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# Disbonding of austenitic stainless steel cladding following high-temperature hydrogen service in hydro processing applications

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**Abstract.** Hydrogen charging and degassing of metal samples with a clad anti-corrosive layer were experimentally studied. Hydrogen charging of the samples was performed in a special chamber with the possibility of recording operating parameters that simulated the full cycle of the oil hydrocracking reactor, according to the requirements of the ASTM G146-01 standard. Cracking control was carried out using ultrasonic testing and acoustic emission signals. The moment of disbonding formation was established. Numerical modeling of hydrogen redistribution in a bimetallic sample with protective surfacing as a result of non-stationary thermal effects was carried out. It was found that heat changes change the diffusion of hydrogen in bimetal, creating non-equilibrium hydrogen oversaturation of local volumes of the fusion zone. The reliability of surfacing depends, in particular, on the kinetics of thermal processes. The critical value of hydrogen concentration was determined.

**Keywords:** Bimetallic fusion, Hydrogen concentration, Disbonding cladding.

## 1 Introduction

Many large pressure vessels operate at high temperatures 445–500°C and at high hydrogen partial pressures 15–17 MPa. These are typically fabricated from low alloy Cr-Mo steel and internally weld overlaid with austenitic stainless steel. After weld overlaid (surfacing), the pressure vessel is subjected to heat treatment at a temperature of 690°C, 24 hours. In this case, carbon diffuses from the base metal into the deposited layer, forming a brittle carbide layer along the fusion boundary [1-4]. During shutdown, hydrogen accumulates at the interface between the cladding and the parent material which occasionally causes disbonding of the stainless layer.

The mechanism of disbonding of the weld metal from the base has not yet been fully elucidated. But the main factor contributing to such destruction is considered to be hydrogen [1, 3-5]. It is shown [4-7] that during pressure vessel operation hydrogen diffuses outwards, distributing along the wall thickness in proportion to its solubility in the metal of the deposited layer, which has an austenitic structure, and mainly in the

metal with a pearlitic structure. During shutdown and cooling, the pressure vessel re-distributes hydrogen and its anomalous accumulation in an amount many times greater than the solubility limit. Released on carbide surfaces, hydrogen, according to Sieverts' law, causes a large increase in pressure, which causes destruction [5].

Therefore, in the future it is important to improve and study the technological schemes of application of surfacing, which would increase the resistance of the weld metal to detachment from the main.

This article presents the results of the study of the influence of surfacing methods and resistance to disbonding of the anticorrosive weld layer made in three ways at different cooling rates after high-temperature hydrogenation.

## 2 Research methodology

Experimental studies were carried out on samples with cladding, which in all characteristics of the base metal and clad, as well as the alloying zone correspond to the structure of the oil hydrocracking reactor. To determine the resistance to delamination of the anti-corrosive clad layer tests were performed according to the requirements of the ASTM G 146-01 standard. To saturation with hydrogen, after saturation with hydrogen and after laying the samples, ultrasound control is carried out. The crack formation was monitored by acoustic emission signals (AES) as soon as the specified temperature was reached [1]. After ultrasonic testing, a metallographic study of the fusion zone of the clad layer with the base metal was carried out at 200x magnification for the presence of disbonding.

### 2.1 Materials

As the main metal, we used steel 2,25Cr-1Mo-V brand SA336M F22V. We executed protective anti-corrosive surfacing in three ways:

- single-layer electroslog (batch I);
- manual two-layer (batch II);
- automatic two-layer cladding (batch III).

For cladding, we used austenitic stainless steel of type 347 (batch I) and 309L + 347 (1st and 2nd layers of batches II and III). The chemical composition and mechanical properties of steels are presented in Tables 1 and 2.

