has experienced recovering heat treatment in vacuum environment, that is, the specimen with hydrogen-attacked cracks was put into the furnace in which the temperature was 650°C, kept for 30 min and then cooled by air. The microcosmic metal structure before treatment appears to be a typical mixed organization of ferrite and pearlite. Having observed and compared the surface of the whole specimen before and after cicatrization treatment, it can be found that the specimen surface has generally turned black but quite shining. The rigidity points that originally have clear protrudings and concavings are now black after cicatrization treatment, and also small and flat with rounded edge. In fact, the cracks are wider, longer and deeper before treatment, with clear-cut edge. After heating, the cracks have obviously become narrower, shallower. Some cracks have become fairly faint, but most cracks do not close up.

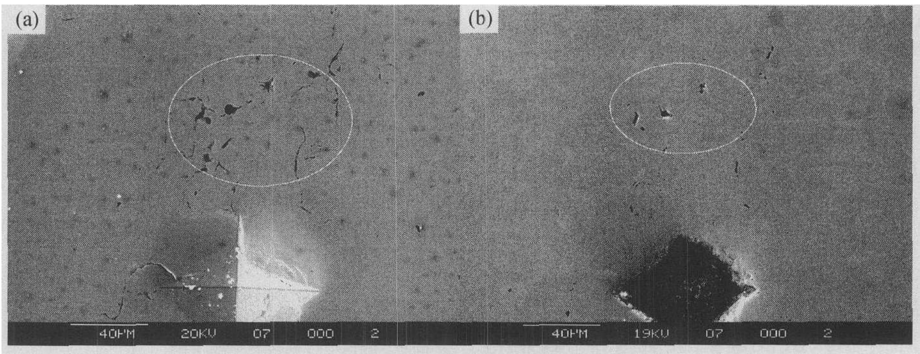

Figure 2 Healing comparison of hydrogen-attacked cracks in 20G steel: (a) cracks appearance after hydrogen-attack, 480°C, 18 MPa, 480 h; (b) the same cracks after heat treatment in vacuum environment, 1000°C, 120 min.

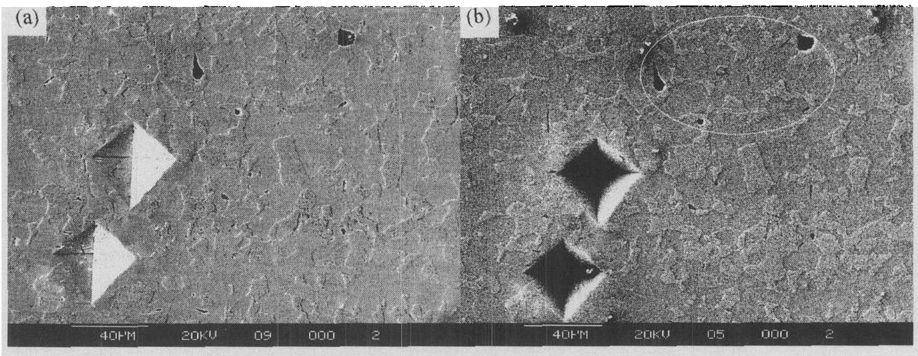

Figure 3 Healing comparison of hydrogen-attacked cracks in 15CrMo steel: (a) cracks appearance after hydrogen-attack, 300°C, 18 MPa, 240 h; (b) the same cracks after heat treatment in vacuum environment, 600°C, 30 min.

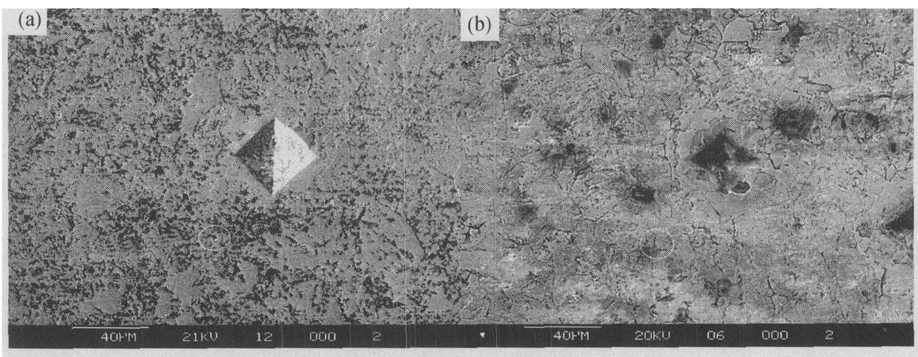

Figure 4 Healing comparison of hydrogen-attacked cracks in 2.25Cr1Mo steel: (a) cracks appearance after hydrogen-attack, 450°C, 18 MPa, 480 h; (b) the same cracks after heat treatment in vacuum environment, 600°C, 30 min.

