Effect of Cu Addition in Pipeline Steels on Microstructure, Mechanical Properties and Microbiologically Influenced Corrosion

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Abstract In the present study, Cu-modified pipeline steels were fabricated to mitigate MIC by the antimicrobial ability of Cu element. The microstructure, mechanical properties and the antimicrobial performance of the Cu-modified steel were systematically investigated. The Cu-modified steels showed good antimicrobial performance with remarkable strength enhancement by nanoscale Cu-rich precipitates and good impact toughness without changing the original base microstructures after the optimal aging treatment of 500 °C/1 h.

KEY WORDS: Pipeline steel; Cu addition; Mechanical properties; Microstructure; Antimicrobial performance

1 Introduction

Microbiologically influenced corrosion (MIC) has been recognized as a major problem in many industries such as oil/gas, and water utilities [1–4]. MIC is thought to be responsible for about 20% of all corrosion damage of metals and building materials [5]. In the natural gas industry, MIC can account for (15–30)% of corrosion-related pipeline failures [5]. It is therefore important to advance our understanding of MIC and take measures to mitigate MIC. Various physical, chemical or biological strategies have been used for MIC control, including biocides, coatings, cathodic

protection and biological competition. These strategies have limitations of being expensive, subject to environmental restrictions and sometimes inefficient. It has been widely accepted that MIC is mainly caused by biofilms formed on a metal surface which can change the electrochemical conditions and thus influence the corrosion processes [3]. Once the biofilms were destructed, MIC could be mitigated. As a common alloying element, copper is well known for its antimicrobial effect. For example, in ancient Egypt, Greece and Rome, silver and copper metals were used to clean wounds [6]. As early as in 1885, Milharde successfully developed a Bordeaux mixture containing Cu ions to kill bacteria. Following this history, many researchers have proved the antibacterial function of Cu ions and also proposed the relevant antibacterial mechanisms, although the exact mechanisms are still not fully understood [7, 8]. What will happen if a higher Cu content was added to pipeline steels? Is it possible to achieve a better combination of strength and antimicrobial activities for pipeline steels? This is a novel and interesting subject. In our recent study, it was reported that addition of Cu to pipeline steels could be exploited as a potential method for obtaining a high-strength steel together with excellent resistance to hydrogen-induced cracking (HIC) [9]. This is because Cu is very special

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alloying element in the steel. Cu could improve mechanical properties and corrosion resistance as well as the cold forming abilities for steels [10–12]. Through adding proper amount of Cu to steels, it could produce fine Cu-rich precipitates by adjusting the aging treatment. These tiny Cu-rich precipitates in nanoscale could be formed in the steels, which is responsible for the strength increase in the steels. Most importantly, Cu is one of the rare metallic elements known to exhibit antibacterial property in stainless steels [13, 14]. This gives us an insight that the addition of Cu to pipeline steels may play an important role in MIC mitigation.

In this study, a series of Cu-modified pipeline steels (1–2 wt% Cu) were fabricated; they show not only better mechanical properties but also strong antimicrobial performance. The effects of aging and Cu content on the microstructure and mechanical properties of the steels were investigated systematically. The age hardening response and corresponding mechanical properties as well as the microstructural evolution of the Cu-modified pipeline steels were studied in a wide range of temperature and time. The antimicrobial performance was verified by electrochemical measurement and surface observation in a near-neutral pH soil environment inoculated with sulfate-reducing bacteria (SRB).

2 Experimental

2.1 Materials

The materials used in this study were newly designed Cu-modified high-strength pipeline steels. They were melted in a 25-kg vacuum induction melting furnace. The analyzed compositions of the steels are listed in Table 1. The Cu-modified pipeline steels are denoted as 1.0, 1.5 and 2.0 Cu according to their Cu content. The X80 steel is also used in this study for comparison. Firstly, the steel ingots were forged into blocks of 70 mm × 70 mm × 80 mm and then austenitized at 1050 °C for 2 h. Then, these blocks were hot-rolled into plates about 9 mm thick under a thermomechanical-controlled processing (TMCP) scheme described in Table 2. After final rolling, the fast cooling rate was achieved by water spray, which was based on the measurement of continuous cooling transformation (CCT) diagram obtained on a Gleeble-3800 hot simulator [15].