**Table 1.** Chemical composition of base and clad metals (%)

| Steel brand    | C    | Si  | Mn  | Cr   | Mo  | V    | Ni  | S     | P     |
|----------------|------|-----|-----|------|-----|------|-----|-------|-------|
| SA336M<br>F22V | 0.15 | 0.3 | 0.5 | 2.85 | 0.7 | 0.27 | 0.4 | 0.015 | 0.012 |
| 347            | 0.09 | 1.2 | 2.0 | 25   | -   | -    | 13  | 0.02  | 0.03  |
| 309L           | 0.03 | 0.8 | 0.7 | 23   | -   | -    | 13  | 0.02  | 0.03  |

**Table 2.** Mechanical properties of materials

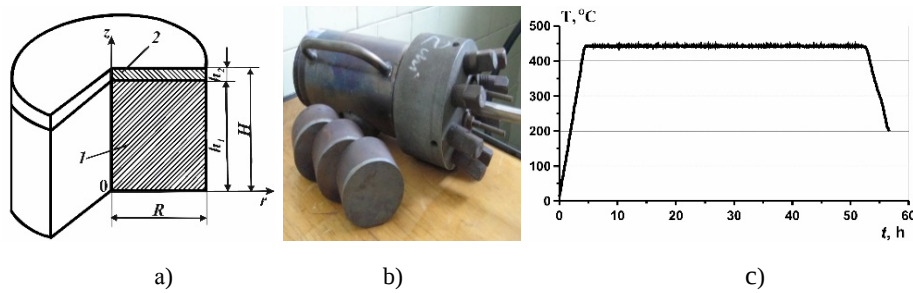
| Steel brand | $\sigma_b$ , MPa | $\sigma_{0.2}$ , MPa | $\delta$ , % | $\psi$ , % | T, K |
|-------------|------------------|----------------------|--------------|------------|------|
| SA336M F22V | 679              | 564                  | 22           | 77         | 293  |
|             | 540              | 470                  | 17           | 75         | 723  |
|             | 490              | 440                  | 19           | 80         | 813  |
| 347         | 560              | 310                  | -            | 25         | 293  |
|             | 412              | 207                  | -            | 40         | 623  |
| 309L        | 590              | 460                  | 40           | -          | -    |

According to the ASTM G146-01 standard, we made 30 cylindrical bimetallic samples 73 mm in diameter and 44 mm in height with a 6 mm thick clad layer. Afterward, the subjects were exposed to intermediate tempering at a temperature of 650÷660 °C for 4.5 h, followed by final tempering at a temperature of 700÷715 °C for 7 h, followed by hydrogen exposure. The samples prepared in this way underwent ultrasonic testing using a UD-12PU flaw detector, with an operating frequency of 5 MHz. 9 samples were taken from each batch, which had no visible defects, 3 pieces for each cooling rate.

## 2.2 Hydrogen charging technique / conditions

The samples were exposed to hydrogen in a special chamber (Fig. 1), which was placed in an electric furnace. During the experiment, control and registration of operating parameters were carried out in accordance with the requirements of the ASTM G146-01 standard:

- heating rate of the samples 80÷100 °C/h,
- tempering temperature 440÷445 °C,
- hydrogen pressure 17,45÷17,75 MPa,
- tempering time 48±1 h.



**Fig. 1.** Scheme of the experimental sample (a) [8], hydrogen charging chambers (b), control schedule of the process of heating, hydrogen charging, and cooling of bimetallic samples (c).

At the end of the hydrogen charging cycle, for a cooling rate of 20°C/h, the chamber was controlled to be cooled together with the oven to a temperature of 20°C. In the other

two cases, at a cooling rate of 100 and 300 ° C / h, the sample chamber was removed from the electric furnace and forced to cool in the air. The heating and cooling temperature were controlled by means of an electronic controller-meter of the RT-0102 type and a thermoelectric converter of the THA-1007 type with the possibility of processing the temperature influence diagram on a computer.

### **2.3 Ultrasonic control of the fusion zone**

Ultrasound testing was performed according to the requirements of the standard ASTM G 146-01 with a sensitivity of  $\varnothing$  3 mm on the flat-bottomed hole on the samples in the area of fusion of the anti-corrosion layer with the base metal. Ultrasound testing was performed both before hydrogen charging - after cladding and heat treatment and after hydrogen charging.

