Technical Report

Super-high Strength Low Alloy Steel OCTG with Improved Sour Resistance

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Abstract

Material design concepts and the applicability of 125ksi (862MPa) grade super-high strength low alloy steel OCTG (oil country tubular goods) for sour service are described in this paper. Following metallurgical techniques were necessary for enhancing sour (SSC) resistance - prevention of pitting by minimizing inclusion size, decrease in dislocation density by high temperature tempering using nano-sized carbides, and improvements of carbides morphologies at grain boundaries - spheroidizing M_3C and preventing $M_{23}C_6$ formation. The developed steel showed superior SSC resistance to conventional steels on the H_2S-pH domain map. The 125ksi sour grade OCTG was commercialized in 2003, the first material of that kind in the world. This new OCTG has been used in deep gas wells in the UK and Norwegian North Sea, and the Caspian Sea.

1. Introduction

In the field of production of oil and natural gas, along with the exhaustion in shallow wells under the environment of low corrosiveness, development of deep wells under highly corrosive environment and high pressure is increasing. Oil wells and gas wells frequently contain corrosive gas of hydrogen sulfide (H_2S) and carbon dioxide (CO_2) gas. In particular, the well environment acidified by the H_2S is called sour environment and is a very severe environment for steel materials. Recently, the demand for natural gas has been sharply rising as a clean energy that emits less CO_2 in combustion compared with oil, and the major oil companies are focusing on the development of natural gas. Unlike oil that exists richly in the geologic strata below 2 000–3 000 m underground, natural gas is deposited in a far deeper and highly corrosive environment; thereby, necessitating production from wells under far harsher conditions.

Steel pipes that are used for the production of oil and natural gas are called as oil country tubular goods (OCTG). As wells go deeper and corrosive environment becomes harsher, higher strength and higher corrosion resistance are required. However, if low alloy steel pipes are exposed to the sour environment, hydrogen embrittlement fracture termed as sulfide stress cracking (SSC) induced by corro-

sion occurs. SSC occurs more frequently in high strength steel. Therefore, SSC has been avoided by limiting the maximum strength of OCTG to 110 ksi (kilo pound per square inch) class and the maximum yield strength to 758 MPa class for OCTG usage (SSC-resistant low alloy OCTG) for a sour environment. Therefore, if the production of high strength steel pipe exceeding the 110 ksi class becomes possible, it can withstand the increase of its own self weight when the well goes deeper and can endure collapse due to pressure. Furthermore, the modified steel pipe can provide a large cost-reduction merit realized by the weight-reduction in the well design by employing pipes having thinner wall thickness.

Authors challenged the research and development of super-high-strength low alloy steel seamless OCTG having compatibly improved sour (SSC) resistance to meet the market needs, and for the first time in the world, they realized practical application of the super-high strength sour (SSC) resistant low alloy OCTG of 125 ksi class (yield strength of 862 MPa class), enabling the exploitation of deep natural gas wells in a highly corrosive environment, which has been possible to date. The realization of sour (SSC) resistant OCTG of 125 ksi class required prevention of SSC by microstructure control and assessment of the application environment. In this study,

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outline of the material design concept and the applicability of the developed steel are discussed.

2. Main Subject

2.1 Material design concept

SSC that develops in a sour environment is a type of hydrogen embrittlement fracture caused by hydrogen generated on the surface of a steel material by the corrosion reaction in an acidic environment. H_2S acts as a strong catalyzer to promote the penetration of hydrogen; therefore, the sour environment can be said to be the severest environment on earth from the viewpoint of hydrogen embrittlement. Namely, SSC occurs in an environment where a large amount of hydrogen penetrates into steel. Compared with other hydrogen embrittlement, such as delayed fracture, compatibility of high strength and prevention of SSC is very difficult to achieve.