2.2 Aging Treatment and Mechanical Properties

Differential scanning calorimetry (DSC) studies were carried out on the 2.0Cu and X80 steels to evaluate the precipitation behavior of Cu. The DSC samples with diameter of 3 mm and thickness of 2 mm were ground to 1000# with sand papers. The test was conducted at a heating rate of 20 °C/min on a SETSYS Evolution 18 DSC thermal analyzer using high-purity argon atmosphere. Based on the results of the DSC experiment, the experimental parameters were selected for conducting the aging treatments. The as-rolled samples were subjected to aging treatment at different aging temperatures for various periods of time. For both the Cu-modified and X80 steels, these included 10, 30 min, 1, 2, 5, 6, 8 and 10 h at 450 °C, and 10, 30 min, 1, 2 and 5 h at 500, 550 and 600 °C. After completion of aging treatment, the samples were air-cooled to the room temperature. Hardness measurements were conducted on polished surface of the samples using a Vickers hardness tester with a load of 500 g for 15 s, and the average value from five different measurements is reported. Based on the hardness measurement, tensile tests were conducted at room temperature at a displacement speed of 5 mm/min on a Schenck 100 kN servo-hydraulic testing machine according to GB/T228.1 specification (Metallic materials. Tensile testing. Part 1: Method of test at room temperature). The tensile specimens with a diameter of 3 mm and a gauge length of 15 mm were machined from the plates, perpendicular to the rolling direction. To assure the reliability of the tensile results, three specimens were tested to obtain the average value. The errors in the yield strength and tensile strength measurement were about ±2% and about ±1% in elongation, respectively. Charpy impact tests were performed at the temperature of −20 °C using the sub-size Charpy V-notch (CVN) specimens of 5 mm × 10 mm × 55 mm according to GB/T229 standard (Metallic materials–Charpy pendulum impact test method). The average of three results was recorded as the impact value for the specimens.

2.3 Microstructural Characterization

Microstructures of experimental steels were observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For SEM observation, the

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

Steel	C	Si	Mn	Mo	Cu	Ni	Nb	S	P	Other
1.0Cu	0.031	0.14	1.09	0.31	1.06	0.32	0.05	0.0011	0.005	0.32Cr
1.5Cu	0.019	0.12	1.03	0.31	1.46	0.31	0.05	0.0011	0.005	0.31Cr
2.0Cu	0.023	0.13	1.06	0.30	2.00	0.30	0.05	0.0010	0.005	0.30Cr
X80	0.028	0.28	1.90	0.22	0.20	0.29	0.08	0.0020	0.012	0.03V

Table 2 Procedure of the thermomechanical control process (TMCP) for the Cu-modified pipeline steels

Steel	Interpass reduction in thickness (mm) and rolling temperature (°C)							Accelerated cooling	
	78 → 62	62 → 45	45 → 30	30 → 24	24 → 16	16 → 11	11 → 9	Water cooling rate (°C/s)	Finishing temperature (°C)
1.0Cu	1025	*	*	894	*	*	835	24	420
1.5Cu	1030	*	*	930	*	*	814	20	416
2.0Cu	1019	*	*	923	*	*	830	27	414

* Temperature not measured during the fast rolling process

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 electropolished 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 using a TEM (FEI Tecnai G² F20) at an accelerating voltage of 200 kV.

2.4 Microbiologically Influenced Corrosion

Soils used in this study were taken from Shenyang, China. The soils were dried at 105 °C for 12 h and then ground to less than 1 mm diameter. The soil solution was prepared by extracting the soil with the distilled water/soil ratio of 5:1. The soil solution was autoclaved at 121 °C for 30 min and stored at 4 °C for use. Table 3 shows the analytical results of the soil compositions. The SRB strains used for this study were isolated from the soils. They were anaerobically incubated in the API RP-38 medium with the following compositions: 0.2 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 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 $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$. The pH of the culture solution was adjusted to 7.1 ± 0.1 by 1 mol/L NaOH. The SRB strains were activated in an incubator for 12 h before the experiment.

For electrochemical measurements, 1.0 Cu and X80 coupons with dimension of 10 mm $\times$ 10 mm $\times$ 5 mm were embedded in an epoxy resin, leaving an exposed area of 100 mm². The coupons were ground to 800# by sand papers, followed by rinsing with alcohol. A standard three-electrode electrochemical cell with 1000 ml solution (950 ml soil solution + 50 ml SRB-inoculated medium) was used for the electrochemical studies. It is composed of

test coupons as working electrodes, a platinum electrode as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. Several coupons were immersed in this cell for surface analysis. Prior to experiment, the cell was purged for 4 h with pure nitrogen gas to establish an anaerobic environment and then 50 ml SRB-inoculated medium was injected into the cell by a syringe. Linear polarization resistance (R_{LPR}) was monitored on 1.0 Cu and X80 coupons under biotic condition for 20 days. The measurements were performed using an EG&G PARSTAT 2273 electrochemical system at temperature of 30 °C. The R_{LPR} was measured in the range of ± 10 mV versus OCP at a scan rate of 0.166 mV/s. After the test, the corrosion products on the surface of the steels were removed according to GB/T 16545-2015 standard and then the pitting morphology was visualized by a field emission scanning electron microscopy (FESEM).

