EVALUATION OF HYDROGEN INDUCED DISBONDING FOR CR-MO-V STEEL / AUSTENITIC STAINLESS OVERLAY

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ABSTRACT

To investigate transition region in welded overlay relating to disbonding crack, the effect of vanadium addition on disbonding of Cr-Mo steels overlay welded with austenitic stainless steel was studied. V modified Cr-Mo steels have a higher resistance to disbonding than V free Cr-Mo steel. One reason is due to the fact that fine vanadium carbide precipated in base metal traps hydrogen and thus decreases the susceptibility to the disbonding. The second is related to the higher stability of the vanadium and stable carbides formed during PWHT, in which the carbon diffusion to the interface is lower than for V free Cr-Mo steel. Decreasing the carbon content at the interface of the weld overlay shows good resistance to the disbonding. Hence, it is important to control the carbon content at the interface of the weld overlay.

KEYWORDS

Cr-Mo steels, disbonding, overlay, pressure vessels, reactor

1. Introduction

The petrochemical refinery industry needs high pressure and temperature reactor vessels for heavy oil treatment under severe operating environment. The operating temperature of the hydroprocessing reactors are at present in the range of 400~480℃ with a corresponding hydrogen partial pressure from 10~35MPa. Currently the thick walled reactor are made by 2.25Cr-1Mo or 3Cr-1Mo steels. The V-modified Cr-Mo steels for high pressure reactors are expected to be used widely in the next decades.

High service temperature and hydrogen partial pressure have been in great demand for low cost and high efficiency of the hydrogenation process. To increase the efficiency of refining equipment, such as hydrocracker, hydrodesulfurizer, etc., the operating pressure has been increased steadily in the last decades and the interest for increasing temperature is also high. Because of this, heavy-wall forgings of the fabrications of these pressure vessels was developed. Moreover, the increase of temperature and partial pressure of hydrogen has led to the development and use of high strength V-modified Cr-Mo steels. The long term operation of this reactor at high temperature and hydrogen pressure will cause various damages to the materials, whose are temper embrittlement[1] and hydrogen assisted degradation such as permanent hydrogen attack[2] and disbonding of the interface between base metal and the cladding layer[3].

In this study the effect of vanadium addition on the susceptibility to disbonding of the Cr-Mo steels overlay welded with austenitic stainless steel and the effective welding processes have been also discussed to improve the resistance to disbonding.

2. Experimental procedures

Table 1 lists the chemical compositions of the base metal and overlay weld metal used in this study. 2.25Cr-1Mo and 2.25~3Cr-1Mo-V steel are the base metal, and STS 309L and STS 347 austenitic stainless steel, overlay weld metal. All materials were forged and preliminary heat treatment(normalizing and tempering) and quality heat treatment(water quenching and tempering) were carried out after rough machining. Strip dimensions are 60~150mm(w) × 0.4 mm(t), strip/flux processes was Submerged Arc Welding(SAW) and Electroslag Welding(ESW). Overlaid plates were heat treated at the temperatures of 690 and 700℃ respectively for 24 hours.

The dimensions of the test specimens are 75mm(l) x 60mm(w) x 50mm(t) and exposed to a hydrogen pressure of 9.8~34.3MPa at 400~575℃ for 48 hours. The generation of disbonding was examined with the C-scanning method using a 15MHz ultrasonic wave. The Vickers hardness tests were conducted on points on a line in the base metal into the weld metal. The microstructure of interface of the base metal and weld overlay was observed using optical microscopy(OM) and scanning electron microscopy(SEM). The morphology and composition of interface in the steels were analyzed with carbon extraction replicas in a scanning transmission electron microscope(STEM) equipped with an energy dispersive X-ray spectrometer(EDX) and Auger Electron Spectrometer(AES).

Table 1 Chemical composition of base metal and overlay weld metal (wt%)

Base Metal	C	Si	Mn	P	S	Ni	Cr	Mo	V
2.25Cr-1Mo	0.13	0.22	0.49	0.003	0.003	0.19	2.24	0.99	0.03
3Cr-1Mo-V	0.14	0.11	0.41	0.009	0.002	0.10	2.90	0.95	0.30
2.25Cr-1Mo-V	0.15	0.09	0.45	0.006	0.001	0.12	2.40	0.98	0.29
Weld Metal	C	Si	Mn	Ni	Cr	Mo	Nb+Ta	Ni_{eq}	Cr_{eq}
STS 309L	0.020	0.82	1.60	11.42	22.60	0.05	0.015	13.36	23.89
STS 347	0.022	0.50	1.77	10.64	19.22	0.05	0.520	12.73	20.28

3. Results and discussion

Samples were prepared after exposed to hydrogen 34.3MPa at 575℃ for 48 hours. Fig.1 shows disbonding crack at an interface. The crack was found to propagate at the overlay/base metal interface or along the coarse grain boundaries developed in stainless steel near the interface.

