SMiRT-12 / K. Kussmaul (Editor)

G14/6

A NEW METHOD TO EVALUATE HYDROGEN-INDUCED DISBONDING SUSCEPTIBILITY IN STAINLESS STEEL WELD OVERLAYS

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ABSTRACT

Aiming at the disbonding problem of stainless steel weld overlay in hydrogenation reactors, this paper presents the concept of the "Disbonding Hydrogen Concentration" C_{dc} and a new method for the evaluation of the resistance to disbonding of the welding clad. The time for disbonding to occur t_{dc} was determined by hydrogen charging tests on clad specimens, and the hydrogen concentration at the locality of the fusion line C_{dc} at time t_{dc} was calculated by simulation computations based upon hydrogen diffusion law. It has been found that C_{dc} value is practically constant for specimens made by a specific manufacturing process and is therefore a material property parameter, which could be used to evaluate the resistance to disbonding of that category of specimen. Using the new method, it is also possible to correlate the disbonding occurring in industrial reactors to the results of specimen tests carried out in laboratories.

1 INTRODUCTION

Since early 1960's, pressure vessels made of Cr-Mo steel and clad with welded stainless steel overlay have been widely used in the petroleum industry for hydrogenation processes. By the 1970's, several cases of underclad disbonding were reported and became a major concern for both the users and manufacturers of hydrogenation reactors. Disbonding could be the chief factor affecting the safe service of those reactors, since underclad cracks could develop and might branch into unfavourable directions. A great deal of research work have been carried out, mainly by the manufacturers, to insure better resistance to disbonding of the welded structures. However, the prevention or lessening of disbonding in in-service reactors has been assessed by very few authors and is still an unsolved safety problem in petroleum production.

2 A BRIEF REVIEW OF THE PREVAILING METHODS OF EVALUATION

A fundamental means to tackle the above problem is the evaluation of the susceptibility to hydrogen-induced disbonding of the stainless overlay. The usual procedure is to charge clad specimens with hydrogen and then measure the degree of disbonding, which is expressed by the percentage of disbonding area in the tested specimens.

Disbonding tests were carried out by Watanabe[1] with hydrogen charging in an autoclave at high temperatures and high pressures. Fig.1 shows the results for one group of specimens made by the same welding process. In this group of test, time of charging was kept as 24h and the rate of cooling kept as 200°C/h, but the temperatures and pressures of charging were different, resulting in different degrees of disbonding. The degrees of disbonding were classified into serious (>5%), light (1-4%) and no disbonding (0%). Based upon such kind of tests, Watanabe proposed that the critical condition for and degree of disbonding can be determined by the proper combination of charging temperature and pressure from those test curves.

The results of disbonding tests carried out by Takeda et al[2] are quite different from those obtained by Watanabe. In their tests, the manufacturing process and size of the specimens were very close to those specimens used by Watanabe, the only difference is that they hand-welded layers of 309 stainless steel to the four outside surfaces perpendicular to the main overlay. Among the tests done by Takeda, the most serious test condition was: temperature 450°C, hydrogen pressure 15MPa, cooling rate 200°C/ h. No disbonding was found under such condition, though according to Watanabe's criterion, disbonding should happen. Obviously, the form of test specimens has great effect on test results.

Kinoshita[3] carried out comparison tests for specimens of different size under the same test conditions. All the specimens were taken from one and the same test plate, but one group of the test specimens has clad areas four times that of the other group. The results showed that the percentage of disbonding area is higher in the bigger specimens. Apparently, the size of the test specimens will affect the test results.

From the above, it can be seen that a common-acknowledged method of evaluation has not yet been established. First, there are a number of testing variables, such as charging temperature, hydrogen pressure, charging time, cooling rate etc., each could be taken as an independent factor, thus a large amount of testing is needed only to get qualitative indications. Secondly, the test results depend very much upon the type and size of specimens. Thirdly, the relative degree of disbonding does not directly reflect the resistance of the structure. Finally, how to relate the testing results on small size testing specimens to the real industrial reactor still remains an unsolved problem. Obviously, the above points also lead to the diversity of testing results reported by different authors[4]. In this paper, the authors try to postulate a material property parameter which can more correctly reflect the disbonding susceptibility of clad structure and can be used to correlate specimen tests to the industrial reactor.

