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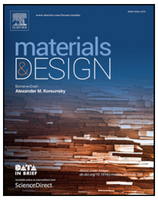

Novel Cu-bearing high-strength pipeline steels with excellent resistance to hydrogen-induced cracking

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ABSTRACT

There is a great challenge to simultaneously improve strength and resistance to hydrogen-induced cracking (HIC) for pipeline steels. In this study, through copper (Cu) alloying, a novel type of pipeline steel was developed to meet the requirement for both high strength and excellent resistance to HIC. The HIC tests of the tentative pipeline steels and the comparison steel were conducted in a hydrogen sulfide (H_2S) saturated solution according to NACE standard. The results showed that an acicular ferrite microstructure with uniformly distributed fine Cu-rich precipitates was obtained by aging at 500 °C for 1 h. Nano-scale Cu-rich precipitates in the new steels were speculated to play a significant role in making precipitation strengthening and providing beneficial hydrogen traps. The Cu-bearing pipeline steel has achieved a high strength grade of API X120 with excellent resistance to HIC.

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1. Introduction

Hydrogen-induced cracking (HIC) is well known as one of the significant hydrogen related problems for pipeline steels serving in the sour environment, namely as the wet corrosive environment containing hydrogen sulfide (H_2S) [1]. There have been numerous efforts to improve both the strength and the resistance to H_2S corrosion cracking for pipeline steels in sour oil and gas environments [2–5]. Unfortunately, it is still very difficult to enhance the strength level of the pipeline steel without reduction of the HIC resistance. This is a great challenge for the current development of pipeline steels. For the conventional pipeline steels, the strength level mainly depends on the manganese content in steels. However, as the manganese content increases, unfavorable microstructures such as large size martensite/austenite (M/A) islands, bainite and martensite are generated, which all deteriorate the HIC resistance of steels [6–10]. Therefore, hydrogen-induced crack usually initiates at the interface between the hard phase and the steel matrix, and then propagates along grain boundaries in higher strength grade pipeline steels such as API X100. Accordingly, the susceptibility to HIC increases with the strength grade [9].

Avoiding the hard phase constituents and employing the beneficial hydrogen traps in high strength grade pipeline steels are expected to be effective in preventing them from HIC. Most importantly, the microstructure with uniformly distributed fine hydrogen traps should maximize the resistance to HIC. Many attempts of using nano-scale carbonitrides in micro-alloyed steels to provide both precipitation strengthening and beneficial hydrogen traps have been made [11–17]. The results revealed that nano-scale carbonitrides are effective in increasing the H_2S resistance of steels. In those attempts, however, the strength grade for pipeline steel could not exceed API X100 (690 MPa) [15].

As previously mentioned, it is important that there is a judicious selection of alloying elements that can meet requirements for both high strength and HIC resistance. Alloying elements commonly used for pipeline steels are Mn, Mo, Cr, Ni, Nb, V, Ti, Cu, etc. [18–21]. Among these elements, Cu is very special because it could produce fine copper-rich precipitates by itself, which are quite desirable to improve both the strength [22–27] and the resistance to HIC for steels [28,29].

Cu has been employed to improve the resistance to HIC for steels in the environment with pH value greater than 4.0 [30]. It is believed that in that environment a stable Cu-containing scaled film can be formed on the surface of pipeline steels, and then their hydrogen permeation rate can be reduced. In this case, the Cu content is usually situated in the range of 0.2–0.7 *wt.%* [31], which seems relatively lower. Therefore, the pH value of the service environment could not go lower than 4.0. What will it happen if the Cu content in the pipeline steels is increased to a high level? Is it possible to achieve a better combination of strength and the resistance to HIC for pipeline steels? Little study has been conducted on this subject. Thus, a novel type of high strength pipeline steel with high Cu content was designed and investigated in the present work. Pipeline steels with different Cu levels in a range of 1–2 *wt.%* were fabricated to examine their mechanical properties and resistances to HIC in an acid solution with pH value of 3.2.

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Table 1
Chemical compositions of experimental steels (wt.%).

Steel	C	Si	Mn	Mo	Cu	Cr	Ni	Nb	V	S	P	Fe
1.0 Cu	0.031	0.14	1.09	0.31	1.06	0.32	0.32	0.05	–	0.0011	0.005	Bal.
1.5 Cu	0.019	0.12	1.03	0.31	1.46	0.31	0.31	0.05	–	0.0011	0.005	Bal.
2.0 Cu	0.023	0.13	1.06	0.30	2.00	0.30	0.30	0.05	–	0.0010	0.005	Bal.
X80	0.046	0.10	1.68	0.19	0.30	0.29	0.20	0.08	0.02	0.0013	0.005	Bal.

2. Experimental

The experimental steels were melted in a 25 kg vacuum induction-melting furnace. The nominal compositions of the steels are listed in Table 1. These newly developed pipeline steels are numbered as 1.0 Cu, 1.5 Cu and 2.0 Cu according to their Cu content designs. The X80 as the comparison is a commercial pipeline steel currently used in the pipeline industry. The steel ingots were forged into blocks of 70 mm × 70 mm × 80 mm and then austenitized at 1050 °C for 2 h. Finally, these blocks were hot rolled into plates 9 mm thick via 7 passes on a trial rolling mill with roll diameter of 450 mm. The finish rolling was carried out at 850 °C, and a fast cooling rate (20 ~ 30 °C/s) after rolling was achieved by water spray. The optimal precipitation behavior of copper was confirmed, and some of the as-rolled plates were aged at 500 °C for 1 h, and then air cooled to room temperature. The schematic diagram of thermo-mechanical controlled processing (TMCP) is shown in Fig. 1.