SSC is characteristically affected strongly by the steel microstructure. Many research aimed at enhancing the sour (SSC) resistance by improving steel microstructure has been conducted.[1] Single-phase martensite structure developed by quench and temper is desirable; the higher the martensite ratio, the more the sour (SSC) resistance is improved. Fine grain size of the prior austenite enhances the sour (SSC) resistance, and addition of Ti and Nb is also found to be effective. Based on this concept, as a low alloy sour (SSC) resistant OCTG having the highest strength, quenched and tempered steel of 110 ksi class (yield strength of 758 MPa class) having, for instance, the chemical compositions of 1%Cr-0.7%Mo-Ti-Nb has been generally used. However, even using this material improving method, compatibility of the super-high strength of 125 ksi class (862 MPa class) and the sour (SSC) resistance could not be obtained.

The authors attempted the unprecedented development of super-high strength sour (SSC) resistant OCTG by clarifying the various microscopic factors in the structure and then by studying the most optimum material that enables establishment of the compatibility of super-high strength and prevention of SSC. In the process from the occurrence of SSC to fracture, the effect of the microstructure is schematically shown in **Fig. 1**. First, a nonmetallic inclusion (hereinafter referred to as "inclusion") exposed on a steel surface becomes the initiation site of corrosion (pitting) and stress concentrates at the bottom of the pit. Hydrogen penetrates into the steel from the H_2S environment and the dislocation in the steel works as a trap site of hydrogen and increases the amount of absorption of hydrogen, supplying hydrogen to the stress concentration site and developing SSC. Furthermore, SSC develops along the carbides at the grain boundaries, propagates, and reaches fracture ultimately. SSC occurs by such a complicated process.

Accordingly, appropriate structure control at these steps is necessary for improving the sour (SSC) resistance of high strength
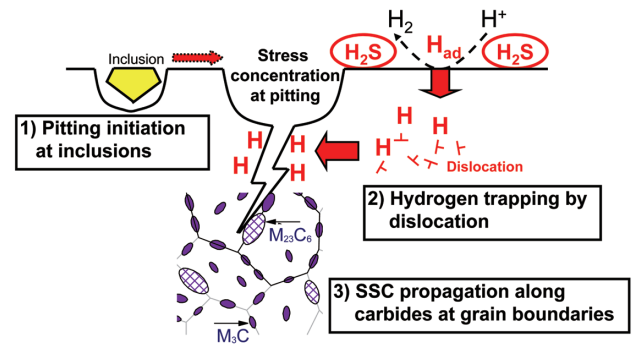

Fig. 1 Process of sulfide stress cracking (SSC) of high strength steel

steel. In the developed steel of 125 ksi class, the effect of the microstructure control, such as prevention of pitting by fining and dispersing inclusions, decreasing in dislocation density by high temperature tempering using nano-sized MC carbides and spheroidizing and fining of carbides at grain boundaries alleviated the unfavorable influence at the respective step and the sour (SSC) resistance was enhanced. The details are described below.

(1) Fining and dispersing of inclusions

Non-metallic inclusions in the steel, such as oxides and nitrides, are produced during the melting operation of steel; they cohere and grow coarse in the cooling process and grow up to the size of approximately several tens micrometer. The effect of inclusions on the development of SSC in conventional steel is shown in **Fig. 2**. Figure 2 shows how an inclusion exposed on a steel surface develops pitting and SSC when the inclusion is exposed to the sour environment. Sour environment is a very harsh acidic corrosive environment and when a coarse inclusion is exposed on a steel surface, as shown in Fig. 2 (a), it becomes an origin-triggering corrosion (pitting), as shown in Fig. 2 (b). As for the operating function of inclusions to corrosion, in case the inclusion is of soluble type, it becomes the origin of the corrosion by dissolving itself. In case of insoluble type, it is considered that it functions to dissolve the neighboring steel by the galvanic effect.