3 MECHANISM OF HYDROGEN-INDUCED DISBONDING AND INFLUENCING FACTORS

Disbonding cracks appear in the locality of fusion line on the side of the stainless clad, along the grain boundary of coarse austenite crystals. The appearance of disbonding fracture surfaces feature typical hydrogen embrittlement fracture. It is commonly acknowledged that the disbonding of stainless steel clad is a kind of hydrogen-induced delayed cracking.

The factors influencing disbonding can be grouped into two categories. The first category is the structural factors, including the type of welding materials, the chemical composition of the welding and the base materials, the welding technology, etc. The resistance to hydrogen-induced disbonding depends on those factors and for a clad structure manufactured according to a specific procedure, it should be constant and could be represented by a certain parameter. The second category is the environmental factors, including the operating temperature, hydrogen partial pressure, exposure time, the cooling down history, etc. Those factors create the condition for disbonding to occur, which in essence is the local hydrogen concentration on the fusion line. For an industrial reactor, the critical condition might be reached during the shut-down process.

The hydrogen diffusion behaviour in a clad structure can be described by the non-uniform solubility diffusion model:

$$\frac{\partial C}{\partial t} = \nabla(DS \cdot \nabla(\frac{C}{S}))$$

where D is the diffusion coefficient, S is the solubility and C is the concentration of diffused hydrogen. Both D and S are the functions of metal structure, environment temperature and hydrogen pressure. The hydrogen diffusion behaviour in clad structures can be analyzed more conveniently utilizing the method of finite element or finite difference to solve the above equation. It has been found that when the environment of the clad specimen changes from high-temperature, high-pressure under hydrogen to ambient temperature and atmospheric pressure without the presence of hydrogen, at a certain time, unusual accumulation of hydrogen will occur on the fusion line on the side of the clad. Referring to the fracture appearance of the disbonding crack, this unusual accumulation of hydrogen is considered to be the driving force of disbonding. Kinoshita[3] carried out experimental measurement of hydrogen content in the locality of fusion line and the results supported the above analysis. This phenomenon is unavoidable during the cooling process of the clad structure. Through simulation computation of the hydrogen diffusion process, it is possible to find out the peak hydrogen concentration at the locality of fusion line.

4 COMPUTER ANALYSES OF DISBONDING PROCESS

Utilizing the non-uniform solubility diffusion model, the authors compiled a two-dimensional finite element computer program to analyze the two-dimensional hydrogen diffusion problem. Following the test conditions shown in Fig.1, we used axi-symmetric model to analyze the hydrogen diffusion processes in various tests. The geometric dimensions of the computer model are shown in Fig.2. The thickness of the model is the same as the clad specimen used by Watanabe, the diameter of the model is equal to the width of the said specimen. The observation point is taken as point O, which is located on the symmetric axis and is 1 μm from the fusion line. Through computation, the variations of the concentration of diffused hydrogen at point O with time are shown in Fig.3. The solid lines show the hydrogen concentration curves in the tests in which disbonding occurred and the dotted lines show those in the tests in which disbonding did not occur. It is apparent that the hydrogen concentration levels in the cases in which disbonding occurred are higher than those in the cases in which disbonding did not occur. It also can be seen that, the more serious the degree of disbonding, the higher the hydrogen concentration at point O. The above results show that the changes in test conditions and their influence on disbonding can be directly reflected by the computational curves of the hydrogen concentration at point O.