Figure 2(a) is the inner structure and crack appearances of 20G steel after hydrogen-attack under conditions shown as follows: 20G steel was heated to 480°C for 28800 min with a hydrogen pressure of 18 MPa. Figure 2(b) is the same place of the same specimen observed at the original place after it has experienced recovering heat treatment in vacuum environment (put into the furnace in which it was 1000°C high, kept for 120 min and then cooled by air). Rising in hydrogen-attack temperature made the hydrogen-attacked cracks become much bigger and more numerous than what emerged at 300°C. And they formed a net along grain boundaries, which made more difficult for cicatrization. More energy is needed, that is, the temperature of heat treatment has to be increased and time for keeping heat has to be prolonged in order to cicatrize larger-sized cracks. After the heat cicatrization, most cracks have become irrecognizable, or even completely cicatrized, and the remaining cracks become slender, small and shallow.

Figure 3(a) is the inner structure and crack appearances of 15CrMo steel after hydrogen-attack under conditions shown as follows: 15CrMo steel was heated to 300°C for 14400 min with a hydrogen pressure of 18 MPa. Figure 3(b) is the crack of the same specimen observed at the original place after it has experienced recovering heat treatment in vacuum environment (put into the furnace in which it was 600°C high, kept for 30 min and then cooled by air). After heat treatment, marks of rigidity have become darker and smaller, and the whole sample has become round and flat. Observing and comparing the crack appearances, it can be found that cavities are numerous with irregular size. After the treatment, cavities become smaller and shallower, but most big cavities do not close up. The cicatrization degree of cracks is well related to the original crack size: small cavities are closed earlier, while bigger cavities have no obvious changes compared with those before treatment.

Figure 4(a) is the inner structure and crack appearances of 2.25Cr1Mo steel after hydrogen-attack under conditions shown as follows: 2.25Cr1Mo steel was heated to 450°C for 28800 min with a hydrogen pressure of 18 MPa. Figure 4(b) is the crack of the same specimen observed at the original place after it has experienced recovering heat treatment in vacuum environment (put into the 600°C furnace, kept for 30 min and then cooled by air). Observing and comparing the crack appearances, it can be seen that cavities before treatment do exist but are quite rare and tiny, so that it can be hardly found. After heat treatment, the original cavities can not be found, but many loose tiny cavities appear in the surrounding organism. At the beginning of hydrogen-attack, the surrounding structure is quite dense and solid. After the cicatrization, it become quite loose, especially in the area that is near the rest cavities, and the loose appearance is more obvious. So called 'loose' is actually an incomplete cicatrication of seeping back carbon which is caused by methane decomposition.

Surfaces of inner cracks are not smooth, in fact, there lie lots of bulges which have existed after the cracks formed. Under the condition of high-temperature heat treatment, these bulges get into touch with each other spontaneously so that tangent cervixes emerge, which provide shortcuts for diffusion weld, as shown in **figure 5**. Tensile force on exterior sunken cervixes of contiguity is equal to a kind of stress that makes the surface of both tangent cervixes nearer and nearer, which results in aftermaths of void content and void existence energy in different areas around cervixes: void content is higher than equilibrium one on the sunken surface of cervixes but lower on the protruding surface of cervixes. This difference in void content drives voids move from "source" to "trap", while atoms that move reversely diffuse to the cervix grooves, which reflects on cervix growth and amalgamation on the protruding tangent point. Void source includes exterior sunken cervixes of contiguity, grain boundary, dislocation, and big cavity. With the condition of this experiment, both opposite protruding crack surfaces contact and fuse gradually, which is actually an atom diffusion process, mainly including superficial diffusion mechanism, grain boundary diffusion mechanism, cubage diffusion mechanism and dislocation diffusion mechanism [7]. During the following process of cicatrisation, because of the property of surface tensility, that is, superficial area intends to be minimum in order to reduce superficial energy, 'separate tiny cracks' hems turn to be smooth and globular little by little. Continuously heated at high temperature, insular cracks shrink constantly until they disappear completely, which are also due to the function of superficial energy. At this point, both superficial diffusion mechanism and cubage diffusion mechanism are still dominant diffusion mechanism [8].

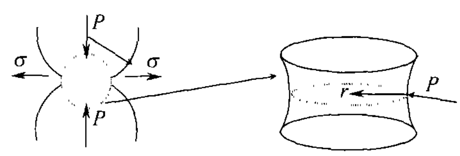

Figure 5 Sketch about how tangent cervixes come forth from protruding surfaces of inner cracks.

The conglutination process about hydrogen-attacked cracks is discussed from the point of view of energy analysis. Imagine interphase does move when heated, which bring about cubage change dV and acreage change dA. The total free energy change per cubage unit is ΔG; the surface tensility is γ; the distortion energy leaded by methane bubbles' growth is E_s. According to the energetic equilibrium relation,

$$\Delta G = -E_s + \gamma \cdot dV/dA \quad (1)$$

If it is bended circularly with the radius r, $dV/dA = 2/r$, then the equation above is:

$$\Delta G = -E_s + 2\gamma/r \quad (2)$$

The condition under which hydrogen-attacked bubbles or cracks can be healed is $\Delta G \le 0$, therefore,

$$E_s \ge 2\gamma/r \quad (3)$$

Hence, the impetus of hydrogen-attacked crack healing is distortion energy E_s leaded by methane bubbles', which is resistance during the growth course of methane bubbles. Under the prerequisite that both iron and carbon atoms diffuse at a high speed in steel, the qualification of healing of hydrogen-attacked cracks is that E_s is more than $2\gamma/r$. But for carbon steel, because the diffusion speed of iron and carbon atoms is relatively slow when heated at 650°C so that it controls all cicatrization course, and cracks can not be healed completely. According to the experimental results, the specific critical temperature and heating time which may lead to the thorough healing for carbon steel is still pending to be studied in the work aftertime.

