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Microbial corrosion resistance of a novel Cu-bearing pipeline steel

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ABSTRACT

Microbiologically influenced corrosion (MIC) is becoming a serious problem for buried pipelines. Developing environmentally friendly strategies for MIC control is increasingly urgent in oil/gas pipeline industry. Copper (Cu) in steels can not only provide aging precipitation strengthening, but also kill bacterium, offering a special biofunction to steels. Based on the chemical composition of traditional X80 pipeline steel, two Cu-bearing pipeline steels (1% Cu and 2% Cu) were fabricated in this study. The microstructure, mechanical properties and antibacterial property against sulphate-reducing bacteria (SRB) and *Pseudomonas aeruginosa* (*P. aeruginosa*) were studied. It was found that the novel pipeline steel alloyed by 1%Cu exhibited acicular ferrite microstructure with nano-sized Cu-rich precipitates distribution in the matrix, resulting in better mechanical properties than the traditional X80 steel, and showed good MIC resistance as well. The pitting corrosion resistance of 1% Cu steel in as-aged condition was significantly better than that of X80 steel. A possible antibacterial mechanism of the Cu-bearing pipeline steel was proposed.

1. Introduction

Pipeline steels for transportation of oil and gas have been under development for several decades. The micro-alloyed pipeline steel is still a research hotspot due to the increasing pipeline construction around the world. The modern high performance pipeline steels are developing for high strength, high toughness, heavy wall, high deformability and sour resistance [1]. These steels are mainly based on the Fe-Mn-Mo-Nb alloy concept with ultra-low carbon content. Combining the thermo-mechanically controlled processes (TMCP) and properly cooling rate, the acicular ferrite or dual-phase microstructures, such as ferrite + bainite and bainite + martensite/austenite (M/A) islands, could be achieved. The acicular ferrite microstructure could produce a better properties combination, including high strength, excellent toughness, good hydrogen sulfide (H_2S) resistance and superior fatigue property [2–5]. The dual-phase microstructure showed high strength and high toughness as well as high deformability [6,7]. These pipeline steels with different properties have been studied intensively in the past years, aiming to respond to various severe environmental conditions.

However, with increase of the pipeline failure cases due to microbiologically influenced corrosion (MIC) in recent years, the problem of MIC on buried pipelines has attracted considerable attentions over the world. For example, the MIC phenomenon of underground pipeline was identified under the disbonded area, and sulphate-reducing bacteria (SRB) and acid producing bacteria (APB) were confirmed as the mainly microbes involved in the corrosion process [8]. The similar failure case also occurred in Germany. Enning and Garrelfs [9] reported that the external corrosion caused by SRB was observed on a buried gas transmission pipeline in bog soil. An oil leakage accident occurred on an X52 pipeline in the north of Iran and the field investigation showed that a SRB induced pitting corrosion was responsible for the stress corrosion cracking (SCC) [10]. Besides, Bhat et al. [11] reported that an 8-in oil dispatch pipeline failed from the internal corrosion within eight months of commissioning. One of the reasons was the extremely high microbe content. Another lesson on the pipeline failure was microbiological corrosion at Prudhoe Bay [12]. It was the largest spill for Prudhoe Bay oil field in the history and caused great economic loss.

MIC has been considered to be a major cause of pipeline failures [13]. It has been reported that more than 20% of pipeline system failures was related to microorganisms [14]. It is therefore important

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to improve our understanding of MIC and take measures to mitigate the MIC. Based on the up-to-date MIC research progress, it is well accepted that MIC is mainly caused by biofilm formed on the metal surface, which can change the electrochemical conditions and thus influence the corrosion processes [15]. According to this viewpoint, once the biofilm was destructed, MIC could be mitigated. Therefore, various physical, chemical or biological strategies have been used to control the occurrence of MIC, including pigging, biocides, antibacterial coating, cathodic protection and biological competition etc. [16–18]. However, these strategies have limitations of high cost, environment damage, and low efficiency. Accordingly, there is an urgent need to develop environmentally and friendly green strategies for MIC control.

However, up to now, no study has been found to attempt to solve the MIC of pipeline steel from the aspect of material itself. Therefore, development of novel pipeline steels with resistance to MIC is a promising and environmentally friendly method. Copper (Cu) is well known for its inherent antimicrobial performance and is the focus of interest for potential application as an element in antibacterial metal materials [19–23]. For example, the Cu-bearing antibacterial stainless steel, characterized by continuous release of trace amount Cu ions with antibacterial function, provides an analogy for development of the MIC resistance pipeline steels [24,25]. Furthermore, Cu can play many beneficial roles in steels, such as exerting a vigorous effect on hardenability [26], enhancing strength via precipitation strengthening [27], improving fatigue resistance [28], reducing susceptibility of hydrogen embrittlement [29], and improving uniform corrosion resistance [30]. Most recently, the presence of Cu-rich nano-precipitates in Cu-bearing pipeline steel was reported to benefit the resistance to hydrogen-induced cracking (HIC) [31].