In disbonding tests, the disbonding defects usually initiate only after a certain time after the specimens are cooled down to ambient temperature and develop during a certain period, then the cracks no longer grow. Through observations during the authors' own tests, it has been found that when the computed hydrogen concentration at point O begins to drop, the development of disbonding is close to an end. Therefore, we can deduce that the usual hydrogen diffusion behaviour is the fundamental driving force in the disbonding of clad structures.

5 A NEW METHOD TO EVALUATE THE RESISTANCE TO DISBONDING

Following the argument in the above section, the authors postulate that there exists a critical value of hydrogen concentration at the fusion line which will cause disbonding and term this value as the Disbonding Hydrogen Concentration C_{dc}. For a group of specimens cut from the same test plate which is made under a specific manufacturing procedure, the C_{dc} values should be practically constant and can be used to as a parameter to evaluate the resistance to disbonding.

The procedure for the determination of the C_{dc} value of a clad specimen adopted by the authors is described in the following text.

After charging the specimens under high-temperature high-pressure hydrogen and cooling down to ambient temperature, ultrasonic detection is immediately followed. When a signal of the intensity of $\phi 2+6$dB is detected, it is considered that disbonding occurs. The time for the first detection is recorded and marked as t_{dc}. The ultrasonic monitoring is continued until all the signals are stable. Then, the variation of test conditions (temperature, pressure, time) is input into the two-dimensional computer program for simulation computation and the curve for the change of hydrogen concentration at the fusion line with time can be obtained. From this curve, at the point t_{dc}, the corresponding hydrogen concentration is the Disbonding Hydrogen Concentration C_{dc}, as shown in Fig.4.

The authors carried out disbonding tests on 8 types of specimens. For each type of specimen, the test conditions varied from mild to serious. The results show that, for the same type of specimen, under various test conditions, the C_{dc} values derived from the test pieces differed not much. Moreover, if the hydrogen concentration at the fusion line is lower than C_{dc}, no disbonding was found. On the other hand, for different types of specimen, there is apparent difference between the C_{dc} values for each type. Table 1 shows some typical results.

Through disbonding test and computer simulation, we can get the C_{dc} value of a specimen of one type, and after that we can predict the disbonding behaviour of the same type of specimen under different test conditions. Thus, we can design the minimum number of tests needed to establish the C_{dc} value of that type of specimen. To compare the resistances to disbonding of specimens made by different manufacturing processes, their C_{dc} values can be used as a fairly reliable parameter. More importantly, in a real hydrogenation reactor, the change of hydrogen concentration at the fusion line with time during shutdown can be calculated by computer simulation, and the values can be used to compare with the C_{dc} values of the weld-test specimens, in order to judge whether disbonding will or will not occur. Thus, it is possible to link the assessment of in-service hydrogenation reactors with the laboratory disbonding test results of weld-test specimens more reasonably.

6 CONCLUSIONS

1. The disbonding of the stainless steel overlay is closely related to the concentration of the diffused

hydrogen at the locality of the fusion line.

2. Using the method of determining the Disbonding Hydrogen Concentration, it is possible to obtain objective evaluation of clad structure through a limited number of tests and computer simulation.

3. The Disbonding Hydrogen Concentration can be considered as a material property parameter, making the quantitative evaluation of the susceptibility to disbonding of stainless overlay possible.

4. The establishment of the new method of evaluation is an effective means for assessing in-service reactors based on laboratory hydrogen-charging disbonding tests on small specimens.

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Table 1. Typical Values of C_{dc}

Specimen type	Test No.	State of Disbonding	Time t_{dc}(h)	Disbonding Concentration C_{dc}(ppm)
Type I	1	No	/	/
	2	Light	110	218
	3	Light	136	224
Type II	1	No	/	/
	2	Light	165	239
	3	Light	231.5	249