It was reported that [9] hydrogen-attack caused the quantity of dislocations to increase greatly in materials. In cracks there exist many high-pressured methane bubbles, which produce somewhat stress on the surfaces of cracks around it. The specimen was heated above its austenitic temperature, then cooled down. When distorted austenite around cracks cools down, both dislocation and stress boost ferrite to form nucleus, which takes effect on the final minute microstructure and thus minute ferrite organism appears. This point can be proved by the experimental results.

During the course of recovering treatment, heating makes dislocation content in the damaged crystals decrease and dislocation status change, which induces polygon structure to come into being gradually [9]. This process reduces to some degree the possibility that dislocation areas with high density make it easy for phase transformation to engender nucleus of new phase, for dislocations can serve as favorable positions when new nucleus are born. At the same time this process brings about the deflected assemblage of carbide on the dislocation nets, which produces new different grain boundaries when growing, and these new boundaries are favorable position for nucleus' being in the course of phase transformation after cooled down. As the experimental results prove, cracks in materials bring about stress which work on the process of phase transformation [10]. Meanwhile, phase transformation has some retroaction on crack cicatrization. Around cracks ferrite produce nucleus and then grow up, which leads to stress on cracks. This action performs an effect just like loading a kind of microcosmic stress so as to accelerate crack conglutination.

15CrMo steel and 2.25Cr1Mo steel are chiefly chosen to produce high-temperatured pressure vessels that have hydrogen inside. Alloy elements in steel have two important effects. First, they bring forth more stable carbide ($Cr_{23}C_6$, $(Cr,Fe)_7C_3$, Mo_6C, *etc.*) and decrease carbon content a_c which balances with that in carbide [11], resulting in reduction of methane pressure. Second, alloy elements improve the creep intensity, that is, they enhance the value of elastic compliance "C". Both of these effects advance steel's resistance quality to hydrogen-attack. From the view of experimental results, cracks in alloy steel with Cr and Mo elements are intended to shrink when heated at high temperature. Because of reasons above mentioned, cracks in alloy steel are small in both quality and size. After heated, that is, input energy, cracks intend to cicatrize to some degree. The healing mechanism about alloy steel is still thermal diffusion. The necessary condition of hydrogen-attacked cracks for self-healing is that both carbon atoms and iron atoms in steel diffuse rapidly, and the impetus is distortion energy E_s leaded by growth of methane bubbles. Under the prerequisite above mentioned, the qualification of healing of hydrogen-attacked cracks is that E_s is more than surface tensile force energy so that E_s can overcome it.

From the discussion above, it is concluded that the impetus of cicatrization is surface energy brought when crack surfaces come into being, distortion energy leaded by microstructural change when cracks expand, and energy input from outside by means of heating as well. Within a certain range, with temperature T increasing and time t prolonging, inner cracks get more energy from outside. Correspondingly their driven energy mounts up, which certainly accelerates the healing process. Furthermore, raising T and prolonging t also reflect on growth of inner crystals, which causes stress to crack around it. This action performs an effect just like loading a kind of microcosmic stress, plastic deformation bringing about distortion. Its mechanism is equal to solidity weld. Considering these two factors, it is found that increasing T and t do good to crack healing.

4 Summary

(1) The experimental results of hydrogen-attacked cracks for self-healing in 20G carbon steel, 15CrMo steel and 2.25Cr1Mo steel by in-situ observations of recovering heat treatment of preset split specimens in vacuum is reported. The research proves that thermal diffusion is the mechanism of hydrogen-attacked cracks for self-healing, which happens when iron and carbon atoms diffuse at the high enough speed in steel and the plasticity deformation energy (E_s) led by methane bubbles exceeds and overcomes surface tensile force energy. In addition, phase transformation and stress-stain relationship also have positive effects

on the process.

(2) For hydrogen-attacked specimen made of 20G steel, cracks are not conglutinated completely when maintained at 650°C. Carbon atoms and iron atoms diffuse slowly in the condition and the healing process is controllable. While heated at 1000°C, cracks close obviously, however outside energy is not high enough to make cracks close entirely.

(3) For hydrogen-attacked Cr-Mo specimens, cracks only close partly at 650°C since diffusion speeds of carbon atoms and iron atoms are relatively slow, which in turn limits the healing degree. The healing degree is well related to the size of cracks, and short cracks close easier.

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