3 Results

3.1 DSC Study

DSC scans of the as-rolled steels of 2.0Cu and X80, measured from 150 °C to 650 °C, were recorded and are shown in Fig. 1. It is interesting to note that there are three similar exothermic peaks at low temperature (< 500 °C), which may be related to tempering of microstructure and recovery of locations therein [16]. The DSC curve of the 2.0Cu steel exhibits an extra exothermic peak at temperature around 550 °C. The corresponding exothermic peak in the case of the X80 steel was not observed. The extra exothermic reaction at 546 °C for the 2.0Cu steel indicates the Cu precipitation process.

Table 3 Compositions of the used soil ($\mu\text{g/kg}$ soil)

pH	Chemical composition								Organic content	Whole nitrogen content	Total salt content
	NO_3^-	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	K^+	Na^+			
7.75	46	31	48	234	57	32	2	14	2.26×10^4	910	464

3.2 Age Hardening

Based on the DSC results, the X80 steel and the Cu-modified steels were aged at 450–600 °C for various periods of time. The Vickers hardness of the four steels as a function of aging time is shown in Figs. 2 and 3. The hardness of the X80 steel shows slight change upon aging from temperature of 450–600 °C (Fig. 2a). After adding (1–2)% Cu to the steel, there is an obvious change in hardness, as can be observed in Fig. 2b–d. The hardness reaches the highest values of 235, 257 and 280 HV for the 1.0, 1.5 and 2.0Cu steels, respectively, if the aging time is fixed at 1 h. Moreover, at 500 °C, the peak hardness was reached for the steels after aging for 1 h. With further increase in the aging time, the hardness decreases, indicating that an over-aging effect occurs. This reduction in hardness is attributed to the combined effect of microstructural softening due to recovery and coarsening of Cu-rich precipitates at higher aging temperatures and for a longer aging time. However, the peak-aging has not been reached aging at 450 °C within 5 h. Extending the aging time up to 10 h, the highest values of 251, 272 and 288 HV for the 1.0, 1.5 and 2.0Cu steels, respectively, were reached at around 6 h (Fig. 3a). In order to analyze the effect of aging temperature on peak-aging time, the curves of hardness versus aging time at different aging temperatures are presented in Fig. 3. As can be observed, the peak-aging time was around 6, 1, 0.5 h and 10 min for the Cu-modified steels aged at 450, 500, 550 and 600 °C, respectively. Obviously, the peak-aging time decreases with increase in the aging temperature.

The increase in hardness on peak-aging, ΔH_{peak} , is summarized in Table 4. For the same Cu content, ΔH_{peak} decreases as aging temperature increases because of over-aging (in terms of temperature) effect and aging softening

due to recovery at higher temperatures. Moreover, ΔH_{peak} reached the highest value for the 1.5Cu steel at all the aging temperatures, indicating that the optimal Cu content is 1.5% with the highest hardness increase.

3.3 Tensile Properties

Room temperature tensile and impact tests were performed to investigate the influence of aging on mechanical properties of the Cu-modified pipeline steels. The tensile and impact specimens of three Cu-modified steels were aged at 450 °C for 6 h and 500 °C for 1 h, corresponding to the peak precipitation strengthening as identified above. For comparison, the tensile and impact tests were also conducted on the specimens aged at 550 °C for 1 h. Firstly, the mechanical properties, namely yield strength, tensile strength, elongation and impact toughness of three Cu-modified steels and the X80 steel in as-rolled condition are presented in Table 5. It can be found that with increase in the Cu content, the strength of the steels was increased and impact toughness was decreased. It can also be observed that the hot-rolled Cu-modified steels showed lower yield strength compared to the X80 steel. There may be two reasons for this phenomenon. (a) Hot-rolled Cu-modified steels have lower C (1.5 and 2.0Cu steels) and Mn contents compared to the X80 steel, which are two major strengthening elements in these steels. (b) Although the 1.0 Cu steel has higher C content than the X80 steel, solid solution strengthening effect of Cu is very small because of its similar radius to Fe atoms. Nonetheless, the as-rolled 2.0Cu steel displays a higher tensile strength than the X80 steel. The Cu-modified steels in as-rolled condition have lower yield/tensile ratios. It is believed that the deformability of the steel is improved by lowering yield/tensile ratio [17]. Therefore, the Cu-modified steels possess higher deformability than the traditional X80 steel. This is confirmed by the Cu-modified steels exhibiting higher elongations than the X80 steel. The tensile results for the Cu-modified steels subjected to aging after hot rolling are presented in Fig. 4. Compared with the as-rolled steels, both yield strength and tensile strength of the aged steels are remarkably improved, which evidently proved that the precipitation strengthening in steels took place through aging. The yield strength and tensile strength are well in agreement with the results of age hardening in Sect. 3.2. The optimum strength values were reached in the condition of aging at 450 °C for 6 h and 500 °C for 1 h. Figure 5 presents the increment of strength between the different Cu-modified steels as-rolled and aged at 500 °C for 1 h. Substantial increases in yield strength and tensile strength are observed in the Cu-modified steels. There are about 200, 215 and 225 MPa increments of yield strength for the 1.0, 1.5 and 2.0Cu steels, respectively, and there are about

