High Cr Stainless Steel OCTG with High Strength and Superior Corrosion Resistance†

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Abstract:

New martensitic stainless steea 2environments is 160°C. UHP15Cr

has high strength, with Yield strength (YS) exceeding 861 MPa, and can be used in high CO_2 environments at temperatures up to 200°C. These new martensitic steel pipes show excellent properties in sweet, high temperature, high CO_2 environments and slightly sour environments containing small amounts of H_2S where conventional 13Cr pipes could not be used.

1. Introduction

The martensitic stainless steel pipe API-13Cr, which

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OCTG must be obtained by cold drawing, resulting in substantially higher costs. Therefore, there was strong demand for the development of new OCTG which possess high corrosion resistance superior to that of API-13D l 3D l p ` l

This paper clari f es the effects of environmental factors and alloying elements on the corrosion resistance of martensitic stainless steel, and describes the history of development of HP13Cr and UHP15Cr with improved CO_2 corrosion resistance and SSC resistance, as well as their application limits in oil and gas environments.

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Increasing the contents of alloying elements such as Cr, Ni, Mo, Cu is effective for improving corrosion resistance. In particular, Cr is the most effective element for improving CO_2 corrosion resistance[9]. However, Cr also promotes the formation of ferrite. Alloying element addition was therefore studied based on the concept of HP13Cr, controlling the Ni balance in consideration of hot workability while at the same time also considering sour resistance.

3.2 Experimental Procedure

As sample materials, small steel ingots with HP13Cr steel as the base composition and varied contents of Cr, Ni, Mo, and Cu were used. The range of chemical compositions of these samples is shown in **Table 4**.

CO_2 corrosion resistance was evaluated using plate-shaped immersion test specimens. The corrosion test was performed by immersion in an autoclave using specimens 3 mm$t$ × 25 mm$w$ × 50 mm$l$ taken from the center of thickness of the sample materials. CO_2 corrosion resistance was evaluated by the general corrosion rate (mm/y) converted from weight loss.

3.3 Corrosion Resistance

The effect of alloying elements on CO_2 corrosion resistance under a condition of 200°C is shown in **Fig. 6**. In a CO_2 environment at 200°C, increasing Cr, Ni, Mo, and Cu is effective for improving corrosion resistance, and particularly in high CO_2 environments, an increased content of Cr is most effective for enhancing CO_2 resistance. To reduce the corrosion rate in a 200°C environment with a partial pressure of CO_2 of 10 MPa to 0.127 mm/y or less, it is necessary to secure a CO_2 corrosion index (CCI: Cr + 0.65 Ni + 0.6 Mo + 0.55 Cu) stainless steel pipes by cold drawing, it is considered that the strength of this type of steel decreases when dislocations are released at high temperature. On the other hand, because strength is secured in UHP15Cr by microstructure and precipitation control, this steel has the distinctive feature of a small decrease in strength even at high temperatures.

The CO_2 corrosion test results of HP13Cr-1, HP13Cr-2, and UHP15Cr steel pipes are shown in **Fig. 8**. The limit in judging the applicability of the steels was a corrosion rate of 0.125 mm/y. The application limit is affected by the partial pressure of CO_2 gas and temperature. For example, the limit temperature for application of API-13Cr steel pipes under a condition of CO_2: 3 MPa is 100°C. In contrast, the limit temperatures for HP13Cr and UHP15Cr are 160°C and 200°C, respectively.

The SSC test results for the HP13Cr-2 and UHP15Cr steel pipes are shown in **Figs. 9** and **10**. The critical concentration of H_2S becomes high with the increase of pH. With HP13Cr, under a condition of pH3.0, SSC occurred even with a partial pressure of H_2S of 0.001 MPa, but at pH4.0, the critical partial pressure of H_2S at which SSC does not occur is 0.01 MPa. UHP15Cr displayed excellent resistance to SSC, in spite of its high strength of 125 ksi grade, and its critical partial pressure of H_2S at pH4.5 was 0.01 MPa.

The fracture surface of a test specimen of a UHP15Cr steel pipe after the SSC test is shown in **Photo 1**. Sulfde stress corrosion has originated at a pit and propagated by hydrogen embrittement. The excellent SSC resistance of UHP15Cr is attributed to improved pitting resistance resulting from its increased Cr content.

5. Conclusion

(1) A new steel pipe with excellent CO_2 corrosion resistance, HP13Cr-1, was developed. HP13Cr steel has high CO_2 corrosion resistance in comparison with API-13Cr and can be used at high temperatures up to 160°C even under high partial pressures of CO_2. The excellent CO_2 corrosion resistance of HP13Cr is considered to be the result of (a) reducing the amount of Cr carbides, which form cathode sites in the corrosion reaction, by reducing the content of C, (b) increasing the content of Cr, which is effective for improving corrosion resistance, by reducing the amount of Cr carbides, and (c) suppressing the corrosion reaction by addition of Ni, which has only a slight tendency to ionize under high temperature, high partial pressure of CO_2 condition.

(2) A steel pipe which possesses excellent sour resistance in addition to CO_2 corrosion resistance, HP13Cr-2, was also developed. HP13Cr-2 has high sour resistance in comparison with HP13Cr-1, which was achieved by increasing the Mo content to 2%. It is considered that improved pitting resistance together with reduced permeation of hydrogen into the steel, which result from the increased Mo content, contribute to improved sour resistance.

(3) A steel pipe with high strength and excellent CO_2 corrosion resistance at temperatures up to 200°C, UHP15Cr, was developed. The UHP15Cr steel pipe possesses not only CO_2 corrosion resistance, but also excellent properties in sour environments. In comparison with duplex stainless steels, UHP15Cr shows only a small drop in yield strength (YS) at high temperatures and possesses high strength even in 200°C high temperature environments.

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