### **2.4 Acoustic emission control**

The crack formation was monitored by acoustic emission (AES) signals immediately after reaching the specified temperature, and the information parameter was the sum of the AES amplitudes in the observation time interval [9]. The peculiarity of this experimental technique is that along with the use of the main channel of AES registration, a known method of protection against background interference was used, selecting the latter with an additional channel and carrying out appropriate processing of information obtained by two channels according to [9, 10].

ES devices of serial production of the AF-15 type were used in the experiments. The bandwidth of the AES resonant piezoelectric transducers and filter units of the device was 0.2 - 0.4 MHz, and the total gain of the path of the main channel was equal to 70 dB. The time base of continuous AE control was limited to 30 h. The distribution of the sum of the AES amplitudes depending on the cooling rate at the base time interval is shown in Fig. 2

### **2.5 Metallographic research**

According to the ASTM G146-01 standard, macro sections of the fusion zones of the anticorrosive layer with the base metal were made. A study of the fusion zone before and after etching was carried out at a magnification of  $\times 200$  at various cooling rates of the samples.

## **3 Determination of residual hydrogen in clad steel**

The distribution of hydrogen concentration was determined in a cylindrical bimetallic sample 73 mm in diameter and 44 mm in height with a clad layer 6 mm thick (Fig. 1) by solving the Fick equation [7, 11]

$$\frac{\partial C}{\partial t} = \nabla(D(T)\nabla C), \quad (1)$$

where  $C = C(x, y, z, t)$  – concentration of hydrogen in the body,  $D(T)$  – diffusion coefficient, which depends on time and temperature.

First, we considered the sample hydrogen charging at a pressure  $P_{avt} = 17 \text{ MPa}$  and a temperature  $T_0 = 440^\circ \text{C}$  at a zero initial condition and boundary conditions on all surfaces of the cylinder as follows  $C_i = K_{s_i}(T_0)\sqrt{P_{avt}}$ , where  $K_{s_i}$  – hydrogen solubility,  $i = \gamma, \alpha$  refers to the cladded materials and the base. From a practical point of view, the solution of this problem makes it possible to determine the time when it can be assumed that an equilibrium hydrogen distribution is achieved everywhere in the sample for the given values  $P_{avt}$  and  $T_0$ .

Next, the problem of hydrogen degassing during cooling of the sample was solved. The boundary conditions on all surfaces of the sample for the temperature problem were set according to the chronograms of sample cooling recorded in the experiments (Fig 1.c). For the diffusion problem, the conditions for degassing the metal into the environment with hydrogen pressure were set  $P = 0$ . The stationary hydrogen distribution  $C_{0i}$  from the previous problem was taken as the initial condition. The cooling rate, as in the experiments, was respectively: 20; 100 i  $300^\circ \text{C/h}$ .

In work [12] it is shown that the width of the transition zone between the surfacing and the base metal, where the chemical composition changes gradually, is from 30 to 300  $\mu\text{m}$ . However, the diffusion and solubility coefficients of hydrogen do not change gradually within this region. The transition zone for them is less than 20 or 30 microns. Therefore, in the calculations, it can be assumed that they change sharply at the fusion boundary of materials, which is modeled by the line:

for steel base:

$$K_{s_\alpha}(T) = \begin{cases} 78.4 \exp(-2980/T), T \geq 573K \\ 13.9 \exp(-1989/T), T < 573K \end{cases}, \quad (2)$$

$$D_\alpha(T) = 2.06 \cdot 10^{-7} \exp(-2410/T) / [1 + 0.55 \cdot 10^{-4} \exp(3480/T)], \quad (3)$$

for steel cladding:

$$K_{s_\gamma}(T) = 46.8 \exp(-980/T), \quad (4)$$

$$D_\gamma(T) = 1.33 \cdot 10^{-6} \exp(-6610/T) / [1 + 3.62 \cdot 10^{-4} \cdot \exp(280/T)] \quad (5)$$

Values  $K_s$  are specified in units  $\text{ppm}/\sqrt{\text{MPa}}$ ;  $D$  - in  $\text{m}^2/\text{s}$ ; and the temperature in degrees Kelvin.