Fig. 1 DSC thermograms showing the additional exothermic peak at 546 °C for the 2.0Cu steel compared with the X80 steel

Fig. 2 Hardness of various Cu-modified steels as a function of aging time **a** X80 for comparison, **b** 1.0Cu, **c** 1.5Cu, **d** 2.0Cu

70, 150 and 150 MPa increments of tensile strength for the 1.0, 1.5 and 2.0Cu steels, respectively. These results once more suggest that the optimal Cu content in the present investigation is 1.5%.

3.4 Impact Toughness

Figure 6 shows the effect of Cu content on the impact toughness of as-rolled steels and those aged at various temperatures and times. The impact result of the X80 steel is also given in Fig. 6 for comparison. As can be seen, the impact toughness is decreased with increase in the Cu content, and the 1.0Cu steel in as-rolled condition displays comparable impact toughness with the X80 steel. For as-rolled steels, Cu contributed to the strength via solution strengthening. For aging steels, Cu mainly contributed to the strength by precipitation strengthening. Both the strengthening techniques could increase the strength with increase in Cu but decrease in toughness. Therefore, the more Cu the steel contains, the lower the impact toughness of the steel was obtained in the present study. Moreover, the impact toughness was deteriorated after aging treatment. For the same Cu content, there is some increase in impact toughness with the increase in the aging

temperature for the Cu-modified steels. Aging at 550 °C for 1 h has resulted in slightly higher energy absorption than aging at 500 °C. However, the tensile stress, especially for the 2.0Cu steel, was reduced significantly after aging at 550 °C (Fig. 4). Thus, the above results indicate that the aging treatment at 500 °C for 1 h provides an appropriate condition for obtaining a substantial strength response with good impact toughness.

3.5 Microstructural Characterization

Figure 7 shows the representative SEM micrographs of the Cu-modified steels and the X80 steel, in the as-rolled and aged conditions. For the as-rolled samples, it can be seen that the 1.0Cu steel presents a polygonal ferrite (PF)-dominated microstructure (Fig. 7a). The microstructure is not homogeneous, and the grain size varies in the range of 2–10 μm . It is clear to distinguish the grains according to their sizes. When the Cu content is increased to 1.5%, the steel consists of a quasi-polygonal ferrite (QF)-dominated microstructure mixed with polygonal ferrite (PF) with grain size changing from 4 to 10 μm (Fig. 7b). It can be seen that the microstructures of the as-rolled 2.0Cu steel (Fig. 7c) and the X80 steel (Fig. 7d) exhibit a typical

Fig. 3 Hardness as a function of aging time at different aging temperatures, **a** 450 °C; **b** 500 °C; **c** 550 °C; **d** 600 °C

Table 4 Increase in hardness (HV) due to peak-aging at different aging temperatures

Steel	450 °C	500 °C	550 °C	600 °C
1.0Cu	58.0	41.0	36.3	24.0
1.5Cu	70.0	54.6	50.3	41.3
2.0Cu	65.3	53.5	44.3	28.0

acicular ferrite (AF) microstructure. A remarkable characteristic of this type of microstructure presents a unique and irregular configuration, which has various grain sizes distributed in a chaotic manner with random orientations [18]. Obviously, the microstructure of the 2.0Cu steel is more uniform than those of the 1.0 and 1.5Cu steels. In

contrast to the as-rolled samples, the microstructures of the aged samples subjected to 500 °C/1 h still keep the same ferrite characteristic but become homogeneous (Fig. 7e–h). The non-uniform grain size and acicular ferrite characteristics as well as Cu-rich precipitates have been reported in one of our previous work [9]. The precipitates in both 1.0Cu steel and 1.5Cu steels show a size with diameter of about 10 nm, while they are about 20 nm in the 2.0Cu steel. The Cu-rich precipitates became denser with increase in Cu content in the steel.