Microstructures of experimental steels were observed using optical microscope (OM) and transmission electron microscope (TEM). For the OM observation, samples were mechanically ground to #2000 with sand papers, polished, and then etched in a 2% nital solution. 300 μm thick disks were first mechanically thinned to foils about 50 μm thick and then electro-polished by a twin-jet electropolisher in a solution of 8 vol.% perchloric acid and 92 vol.% ethanol. These foils with very tiny holes were examined by a TEM (FEI Tecnai G^2 F20) at an accelerating voltage of 200 kV.

The tensile specimens with diameter of 3 mm and gauge length of 15 mm were machined from the plates perpendicular to the rolling direction. The geometric sketch of tensile specimen is shown in Fig.2.The tensile tests were conducted at room temperature at a tensile speed of 5 mm/min on a SCHENCK-100KN servo-hydraulic testing machine according to GB/T228.1 specification: Metallic materials tensile testing part 1-method of test at room temperature. In order to assure the reliability of the tensile results, three parallel samples were tested to get the average value. The error in yield strength and tensile strength measurement was noted as ~ ± 2%, and in elongation ~ ± 1%.

The HIC test was performed in accordance with NACE Standard TM 0284-2003. The specimens used in this test were 100 mm long and 20 mm wide, and identical to thickness of the plate. Fig. 3 shows the orientation of specimen and the faces to be examined. The samples were immersed in the Solution A (5.0 wt.% NaCl and 0.50 wt.% CH3COOH in distilled water) at ambient temperature and normal pressure, and the duration time was 96 h. The residual oxygen in the airtight vessel was purged by pure nitrogen for 2 h, and then hydrogen sulfide (H_2S) was charged into the solution for 24 h to keep the H_2S saturated. After the HIC test, the surface blistering was carefully examined under a Hitachi S-3400 N scanning electron microscope (SEM). The crack length ratio (R_{CL}), crack thickness ratio (R_{CT}) and crack sensitivity ratio (R_{CS}) were obtained.

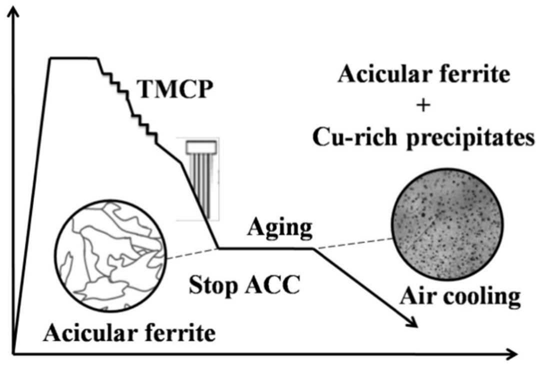

Fig. 1. The schematic diagram of thermo-mechanical controlled processing.

3. Results and discussion

Microstructure plays a very important role in the HIC resistance of steels. Fig.4 shows the microstructures of the newly designed pipeline steels and X80 steel. It can be seen that 1.0 Cu steel shows a polygonal ferrite (PF) dominated microstructure, as shown in Fig. 4a(i). The grain size is not uniform, varying in range of 2–10 μm. When the Cu content was increased to 1.5 wt.%, the microstructure presents a quasi-polygonal ferrite (QF) dominated microstructure plus a few polygonal ferrite (PF) with grain size of 4–10 μm, as shown in Fig. 4b(i). Whereas it can be seen that the microstructures of the as rolled 2.0 Cu steel (Fig. 4c(i)) and X80 steel (Fig. 4(d)) exhibit a typical acicular ferrite characteristic, i.e., non-equiaxed or non-polygonal various-size grains distributed in random orientations.

In contrast to the as-rolled samples, the ferritic microstructure of the aged samples became homogeneous, as shown in Figs. 4a(ii), b(ii) and c(ii). The non-uniform grain size characteristics were confirmed by TEM observation shown in Figs. 5a(i), b(i), and it is easy to distinguish the grains according to their sizes. Figs. 5c(i), d confirm that the acicular ferrite is characterized by an assemblage of interwoven nonparallel ferrite laths. All the Cu-bearing steels aged at 500 °C for 1 h show a large number of fine Cu-rich precipitates in steel matrix, as shown in Figs. 5a(ii), b(ii) and c(ii). The precipitates in both 1.0 Cu steel and 1.5 Cu steel show a size with diameter of ~10 nm, while ~20 nm in the 2.0 Cu steel. The Cu-rich precipitates became denser with increase of Cu content in the steel. These nano-scale Cu-rich precipitates potentially provide numerous sites for the re-distribution of hydrogen atoms in the steel.

Hydrogen blistering is a good reflection of the susceptibility to HIC for steels. The HIC test was conducted on the Cu-bearing steels and X80 steel. Fig. 6 shows the macro-photographs of these five steels after HIC test, and the hydrogen induced blistering (HIB) on X80 steel (Fig. 6a) and Cu-bearing steels (Figs. 6b, c, d, e) can be compared. Some HIBs with diameter of around 5 mm were observed on the surface of X80 steel, whereas there was no HIB on the surfaces of those Cu-bearing steels, which implies that the newly designed pipeline steels exhibited excellent resistance to HIC. EDS analysis taken from one of these HIBs showed that Fe, Mn and S were present, as shown in Fig. 6①, indicating that the hydrogen related corrosion occurred [9]. Whereas the EDS analysis on the 2.0 Cu as-aged steel surface showed that Fe, Mn,

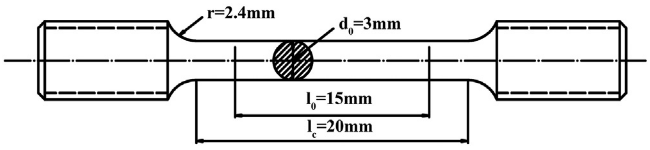

Fig. 2. The geometric sketch of tensile specimen.

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