Stress is concentrated at the bottom of the pitting formed on the surface of a steel surface, and SSC develops at the bottom of the pitting, as shown in Fig. 2 (c). The figure shows a fracture surface of a round bar-type tensile strength test piece after being used for the test of SSC. Ultimately, cracks cause fractures in a pipe, as shown in Fig. 2 (d). For line pipe steel, a phenomenon termed as hydrogen-induced cracking (HIC) is well known, which is an internal cracking caused by the concentration of hydrogen on inclusions in the steel, in particular around the elongated MnS.[2] However, the phenomenon shown in Fig. 2 is not the internal cracking like HIC, but the phenomenon in high strength steel OCTG in which SSC is developed,
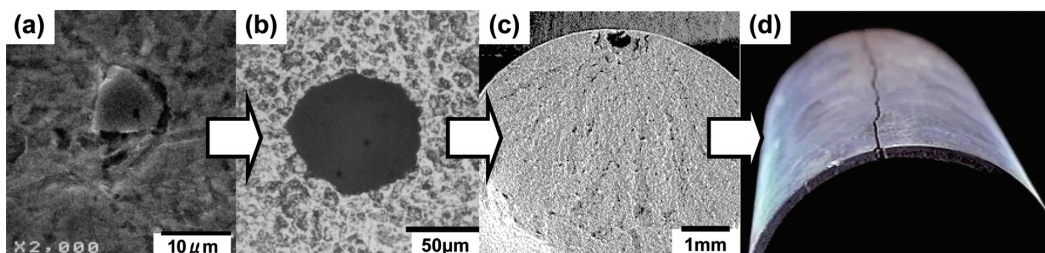

Fig. 2 Process of SSC at inclusions on conventional steels
(a) Large inclusion, (b) Pitting initiation at the inclusion, (c) SSC at the pitting, (d) Failure of the pipe
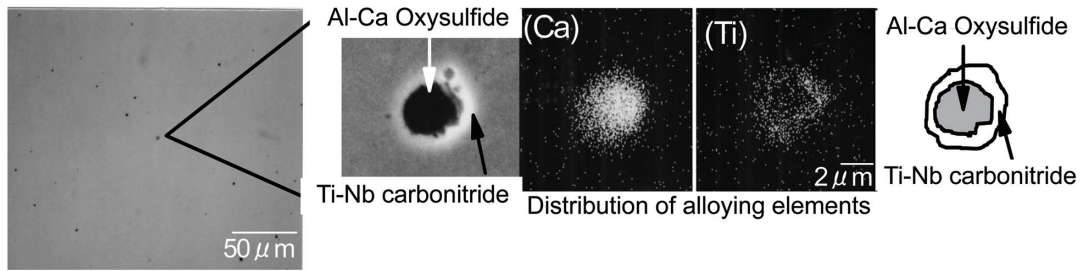
Fig. 3   Fine multi-component inclusions

starting at a pitting formed by an inclusion on a steel surface.

It's needless to state that decreasing of inclusion-forming impure elements, such as S, O, and N is effective in decreasing inclusions. For super-high strength sour (SSC) resistant steel, decreasing of impurities at the highest level is also required. Moreover, the larger the diameter of an inclusion, the larger the diameter of the pitting becomes (Fig. 2 (b)). The prevention of pitting by controlling the growth of inclusions and fining them was also investigated. The inclusions shown in the electron microscopic photos in **Fig. 3** are complexes of heterologous inclusions with appropriate addition of trace elements.[3] Al and Ca join with O and S to form oxysulfide of Al-Ca of the inner core, which is fined and dispersed in the steel during solidification of the molten steel, suppressing the growth of coarse inclusions of oxysulfide system.

This technology is similar to the one that prevents the growth of coarse MnS in the aforementioned line pipe steel, and its finding is being employed.[4] Furthermore, carbonitride of Ti-Nb is adsorbed to the inner core and forms an outer shell and formation of a coarse carbonitride is suppressed. Employing this technology, inclusions are fined and dispersed, preventing SSC originating at pitting. Thus, for enhancing the sour (SSC) resistant, inclusion control at a high level is sought after, which has been used for development of the steel making technology in recent years.

(2) Decreasing of dislocation density using nano-sized carbides

The strength of low alloy OCTG is adjusted by quenching and tempering heat treatment after pipe-forming. Dislocation is introduced in quenching the heat treatment and serves to enhance strength. However, dislocation works as a trap site of hydrogen and becomes a promoting factor for SSC. Namely, as long as the strengthening mechanism is based on dislocation strengthening, enhancing strength and prevention of SSC cannot compromise with each other and more frequent occurrence of SSC at higher strength level cannot essentially be helped. As a method for enhancing strength to become compatible with decreasing dislocation density, formation of nano-sized carbide by adding alloying element of V is effective as stated below.