The 2.0Cu steel was selected to investigate the effect of aging on the Cu-rich precipitate evolution. Figure 8 shows the bright-field TEM micrographs of steels after aging at different temperatures and time. High-density particles

Table 5 Mechanical properties of the as-rolled steels

Steel	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Impact toughness (–20 °C) (J)
1.0Cu	443	651	30.0	141
1.5Cu	513	645	28.0	82
2.0Cu	608	759	25.0	66
X80	608	677	23.5	140

Fig. 4 Variation of yield strength (YS) and tensile strength (TS) with Cu content for the as-rolled and aged (450 °C/6 h, 500 °C/1 h, 550 °C/1 h) steels. Open and filled symbols represent YS and TS, respectively

Fig. 5 Increment of strength between as-rolled and aged steels with different Cu content

could be observed in the steel aged at 450 °C for 6 h (Fig. 8a). This is consistent with the result of hardness measurements in Fig. 3a. It can be found that there are very fine precipitates interacting with the dislocations in the steel aged at 500 °C for 10 min (Fig. 8b). The Cu-rich precipitates have not enough time to precipitate completely during this short time. However, the hardness increase is higher compare with other steels (Fig. 3b), indicating that the formation of Cu-rich precipitates should be very fast in the 2.0Cu steel. When the steel was aged at 500 °C for 5 h, the precipitate size was bigger and the density of precipitates was larger (Fig. 8c). The same trend was also observed in the steel aged at 550 °C. The precipitate size and the number density were increased with increase in the aging time (Fig. 8d–f). Figure 9 shows the average size determined by image analysis, which demonstrates this trend for the 2.0Cu steel under different aging conditions. Upon aging at 500 °C, the average size of the Cu-rich particles increases continuously from 11 ± 2 nm aged for 10 min to 16 ± 4 nm for 1 h and further to 26 ± 6 nm for

Fig. 6 Variation of impact toughness at –20 °C with Cu content for the as-rolled and aged (450 °C/6 h, 500 °C/1 h, 550 °C/1 h) steels

5 h. Aging at 550 °C, the average size of the Cu-rich particles increases from 20 ± 4 nm aged for 10 min to 24 ± 6 nm for 1 h and further to 34 ± 7 nm for 5 h.

3.6 Antimicrobial Performance

The 1.0Cu steel (aged at 500 °C for 1 h) and X80 steel were used to verify the effect of Cu on the antimicrobial performance in the soil environment. The linear polarization resistances (R_{LPR}) of the two steels are compared in Fig. 10 as a function of time. As can be seen, the two steels show the similar R_{LPR} values during the initial 4 days. From the day 2 to 6, R_{LPR} of the X80 steel declines sharply and reaches a minimum of $5.2 \text{ k}\Omega \text{ cm}^2$ on day 6, and then gradually increases to a steady state of $8.2 \text{ k}\Omega \text{ cm}^2$. In contrast, R_{LPR} of the 1.0Cu steel increases from $11.4 \text{ k}\Omega \text{ cm}^2$ on day 5 to $22.6 \text{ k}\Omega \text{ cm}^2$ on day 9, and then the 1.0Cu steel is typically $11\text{--}17 \text{ k}\Omega \text{ cm}^2$ noble than that of X80 steel. It is known that the corrosion rate is inversely related to the R_{LPR} value. This clearly indicates that SRB-influenced corrosion is inhibited by the nanoscale Cu-rich particles in the matrix of the 1.0Cu steel. The growth curve of SRB as a function of time is also shown in Fig. 10. The planktonic SRB experiences a rapid growth during the first 3 days, reaches the maximum from day 4 to 6 and then decreases sequentially. The trends of R_{LPR} match well with the growth phase of planktonic SRB.

Figure 11 shows the corroded appearance of two steels after 20 days exposure to SRB-inoculated soil solution. For the 1.0Cu steel, the scratches from pretreatment are clear on the surface (Fig. 11a). Some tiny pits are observed on the surface. However, there are more pits on the X80 coupon than that of on the 1.0Cu coupon, and these pits are of high-density and larger diameter. It is apparent that SRB induced serious pitting corrosion on the X80 steel compare

Fig. 7 SEM microstructures of Cu-modified pipeline steels and the X80 steel, **a** 1.0Cu steel as-rolled; **b** 1.5Cu steel as-rolled; **c** 2.0Cu steel as-rolled; **d** X80 steel as-rolled; **e** 1.0Cu steel 500 °C/1 h; **f** 1.5Cu steel 500 °C/1 h; **g** 2.0Cu steel 500 °C/1 h; **h** X80 steel 500 °C/1 h