It should also be noted that for an inhomogeneous body, which is, in particular, a bimetallic compound, at different solubility coefficients  $K_{s_\alpha} \neq K_{s_\gamma}$  at the interface

between the materials, there will be a discontinuity in the magnitude  $K_s$  of the first kind. Therefore, in order to ensure the requirement of flow continuity, which will at the same time meet the condition of continuity throughout the body of the chemical potential, which is determined by the value of the ratio  $C/K_s$ , the solution of the hydrogen mass transfer problem (4) - (5) will be sought in the class of functions discontinuous at the surface of materials such that the equality should hold:

$$\frac{C_1}{K_{s_a}} = \frac{C_2}{K_{s_y}}, \quad (5)$$

where  $C_1$  and  $C_2$  values of hydrogen concentration in the base and the cladding, respectively.

The problem of heat and mass transfer formulated above was solved by the finite element method (FEM) [13]. The heat and mass transfer problem formulated above was solved by FEM. To do this, the area  $0 \leq r \leq R$ ,  $0 \leq z \leq H$  was divided into 6426 quadrangular linear finite elements (6515 nodes). Moreover, for both materials, the elements that are directly adjacent to the boundary of the separation of materials (bases and cladding) have the form of rectangles of size  $196,2 \times 10 \mu\text{m}$ , where their longer sides correspond to the radial direction. As the elements move away from the boundary of the section, their sizes increase. For high-temperature hydrogen charging, Fick's equation (1) was solved in two-time steps  $\Delta t = 2$  min and  $\Delta t = 4$  min. The relative calculation error was not more than 0.5%. During degassing, the problem was solved between 0 and 10000 h for all three cooling rates. A variable time step  $\Delta t$  was used during the calculation.

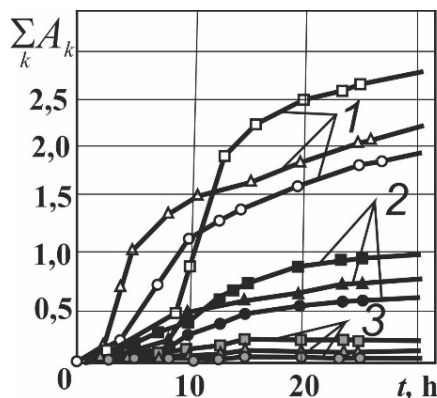
As a result of calculations, the change of hydrogen concentration in potential zones of hydrogen damage was determined over time. Next, having established from the experiments the moment of the beginning of crack formation, we assume that the calculated concentration corresponding to this moment and place is critical.

## 4 Results and discussion

### 4.1 Acoustic emission control

As expected, the most acoustically active samples were cooled at the maximum speed  $300^\circ\text{C/h}$ . Moreover, the process of crack formation in the samples can be divided into the following stages. The first, incubation, is marked by the fact that for the initial 2-3 hours of observations no AES is registered. After that, single AES of insignificant amplitudes appears for 3 - 4 h, which corresponds to the processes of plastic deformations and the formation of microcracks. The second stage begins at 5 - 6 hours of the experiment when the processes of macrocracking start to develop intensively. It is during this period that the determining amount of the AES is recorded, which possibly corresponds to the unification of micropores and the initiation of a crack.

After such rapid radiation of AES, which ends after 9 h, there is a period of "silence" lasting about 3... 3.5 h, followed by the third stage of ES generation, when slight radiation of ES with single discrete AES is restored until the end of the experiment, i.e. passes the final phase is the propagation of the crack. Therefore, we believe that in this case, the critical moment of damage is  $t_{cr} = 10,5$  h, after reaching room temperature.