Figure 4 (a) shows the difference in yield strength after tempering of the conventional steel (0.7% Mo steel with no V added) and that of the developed steel (0.7%Mo-0.1%V, V added steel). In the developed steel, V and Mo, both having high carbide forming capability, join C and form nano-sized tetragonal MC carbides (M=V, Mo).[5, 6] With this MC carbide causing precipitation strengthening, the tempering temperature at the final heat treatment can be elevated and made higher than that of the conventional steel.

In Fig. 4 (b), half peak widths of (211) plane in X-ray diffraction of the conventional steel (0.7% Mo steel with no V added) and that of the developed steel (0.7%Mo-0.1%V, V added steel) are shown. This value is considered to denote the dislocation density. As
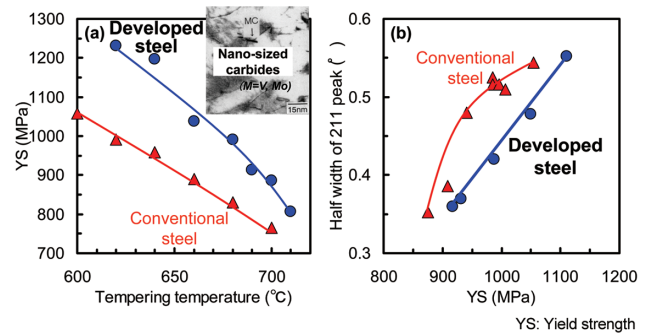

Fig. 4   (a) High temperature tempering and (b) Decrease in dislocation density using nano-sized carbides

strength increases, the half-width value tends to increase, and therefore dislocation increases. However, in the case of the developed steel, decreasing of the half-width value is possible by tempering at an elevated temperature by adding V. It means that with tempering at a high temperature, dislocation developed at the quenching heat treatment can be eliminated. Thereby, enhancing strength and decreasing dislocation can be made compatible.[7-9] Specifically, by changing the dislocation-strengthening mechanism to precipitation-strengthening mechanism, decreasing of the influence of dislocation on SSC is possible while maintaining high strength.

The MC carbide acts as a hydrogen trap site more strongly than dislocation[5, 6] and is said to be effective in preventing embrittlement caused by small amount of hydrogen, such as delayed fracture. However, similar to the case of an oil well environment where a great amount of hydrogen continuously penetrates, its effect as a hydrogen trap site is low,[6] and the effect of the abovementioned tempering at an elevated temperature is considered to be large for enhancing sour (SSC) resistance.

(3) Improvement of morphologies of carbide at grain boundaries

At tempering of steel pipes at the final stage of heat treatment, alloy carbides of various types precipitate. In the conventional steel, intergranular fracture-type SSC is more likely to occur along with enhancing of strength and, sour (SSC) resistance is deteriorated. This phenomenon is considered to be attributed to carbides precipitated at prior austenite grain boundaries. Improvement of carbide morphologies at grain boundaries is also effective in enhancing sour (SSC) resistance. Such an example of such is introduced in previous studies.[7-9]

Figure 5 (a)–(c) show comparisons of the results of observation of precipitation morphologies of carbides for a conventional steel (1%Cr-0.7%Mo steel with no V added) and the developed steel (0.5%Cr-0.7%Mo-0.1%V steel) both having the yield strength of approximately 130 ksi (896 MPa). The observation was made with
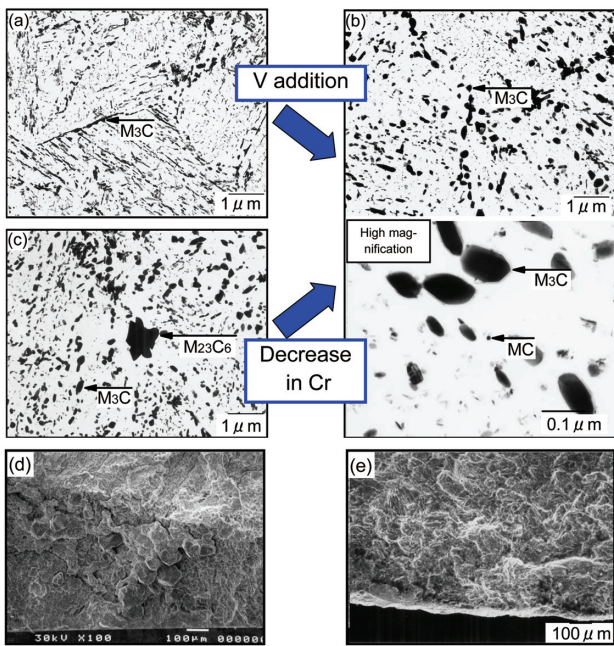
Fig. 5   Effect of carbides at grain boundaries on SSC (a)(c)(d) Conventional steels, (b)(e) Developed steel