Fig. 8 Bright-field TEM micrographs showing nanoscale copper-rich precipitates in the 2.0Cu steel under different aging conditions, **a** 450 °C/6 h; **b** 500 °C/10 min; **c** 500 °C/5 h; **d** 550 °C/10 min; **e** 550 °C/1 h; **f** 550 °C/5 h

Fig. 9 Average size of Cu-rich precipitates in the 2.0Cu steel under different aging conditions

Fig. 10 Variations of R_{LPR} with exposure time for X80 and 1.0Cu steels in the soil solution with SRB

with 1.0Cu steel. The values of R_{LPR} of two steels match well with the corroded appearance.

4 Discussion

4.1 Effect of Aging on Hardness for Cu-modified Steels

From the thermodynamic point of view, the age hardening behavior of Cu in steel depends on the Cu content, aging temperature and time. Only an overall effect can be observed on the aging curves (Figs. 2, 3). It is noted that typical age hardening and over-aging softening behavior was observed in the Cu-modified steels, and the extent of age hardening was increased with decreasing aging temperature (Fig. 2b–d). This effect can be attributed to the finer precipitate dispersions generated at lower aging temperature (Fig. 8a). In addition, the increment of hardness is significantly increased with increase in the aging

temperature and Cu content in a short aging time (Fig. 3). This means that there is no significant free energy barrier for the nucleation process at these temperatures [19]. Seko *et al.* [20] reported that the critical energy required for nucleation was very low in a binary Fe-Cu alloy. Viswanathan *et al.* [21] reported that there was no incubation period for the onset of Cu-rich precipitation in the 17-4 precipitation hardening stainless steel. Same result was also reported by Mirzadeh and Najafizadeh [19]. These simulation predictions and experimental results are all in agreement with the present results, where the Cu-modified steels had a very short incubation period for the Cu-rich phase precipitation (Fig. 3). Therefore, the precipitation and coarsening of Cu-rich particles are mainly determined by the diffusion of Cu atoms. The size of Cu-rich precipitates in the steel matrix can be described by the following equation [22]:

$$S = \alpha(Dt)^{1/2}, \quad (1)$$

where S is the average size of Cu-rich precipitates, α is determined by the concentration difference of Cu between the Cu-rich precipitate and the steel matrix, t is the aging time and D is the diffusion coefficient of Cu. D is determined by the following Arrhenius equation:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (2)$$

where D_0 is a constant determined by the diffusion mechanism and materials, R is the ideal gas constant, T represents the temperature in Kelvin and Q is the activation energy for the diffusion of Cu atoms.

A higher Cu content increases the average size of Cu-rich precipitates and the number density of Cu-rich precipitates [9]. With increasing aging temperature, the diffusion coefficient D in the above equations would increase rapidly, and with prolonging aging time t , the size of Cu-rich precipitates would also increase. Both parameters could increase the size of Cu-rich precipitates in the steel matrix. Consequently, the over-aging softening and coarsening behavior of Cu-rich precipitates in the Cu-modified steels are apparent after aging at 550 °C for 5 h (Fig. 8f).

On the other hand, the age hardening results indicate that the aging response was significantly accelerated by aging temperature for the Cu-modified steels. The Cu-modified steels reached peak hardness after about 6 h aging at 450 °C and 1 h at 500 °C. However, it was about 0.5 h at 550 °C and 10 min at 600 °C (Fig. 3). The elevated temperature accelerates aging of the Cu-modified steels because of increasing diffusion rate of Cu, which in turn enhances both nucleation and growth of Cu-rich precipitates. In the present study, the 1.5Cu steel was selected to analyze the effect of aging temperature on the peak-aging

Fig. 11 Morphologies of 1.0Cu steel **a** and X80 steel **b** exposed to soil solution with SRB after removing corrosion products

time. According to the method applied by Rana *et al.* [23] for age hardening of Cu-alloyed IF steel, at any fixed temperature T , the extent of aging is governed by the temperature-corrected time P , defined by

$$P = \frac{t}{T} \exp\left(-\frac{Q}{RT}\right), \quad (3)$$

where t is the aging time, Q is the effective activation energy and R is the ideal gas constant. Equation (3) provides a useful way for comparing aging data at different aging time and temperatures. From Eq. (3), the peak-aging time, t_{peak} , can be defined as

$$t_{\text{peak}} = (T \cdot P_{\text{peak}}) \cdot \exp\left(\frac{Q}{RT}\right), \quad (4)$$

where P_{peak} is the temperature-corrected peak-aging time, s/K. Taking experimental t_{peak} values of 6 h, 1 h, 0.5 h and 10 min, and using the values of the corresponding T in the experiment, ideally a linear plot of $\ln(t_{\text{peak}}/T)$ against $1/RT$ can be made from Eq. (4). The slope of the curve is Q and