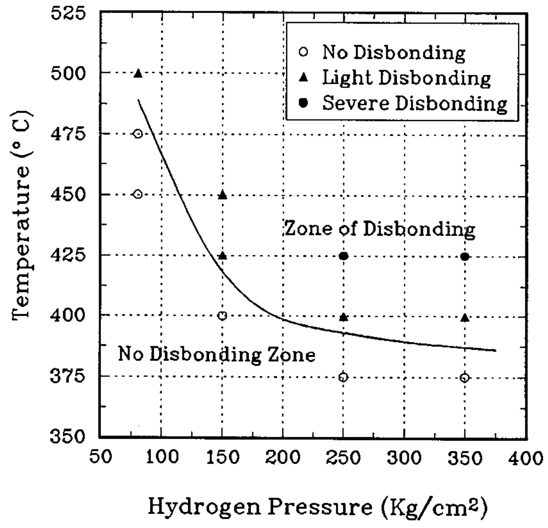

Fig.1 Effect of Test Conditions on Disbonding[1]

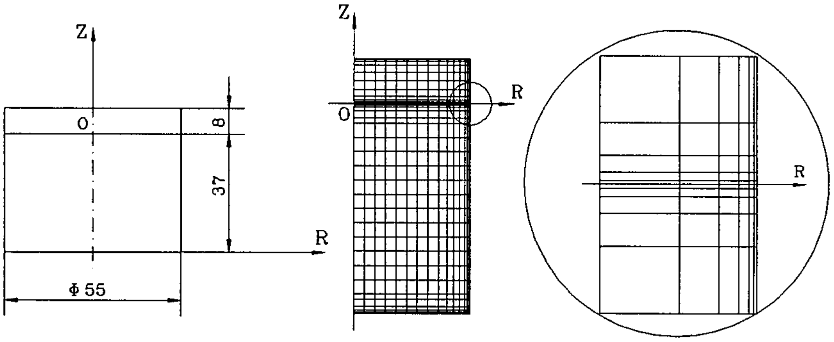

Fig.2 Geometric Dimensions of Computation Model

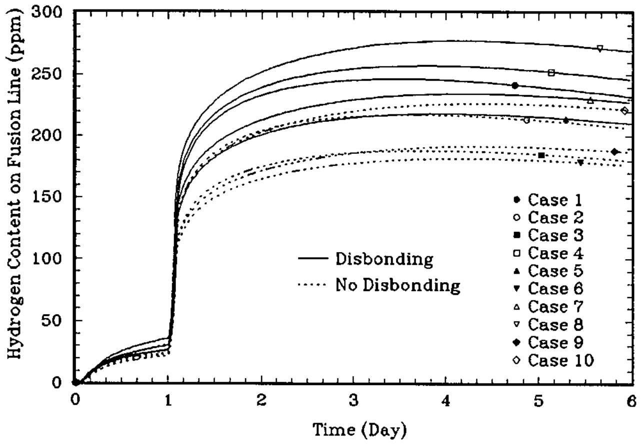

Fig.3 Simulated Hydrogen Concentration at Fusion Line vs. Time

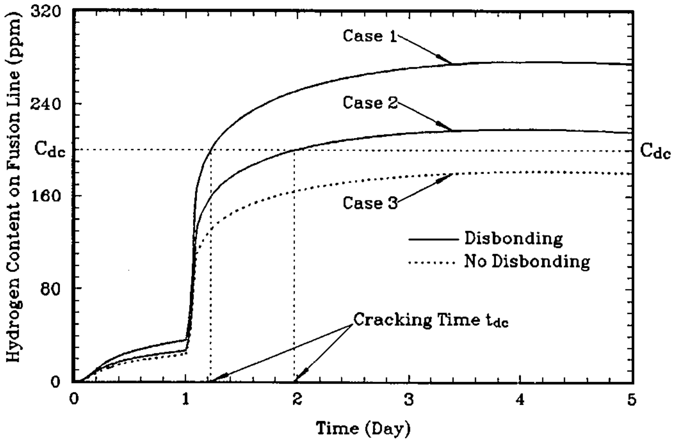

Fig.4 Procedure for Evaluating C_{dc}