**Fig. 2.** Dependence of the final count of the sum of the amplitudes of the ES signals on the observation time for different cooling rates of the samples: 300 (1); 200 (2) and 20 (3) °C/h.  
□ - I batch, Δ - II batch, ○ - III batch

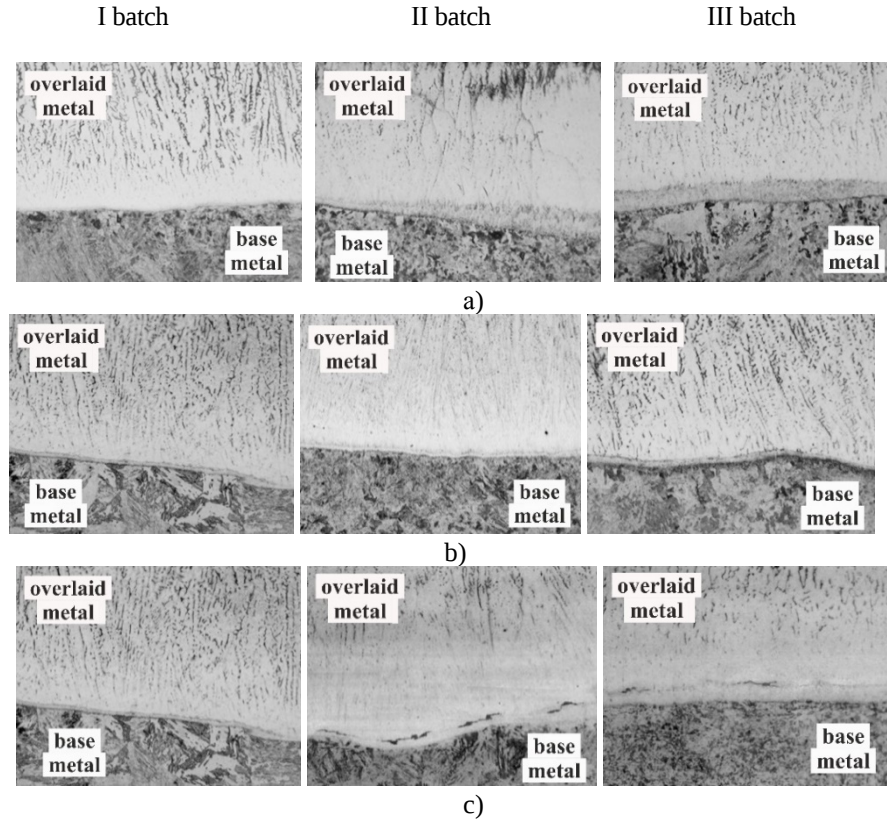
Samples cooled at a rate of 100 °C/h occupy an intermediate position in terms of ES activity. For samples cooled at a rate of 20 °C/h, ES signals are not recorded throughout the observation interval, indicating the absence of disbonding in them.

#### 4.2 Ultrasound and metallographic analysis

168 hours after hydrogen charging, the samples were subjected to ultrasonic testing for disbonding. It was established that at the cooling rate of the samples 300 °C/h the area of disbonding is 15-20% of the cladding area. At the cooling rate of 100 °C/h disbonding does not exceed 5% of the sample area that meets the requirements of ASTM G146-01 standard. In samples that were cooled at the rate of 20 °C/h, ultrasonic testing practically did not reveal any defects.

According to the requirements of ASTM G146-01, microsections of the fusion zones were manufactured and investigated at various cooling rates of the samples. Zones of fusion after etching in Marble reagent and magnification of 200 times are shown in Fig.3. For cooling at a rate of 20 °C/h, the fusion zone is typical for joining a pearlitic base metal with austenitic cladding. At cooling rates of 100 and 300 °C/h along the carbide layer fusion boundary, cracks formed on the side of the stainless steel cladding.

As can be seen from the figure, the most resistant to disbonding turned out to be samples with a single-layer cladding applied by a manual electroslag method (batch I), which is confirmed by acoustic and ultrasonic testing.