Fig. 12 Experimental peak-aging time of 1.5Cu steel and its predicted peak-aging time

the intercept is $\ln(P_{\text{peak}})$. Thus, for the 1.5 Cu steel, $Q = 127 \pm 13$ kJ/mol and $P_{\text{peak}} = 1.59 \times 10^{-8}$ s/K were calculated by regression analysis with a correlation coefficient of 0.99. This approach describes the temperature dependence of peak-aging time and is illustrated in Fig. 12. Similar result has been reported by Rana *et al.* [23]. The time for peak-aging, t_{peak} , decreases as the aging temperature increases. However, the calculated activation energy from Eq. (4) in this work is higher than that of their result (74 kJ/mol). Nonetheless, this trend agrees well with the calculated activation energy of 109 ± 2 kJ/mol for another Cu-alloyed HSLA steel [24].

4.2 Effect of Cu Content on Microstructure and Mechanical Properties

Cu addition would affect the microstructure of the steels (Fig. 7). The 1.0Cu steel showed a polygonal ferrite-dominated microstructure (Fig. 7a), but the 1.5Cu steel still gave a mixed microstructure of quasi-polygonal ferrite and polygonal ferrite (Fig. 7b). Further increasing the Cu content, an acicular ferrite (AF) microstructure was formed in the 2.0Cu steel (Fig. 7c). It has been known that Cu is an austenite stabilizer in steels and possibly reduces the austenite-to-ferrite transformation temperature. Thus, the high-temperature transformation phase such as pearlite and polygonal ferrite would be suppressed [25]. To verify this possibility, the 1.5 and 2.0Cu steels with similar carbon concentration were selected to measure the continuous cooling transformation (CCT) diagrams. The transformation temperatures of two steels are shown as a function of cooling rate in Fig. 13. It is evident that the austenite-to-ferrite transformation temperature is lowered by adding more Cu, and the lowering austenite-to-ferrite transformation temperature could lead to an increase in the driving force for the acicular ferrite transformation (Fig. 13b).

Accordingly, the microstructure would be transformed from polygonal ferrite to acicular ferrite under a given cooling rate. Furthermore, the solute Cu atoms in austenite were reported to retard the recrystallization of hot-deformed austenite [26]. The 2.0Cu steel retained non-recrystallized austenite before transformation, which made the AF grains more uniform and fine (Fig. 7c).

Cu, as a solid solution strengthening element, contributes to the strength enhancement to a limited extent in the present study (Table 4). However, high-density fine Cu-rich particles could be obtained without changing the base microstructure (Fig. 7). Accordingly, the strength of the Cu-modified steels after aging was remarkably improved by Cu-rich precipitates (Fig. 5). According to the relationship between microstructure and mechanical properties of the Cu-modified steels, it is noted that the highest strength increase occurs in the 1.5Cu steel under the condition of aging at 500 °C for 1 h (Fig. 5). This can be explained by the synergistic effects of microstructure and Cu-rich precipitates. On the one hand, the more Cu the steel contains, the higher the strength of the steel was obtained. On the other hand, higher Cu content in the steel facilitates the coarsening of Cu-rich precipitates, thereby decreasing the hardening effect in the steel. Thus, the optimal Cu content in the present investigation is 1.5%. It was reported that acicular ferrite played an important role in enhancement of both strength and toughness of pipeline steels [27]. It is believed that a higher strength would be achieved if the 1.5Cu steel had an acicular ferrite microstructure. In addition, it is interestingly noted that the impact toughness was sharply decreased in the 1.5Cu steel compared with the 1.0Cu steel, while a slight decrease in impact toughness occurred in the 2.0Cu steel compared with the 1.5Cu steel at a given aging treatment (Fig. 6). In our previous work, EBSD analysis has been proved that acicular ferrite exhibited more bent crack propagation during the fracture compared with polygonal ferrite [28]. In

the present study, the phenomenon could be explained by schematic illustrations of the crack propagation path in QF (1.5Cu) and AF (2.0Cu) microstructures as shown in Fig. 14 [29]. In the QF structure, the crack propagates straight during fracture, changing its path slightly when meeting with new QF grains (Fig. 14a). However, the AF microstructure, including interwoven non-parallel ferrite laths [9, 17], is complex and the crack frequently bends at boundaries (Fig. 14b). The AF microstructure should have higher impact toughness if two steels had the same Cu content. Thus, a sudden decrease in impact toughness occurred in the 1.5Cu steel.