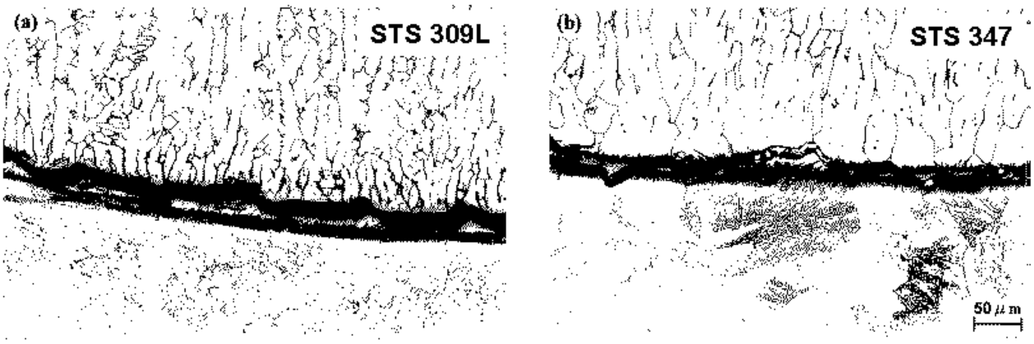


Fig. 1 Optical micrographs of the interface of base metals and stainless steels

(a) 2.25Cr-1Mo / STS 309L+347 (b) 2.25Cr-1Mo-V / STS 347

The predominantly intergranular fracture is also apparent in the SEM fractograph shown in Fig. 2. The dark band (Transition Zone) shown in Fig. 1 is carbide aggregate that precipitates after PWHT, which are mainly Cr-rich carbides.

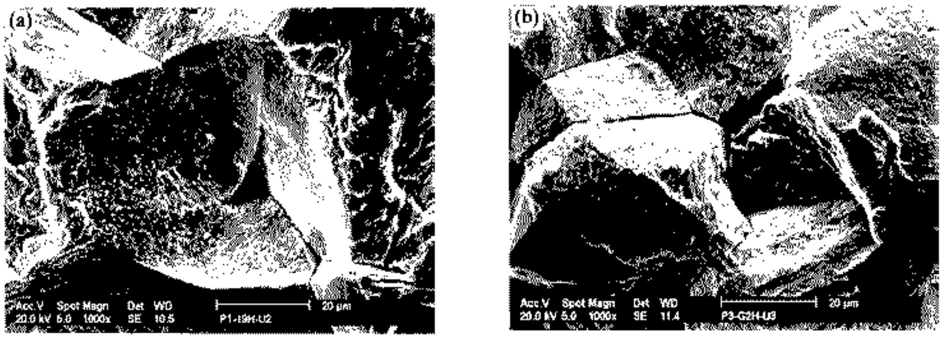


Fig.2 Intergranular fracture surface of disbonding

(a) 2.25Cr-1Mo / STS 309L+347 (b) 2.25Cr-1Mo-V / STS 347

The disbonding tends to occur more extensively when material is hydrogenated under higher pressure at higher temperature, as shown in Fig. 3. Vanadium modified 2.25~3Cr-1Mo steel overlay welded with austenitic stainless steel shows good resistance to disbonding. It has been reported that fine vanadium carbide precipitated in base metal traps hydrogen, and thus decrease the susceptibility to disbonding[4].