**Fig. 3.** Microsection of fusion zones of three batches of samples, depending on the methods of applying anti-corrosion cladding, at different cooling rates: a) – 20°C/h ; b) – 100°C/h ; c) – 300°C/h .

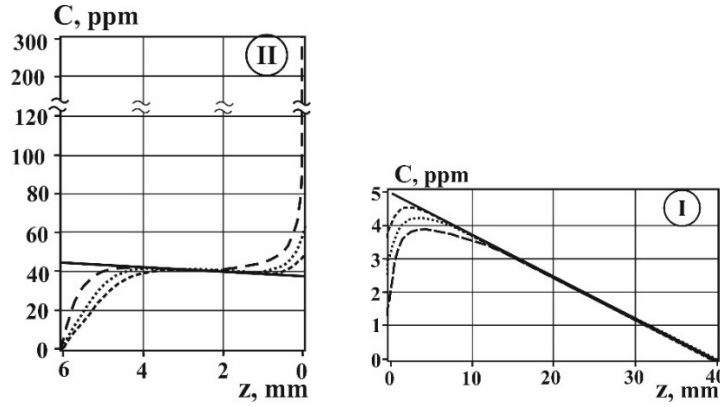
### 4.3 Hydrogen distributions

As a result of a numerical experiment, it was established (Fig. 4) that a non-stationary temperature field leads to the occurrence of peak concentrations in the cladding along the fusion boundary, which is 5-6 times higher than the equilibrium values for hydrogen charging conditions at high temperature and pressure. (Fig.5).

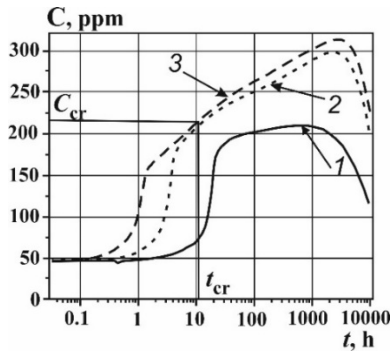
Moreover, with an increase in the cooling rate, the peaks of hydrogen oversaturation of the sample metal grow, and their formation is activated. Since the oversaturation zones are nonequilibrium and the sample is degassing in general, these peaks after a certain time (in this case, after several thousand hours) are smoothed out. (Fig.5).

The duration of the existence of a local over equilibrium supersaturation with metal is rather significant.

Having determined from the experiment the moment of crack formation, we take the calculated hydrogen concentration at the damage site corresponding to this time as critical:  $C_{cr} = C(t_{cr}) = 212\text{ppm}$  (Fig. 5).



**Fig. 4.** Distribution of hydrogen concentration in cladding (II) and in base metal (I) after high-temperature hydrogen charging (1) and cooling at different rates: 2 – 20°C/h; 3 – 100°C/h; 4 – 300°C/h.



**Fig. 5.** Time variation of the maximum hydrogen concentration at different cooling rates: 1 – 20°C/h; 2 – 100°C/h; 3 – 300°C/h.

## 5 Conclusions

A computational and experimental procedure for determining the critical concentration of hydrogen in a bimetallic compound was proposed. The experimental part of the procedure consisted of hydrogen charging of cylindrical samples with cladding in an autoclave and their further degassing. Experiment conditions and results meet the requirements of ASTM G146-01 standard for bimetallic compounds and severe operating conditions for oil hydrocracking reactors. After cooling, the development of damage in the samples was monitored by the method of acoustic emission. The time of the beginning of crack formation was established.

The computational part of the procedure consisted in solving the FEM problem of heat and mass transfer for a cylindrical bimetal sample. An example of numerical modeling of hydrogen redistribution in bimetal due to nonstationary thermal effects is given. It was found that heat exchange changes the hydrogen diffusion in bimetallic elements of structures, creating a nonequilibrium hydrogen oversaturation of the local volumes of the

fusion zone. The reliability of surfacing here depends, in particular, on the kinetics of thermal processes. The hydrogen concentration in the fusion zone, critical for the integrity of the bimetallic compound, has been established.

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