4.3 Effect of Cu on Antimicrobial Performance in Cu-modified Pipeline Steel

Cu is well known for its inherent antimicrobial effects and is the focus of interest for potential application as an element of antibacterial metal materials [13, 14, 30–34]. Actually, the exact antibacterial mechanisms are still not fully understood [8]. However, it has been known that Cu ions possess a strong biocidal capability. Antibacterial effect of Cu is generally contributed to its ability to accept and donate electrons as changing oxidation state between Cu^+ and Cu^{2+} [8]. This allows Cu to act as a catalyst for generation of reactive oxygen species that can cause oxidative damage to vital cell constituents such as proteins, nucleic acids or lipids [35]. Nan *et al.* [30–32] have confirmed that precipitation of Cu-rich phase caused by saturated Cu in the austenitic stainless steel is a crucial factor to kill the bacteria, and the Cu ions released from the Cu-rich phase play a dominant role in the antibacterial effect. Wang *et al.* [33] reported that novel 3Cr13MoCu martensitic stainless steel subjected to solution treatment following aging showed good antibacterial performance. Xia *et al.* [14] believed that inhibition of the biofilm was caused by the Cu ions released from Cu-rich phase in the 2205-Cu

Fig. 13 Continuous cooling transformation diagrams of **a** 1.5Cu and **b** 2.0Cu steels

Fig. 14 Schematic illustrations of the crack propagation path in quasi-polygonal ferrite (QF) of the 1.5Cu steel **a** and acicular ferrite (AF) of the 2.0Cu steel **b**

duplex stainless steel, leading to its effective mitigation of MIC by *Pseudomonas aeruginosa*. In the present study, the number of planktonic SRB reached the maximum from day 4 to day 6. Accordingly, the R_{LPR} values of two steels declined sharply (Fig. 10). For the Cu-bearing steel, Cu ions on the surface released from the Cu-rich phase resulted in SRB death, and the R_{LPR} of 1.0Cu steel was higher than that of X80 steel. As a result, the pits were significantly inhibited by SRB attack. Therefore, 1.0Cu steel presented a good antimicrobial effect and distinctly suppresses the occurrence of pitting (Fig. 11). However, there are still some unknown factors of the novel pipeline steel to be understood. For instance, what is the exact antibacterial mechanism for the Cu-bearing steel? Do the steel release Cu ions like the Cu-bearing stainless steel? Based on the good antimicrobial performance of the Cu-bearing pipeline steel, we will continue to carry out deeper studies to answer the above questions in the near future. In addition, pipeline steels, used for transportation of oil and gas, require high strength and high toughness as well as excellent resistance to HIC [36]. Many issues should be considered, such as possibility to be highly rolled at higher temperature, formability, weldability, etc. Therefore, many studies on development of novel Cu-modified pipeline steels should be pursued in the future. Fortunately, the precipitation of Cu-rich particles in the newly developed Cu-modified pipeline steels is very fast (Fig. 3). Therefore, this new type of pipeline steels may be coiled at temperature range of 500–550 °C after TMCP (Fig. 12). This processing step can be potentially used as the aging treatment for the hot-rolled plates without requiring any additional processing for Cu precipitation.

5 Conclusions

Novel Cu-modified pipeline steels showed the typical age hardening and over-aging softening behaviors at the aging temperature of 450–600 °C from 10 min to 10 h, and the 1.5Cu steel achieved the highest hardness increase after aging at 500 °C for 1 h. The aging response was

significantly more rapid at a higher aging temperature, and the peak-aging time can be well predicted from the hardness results. There is no significant free energy barrier for the nucleation process of Cu-rich precipitates. These make it possible to coil the hot-rolled Cu-modified steel plates after TMCP without requiring any additional processing step for Cu precipitation strengthening.

Cu lowered the austenite-to-ferrite transformation temperature and led to an increase in the driving force for the acicular ferrite transformation. Thus, the microstructures of Cu-modified pipeline steels were transformed from PF-dominated microstructure in the 1.0Cu steel to QF-dominated microstructure in the 1.5Cu steel and further to AF-dominated microstructure in the 2.0Cu steel at a given cooling rate with increase in the Cu content.

The Cu-modified steels showed good antimicrobial performance with remarkable strength enhancement by nanoscale Cu-rich precipitates and good impact toughness without changing the original microstructures at the optimal aging treatment of 500 °C/1 h.

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