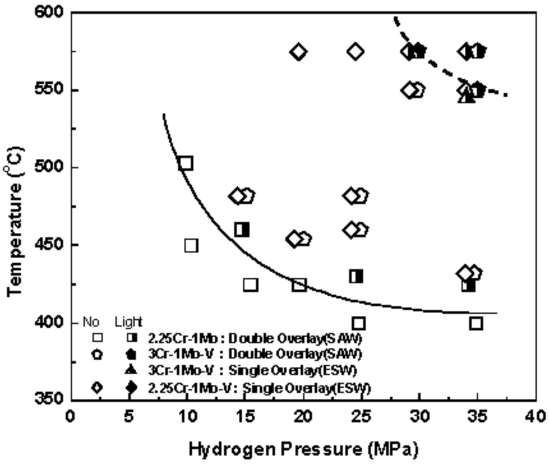
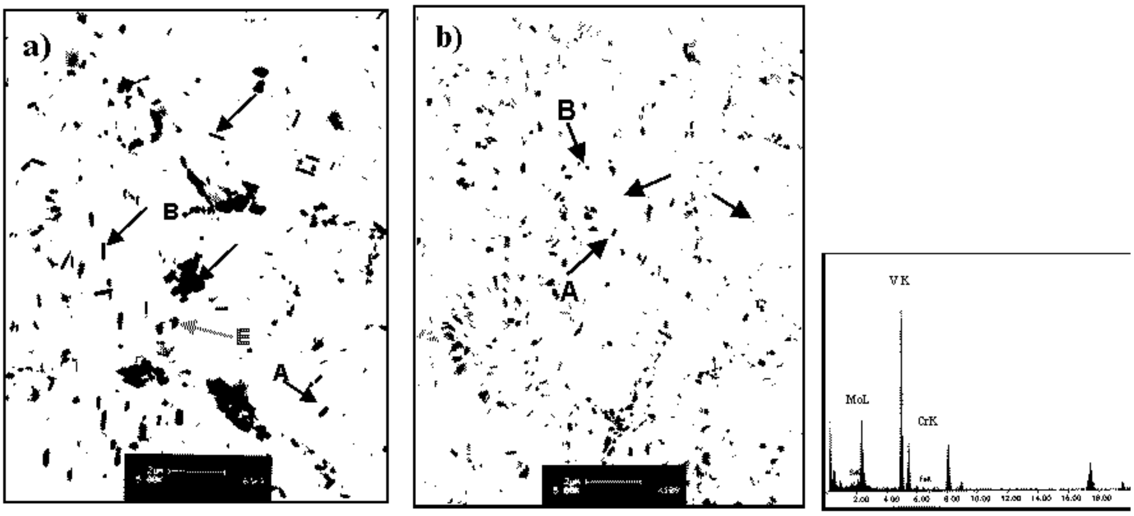


Fig. 3 Effect of hydrogen pressure and temperature on disbonding

Fig. 4 shows the STEM images and EDX spectra for the precipitates in the 2.25Cr-1Mo and V-mod. 2.25Cr-1Mo steels using carbon extraction replicas. The STEM image for the 2.25Cr-1Mo steel indicates that there are four different types in the morphology of precipitates. Coarse granular precipitates exist both in matrix and on grain boundaries. The fine, needle-like carbides (M_2C) existing only in matrix. On the other hand, in the V-mod. Cr-Mo steel, five types of precipitates are observed. However, granular precipitates are small and contain a small amount of vanadium. The finely dispersed V-rich fine carbides(V_4C_3) are precipitates in matrix. The fine precipitates are very different from those in 2.25Cr-1Mo steel, that is, fine precipitates contain V besides Mo and Cr as indicated by EDX spectra. It is well known that the solubility of hydrogen in V-mod. steel is higher than that of V free steel at room temperature[5]. Therefore the carbon diffusion to the interface is lower than for V free Cr-Mo steel. Hence V-mod. Cr-Mo steel effectively decrease the sensitivity to overlay disbonding.



A : M_7C_3 B: $M_{23}C_6$ C:M_2C D:V_4C_3 E:M_3C F:M_6C

Fig. 4 Morphologies of the precipitated carbides with base metals as PWHT

(a) 2.25Cr-1Mo steel (b) 2.25Cr-1Mo-V steel

Fig. 5 shows the micro-hardness profile across overlay and base metal. Vickers hardness tests exhibited that maximum hardness was formed near the interface of the weld overlay and its maximum hardness was more than 350Hv. V-mod. Cr-Mo Steels show hardness difference($\triangle Hv = Hv_{max} - Hv_{in}$) between maximum hardness(Hv_{max}) and hardness of interface(Hv_{in}) of the transition zone is lower than 2.25Cr-1Mo steel. It is concluded from the hardness of interface of the weld overlay as welded state was about 400Hv that M+A microstructure was existed near the interface of the weld overlay.

It is well known that the disbonding is a kind of delayed fracture caused by hydrogen[3] and the sensitivity of the delay fracture depends strongly on the strength and hardness of the steels[6].

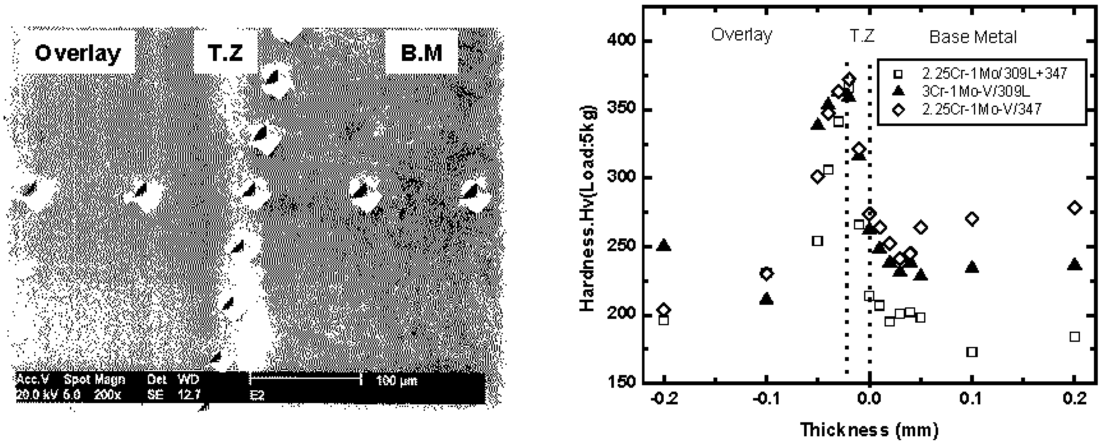


Fig. 5 Scanning electron micrograph and micro-hardness profile across overlay/base metal interface after PWHT