Fig. 6   Effect of Cr and Mo concentration on carbides structures (calculated phase diagram)

an extraction replica method and electron microscope.

In the conventional steel, two types of carbides are observed at the grain boundaries. One is the flattened M_3C carbide (cementite: M=Fe, Cr, Mo), as shown in Fig. 5 (a), which was formed preferentially at the prior austenite boundaries. On the other hand, in the developed steel added with V, nano-sized carbide of MC (M=V, Mo) is formed, having the effect of the elevating tempering temperature. Figure 5 (b) shows the carbide morphology of the developed steel near the grain boundaries. It is confirmed that tempering at an elevated temperature grows and spheroidizes M_3C and has the function of dispersing it uniformly regardless of whether at grain boundaries or within of grains.

Another harmful carbide that exists at the grain boundaries of conventional steel is $M_{23}C_6$ (M=Fe, Cr, Mo), shown in Fig. 5 (c). In the conventional steel containing 1% of Cr, coarse carbides of approximately $1\mu m$ in diameter is precipitated preferentially at the grain boundaries of prior austenite. $M_{23}C_6$ contains considerable amount of Cr and Mo, suggesting that they are formed by absorbing Cr and Mo. Considering that the concentration of Cr and Mo in the steel affects the formation of $M_{23}C_6$, the effect of concentration of the alloying elements on the crystal structure of carbides was estimated thermodynamically using Thermo-calc, as shown in **Fig. 6**. It is shown that the decrease in the contents of Cr and Mo and addition of V further are effective in suppressing $M_{23}C_6$, and it is confirmed experimentally that the decrease in the Cr content suppresses the formation of $M_{23}C_6$, as shown in Fig. 5 (b). Figure 6 suggests that the decrease in the Mo content is effective in reducing $M_{23}C_6$; however, decreasing of Mo is not desirable as Mo is effective in elevating the tempering temperature by forming the MC carbide, as shown in Fig. 4 (a) and Fig. 5 (b). Regarding Cr, it has been confirmed that it does not affect the yielding strength in tempering,[7-9] therefore, decreasing of the Cr content is most desirable in suppressing the formation of $M_{23}C_6$.

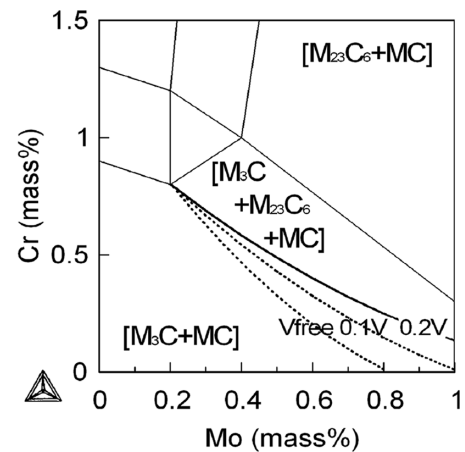The fracture surface of the conventional steel and the developed steel after SSC tests are compared in Fig. 5 (d) and Fig. 5 (e). In the conventional steel, cracking at the grain boundaries of prior austenite is observed (Fig. 5 (d)). In the developed steel, transgranular cracking is observed (Fig. 5 (e)). Therefore, it is confirmed that the difference in the forms of carbides at grain boundaries affects the form of the fracture surface.