In the present work, by using these special functions of Cu in steels, a novel Cu-bearing pipeline steel was fabricated by adjusting carbon (C) and manganese (Mn) contents and making proper Cu alloying design based on an X80 grade pipeline steel that is currently used in oil/gas industry. The microstructure, mechanical properties and antibacterial property of the Cu-bearing pipeline steels with X80 steel as the comparison were studied. The aim of this study is to explore whether the novel Cu-bearing pipeline steel can well balance the mechanical properties and the antibacterial property, which will lay a solid scientific and technological foundation for the development of MIC resistance pipeline steels.

2. Material and methods

2.1. Alloy design

In the novel pipeline steel, the key alloying element is Cu. Through adding proper amount of Cu to the currently used pipeline steels, fine nano-sized Cu-rich precipitates could be formed in the steel matrix by adjusting the aging treatment, which could improve the strength, ductility, HIC resistance and antibacterial property [31,32]. For the conventional pipeline steels, C and Mn are essential and economical alloying elements for solid solution strengthening. In the novel pipeline steels, the contents of C and Mn were reduced. The aim of decreasing the C content is to improve toughness and weldability. Cutting down the Mn content is to avoid the detrimental effect of centerline segregation and improve the resistance to HIC [33]. Meanwhile, for saving cost, the expensive alloying elements titanium (Ti) and vanadium (V) were not added.

Besides the chemical composition design, another important aspect is the microstructure control. Acicular ferrite is one of the most promising microstructures for pipeline steel application. High density tangled dislocations and fine grain size in this microstructure give rise to an optimum strength-toughness combination [34]. Thus, the acicular ferrite is still the goal microstructure of the novel Cu-bearing pipeline steel.

2.2. Materials

The Cu-bearing pipeline steels with different Cu contents were melted in a 25 kg vacuum induction melting furnace. The nominal compositions of the steels are listed in Table 1. For convenience, they are referred as 1.0Cu and 2.0Cu steels according to their nominal Cu contents. The X80 steel for comparison is a commercial pipeline steel currently used in the pipeline industry. Firstly, the steel ingots were forged into blocks of 70 mm × 70 mm × 80 mm and then austenitized at 1200 °C for 2 h. These blocks were hot rolled into 8 mm thick plates under a TMCP scheme recorded in Table 2. After final rolling, a fast cooling was applied to obtain the acicular ferrite, which was based on the measurement of continuous cooling transformation (CCT) diagram obtained on a Gleeble-3800 hot simulator [35]. The optimal precipitation behavior of Cu was confirmed, and some of the as-rolled plates were aged at 500 °C for 1 h, and then air cooled to room temperature [32].

2.3. Microstructure observation

Microstructures of experimental steels were observed using optical microscope (OM) and transmission electron microscope (TEM). For the OM observation, samples were mechanically ground with sand papers, polished, and then etched in a 2% nital solution. For the TEM observation, 300 μm thick discs were first mechanically thinned to about 50 μm thick foils 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.

2.4. Mechanical properties

Mechanical properties were determined by tensile test and impact test. The tensile test was conducted at room temperature at a displacement speed of 5 mm/min on a servohydraulic testing machine according to GB/T228.1 specification. Charpy impact test was performed at temperature of −20 °C using the sub-size Charpy V-notch specimens with size of 5 mm × 10 mm × 55 mm according to GB/T 229 standard.

2.5. Bacterial solution

Antibacterial property was verified using two microorganisms, SRB and *Pseudomonas aeruginosa* (*P. aeruginosa*). The SRB consortium used in this study was isolated from the soil located in Shenyang, China. They were anaerobically cultured in the API RP-38 medium with the following compositions: 0.2 g/L $MgSO_4 \cdot 7H_2O$, 0.5 g/L KH_2PO_4, 10.0 g/L NaCl, 1.0 g/L ascorbic acid, 4.0 g/L sodium lactate, 1.0 g/L yeast extract, and 0.02 g/L $Fe(NH_4)_2(SO_4)_2$. The pH of the medium was adjusted to 7.1 by 1 mol/L NaOH. The electrolyte solution was the NS4 solution [36], a simulated trapped electrolyte with compositions as follows: 0.122 g/L KCl, 0.483 g/L $NaHCO_3$, 0.181 g/L $CaCl_2 \cdot 2H_2O$ and 0.131 g/L $MgSO_4 \cdot 7H_2O$. It was sterilized by autoclaving at 121 °C for 20 min, cooling to room temperature, and then 50 ml of SRB-inoculated API RP-38 medium was injected into an oxygen-free sealed jar with 450 ml of NS4 solution. The total test lasted two months at a constant temperature of 37 °C.

P. aeruginosa was obtained from the Marine Culture Collection of China, Xiamen, China. They were cultivated in 2216E liquid medium that was composed of NaCl (19.45 g), $MgCl_2$ (5.98 g), Na_2SO_4 (3.24 g), $CaCl_2$ (1.8 g), KCl (0.55 g), Na_2CO_3 (0.16 g), KBr (0.08 g), $SrCl_2$ (0.034 g), $SrBr_2$ (0.08 g), H_3BO_3 (0.022 g), $NaSiO_3$

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