Disbonding occurs when the conjunction of hydrogen peak at the interface and of a sensitive microstructure in that area. It has been demonstrated that an increase of carbon content of the interface is a major factor of disbonding sensitivity[7]. Table 2 shows the AES analysis of chemical composition changes of the transition zone(T.Z) of the 2.25Cr-1Mo steel and 2.25Cr-1Mo-V steel before and after disbonding test. The C- and Cr-content near crack in the transition zone was increased after disbonding test. The V-mod. Cr-Mo steel has lower C- and Cr-content than V free steel. These C-content differences decreased the sensitivity to overlay disbonding , due to the fact that fine V carbides in the V-mod. Cr-Mo steel suppressed the carbon diffusion that is related to the disbonding crack of interface of the weld overlay.

Table 2 AES analysis(at%) of the transition zone before and after disbonding

Base metal	analysis	C	Fe	Cr	Ni	Remark
2.25Cr-1Mo	T.Z	17.41	66.04	12.62	3.92	As PWHT
	T.Z near crack	20.32	57.20	18.97	3.51	HID
2.25Cr-1Mo-V	T.Z	8.88	82.01	6.6	2.51	As PWHT
	T.Z near crack	18.11	69.28	11.51	1.1	HID

From Fig. 6 it can be noted that, decreasing the carbon content at the interface of the weld overlay decreased disbonding ratio. For a given carbon content, the resistance to disbonding was higher in V free 2.25Cr-1Mo steel, V-mod. 2.25Cr-1Mo steel and V-mod. 3Cr-1Mo steel, in that order. A single-pass overlay of STS 347(ESW) shows higher resistance to disbonding than two-pass overlay of STS 309L(SAW) plus STS 347(ESW). Hence the development of the effective welding processes to reduce the carbon content at the interface of the weld overlay is important.

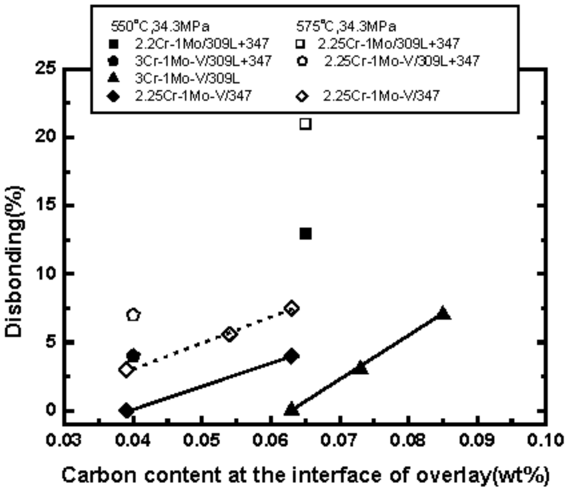


Fig. 6 Influence of C-content at the interface of the weld overlay on disbonding

4. Conclusions

The following conclusions may be drawn from the current investigations on the properties of 2.25Cr-1Mo and 2.25~3Cr-1Mo-V steels for pressure vessels used in the environment of high temperature and hydrogen pressure.

1) V-modified Cr-Mo steels have a higher resistance to disbonding than V-free Cr-Mo steel.

As the result of the higher trapping effect of hydrogen in the base metal, the carbon content differences decreased the sensitivity to overlay disbonding, due to the fact that fine V carbides in the V-modified Cr-Mo steel suppressed the carbon diffusion.

2) The C- and Cr-content near the crack in the transition zone were increased after disbonding test. The V-mod. Cr-Mo steel has lower C- and Cr-content than V free Cr-Mo steel.

3) Decreasing the carbon content at the interface of the weld overlay decreased disbonding ratio. For a given carbon content, the resistance to disbonding was higher in V free 2.25Cr-1Mo steel, V-mod. 2.25Cr-1Mo steel and V-mod. 3Cr-1Mo steel, in that order.

4) A single-pass overlay of STS 347(ESW) shows higher resistance to disbonding than two-pass overlay of STS 309L(SAW) plus STS 347(ESW). Hence the development of the effective welding processes to reduce the carbon content at the interface of the weld overlay is important.

Acknowledgements

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