Based on the abovementioned material design concept, the new chemical composition of (0.5%Cr-0.7%Mo-0.1%V steel) wherein inclusions are fined Cr is decreased and V is added has been proposed as the composition of sour (SSC) resistant OCTG of 125 ksi class (862 MPa class). It has been confirmed that the developed steel has sour (SSC) resistance superior to that of the conventional steel.[7-10]

2.2 Assessment of applicability

For the realization of super-high strength sour (SSC) resistant OCTG, the assessment of its applicability is also an important issue. Applicability thereof is stated below based on the environmental domain map and from the viewpoint of the actual application results in customers.

(1) H_2S-pH domain map

In recent years, a concept of assessing the corrosion resistance of OCTG materials is penetrating wherein development is promoted after grasping the severity of the actual environment correctly based on environmental factors, such as partial pressure of H_2S, pH value, and temperature, and selecting correct materials to meet the requirement. The environment endurable for 125 ksi class sour (SSC) resistant OCTG (test conditions where SSC does not occur) expressed by mapping of H_2S partial pressure and pH value is shown in **Fig. 7**. The assessment of SSC was carried out based on the stipulation of the uniaxial tensile testing[11] of National Association of Corrosion Engineers. The occurrence or non-occurrence of SSC was confirmed by varying the partial pressure of H_2S gas saturated with the balance of CO_2 and by varying the pH value of acetic acid-sodium acetate solution wherein the test piece was immersed for 720 h under the stress of loading at 90% of the actual yielding strength. Several other examples of development of 125 ksi class sour (SSC) resistant low alloy OCTG are reported;[12-17] however, the sour (SSC) resistance in Fig. 7 shows the durability of the developed steel in the environment harsher than other reported cases.

For correct assessment of sour (SSC) resistance, establishment of correct assessment method, which can reproduce the actual envi-
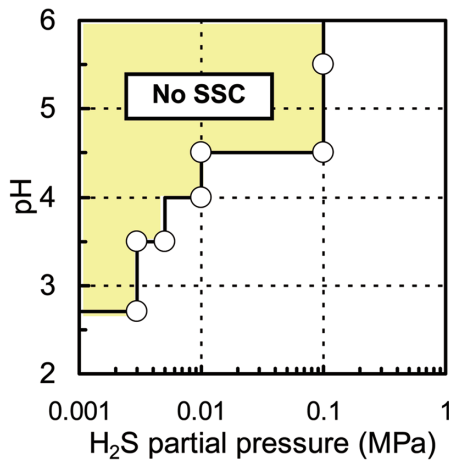
Fig. 7 No SSC conditions of the 125 ksi grade sour OCTG

ronment is also important. Therefore, such improvement efforts as reduction to the maximum extent possible of dissolved oxygen in the test solution since oxygen does not exist in an actual well environment, and use for the test solution of high concentration acetic acid-sodium acetate solution for suppressing pH drift before and after the testing, have been proposed as correct test method, and was established [18] and then Fig. 7 has been worked out.

(2) State of application of the developed product

Recognition of British Petroleum (UK) and Statoil ASA (Norway) of the super-high strength sour (SSC) resistant OCTG applied with this technology was acquired, and, in 2003, for the first time in the world, this product was put into practical use as sour (SSC) resistant OCTG of 125 ksi class (yield strength of 862 MPa class). This OCTG has been used for sour natural gas wells of 4 000–6 000 m class deep in the North Sea and the Caspian Sea without any problem up to present.[19] Along with the increase in global demand for natural gas, the demand is increasing each year.

3. Conclusion

An example of development of low alloy OCTG having super-high strength and sour (SSC) resistance compatibly, which is used in the field of oil and natural gas production, was introduced. Such microstructure optimization as fining and dispersing of inclusions, decreasing of dislocation density using nano-sized carbide and mor-

phology control of carbides at grain boundaries was effective in obtaining the desired performance. Based on this material design concept, sour (SSC) resistant low alloy OTCG having the super-high strength of 125 ksi class (yielding strength 862 MPa class) has been developed and implemented practically. With this developed product, exploitation of deep gas wells reaching as deep as 4 000–, m, which was impossible to develop in the past, has become possible, contributing to the global supply of natural gas, a clean energy. Presently, exploitation of very deep natural gas wells under a highly corrosive environment is being accelerated on a global scale and far greater demand is expected.

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