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Role of inclusions in the pitting initiation of pipeline steel and the effect of electron irradiation in SEM

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ABSTRACT

The role of inclusions in the initiation of corrosion pits for a high strength pipeline steel in NaCl solution was investigated. The inclusions with typical compositions of Al-Mg-Ca-S-O were found typically spherical and responsible for the initiation of circular corrosion pits. The possible formation mechanism of the spherical inclusions and their role in the initiation of pitting corrosion are discussed. The electron irradiation in scanning electron microscopy, including the morphology observation and energy-dispersive X-ray spectroscopy test, was found to have significant influence on the pitting susceptibility around the inclusions.

1. Introduction

One third of the world's oil and gas resources are distributed in the ocean. Subsea engineering technologies are becoming increasingly attractive when the land energy resources are being gradually depleted. High strength low alloy steels (HSLAs), which are widely utilized in the construction of oil and gas pipelines, have been installed not only in the actual underground projects but also in the subsea environment [1–3]. The usage of high strength steel has significantly reduced the construction costs of oil and gas pipelines. However, it is well recognized that the seawater is highly corrosive to various metallic materials including the pipeline steels. The corrosion of these pipelines may become a potential threat to the safety of offshore oil and gas pipelines [4–6].

The failure of offshore structures may cause catastrophic consequences. For example, the Deepwater Horizon oil spill in the Gulf of Mexico in 2010 resulted in the world's largest accidental release of oil (4.9 million barrels) into the ocean in recorded history [7,8]. This accident caused huge economic losses and casualties, as well as serious impacts on coastal and marine ecosystems [9,10]. The failure of subsea pipelines due to corrosion was also reported in the U.S. Gulf of Mexico [11]. Thus, the study of corrosion behavior of structural materials in marine environment is of great significance.

Due to the unique material properties, the corrosion behavior of high strength steel is different from that of other materials [12–15]. Therefore, interest has risen in the study of corrosion behavior of high strength steel in marine environment [16–23]. It has been reported that high strength pipeline steel exhibited very high susceptibility to pitting corrosion, when exposed to aerated NaCl solution [24]. Massive corrosion pits were observed in the X80 pipeline steel after immersion in aerated NaCl solution for 30 min. Also, near-circular pitting morphology has been reported for the corrosion of X80 steel in naturally aerated NaCl solution [24,25], which was very different from the typically irregular corrosion pits reported for other materials [26–30]. The circular corrosion pits reported by Wang et al. [24] were similar to the pitting morphology of Ni-Cr-Mo-V steel in NaCl solution as reported by Yang et al. [31]. Tsutsumi et al. [32] also reported corrosion pits with near-circular shapes for the corrosion of stainless steel under a droplet of chloride solution. Efforts have been made to investigate the formation mechanism of circular pits on the surface of X80 steel in our previous work [24,33–35]. The horizontal propagation of corrosion pits was attributed to the diffusion of chloride ion in the horizontal direction [24]. An image recognition technique was introduced to recognize the diameters and locations of the circular corrosion pits formed on steel surface, indicating lognormal distribution of pit diameters and random spatial distribution of pit locations [34]. Although the initiation and propagation processes of pits have been presented in these studies, the formation mechanism of the circular shapes of corrosion pits is not yet fully understood.

In this paper, the role of inclusions in the formation of circular corrosion pits for high strength pipeline steel in NaCl solution was investigated. The inclusions in a high strength pipeline steel prior to corrosion processes were studied. The possible formation mechanism of the spherical inclusions was discussed. The pitting morphology after immersion tests was analyzed and the initiation sites of corrosion pits were determined.

Furthermore, it is considered that the electron irradiation in scanning electron microscopy (SEM) at high acceleration voltage may cause

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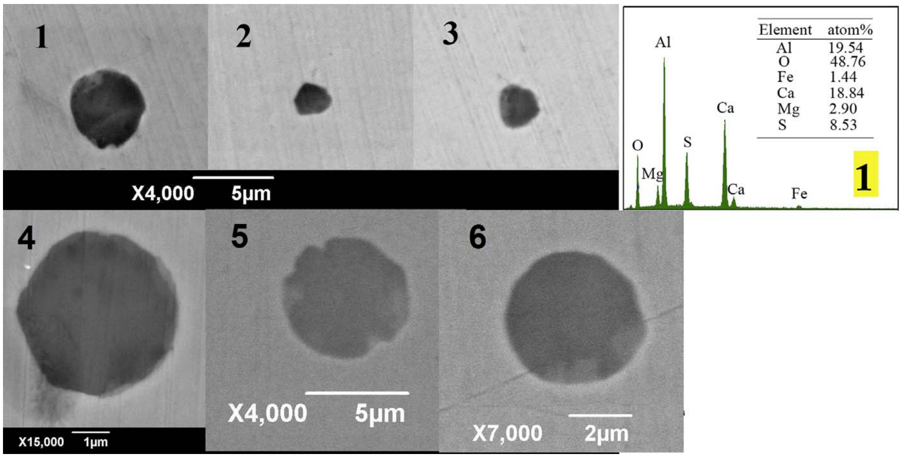

Fig. 1. Spherical inclusions observed on the surface of X80 steel, with the chemical compositions of inclusion 1 shown in the figure on the right.

damage to the sample surface, and consequently affect the corrosion susceptibility. The manner in which the corrosion process could be affected by the electron irradiation is discussed.

2. Experimental

2.1. Material and electrolyte

The material used in this paper was the X80 high strength pipeline steel, provided by the China Special Equipment Inspection and Research Institute (CSEI). The specimens with dimensions of 10 mm × 10 mm × 5 mm were cut from the steel plate (15 mm thick), with the following chemical compositions (wt.%): C 0.07, Mn 1.77, Ni 0.22, Mo 0.21, Si 0.30, P 0.02, S 0.005, Cu 0.22 and Fe balance. The electrolyte used in the corrosion tests was a naturally aerated 3.5 wt.% NaCl solution with a pH of 6.2, which was prepared from analytical grade reagent and distilled water. All the tests were conducted at ambient temperature.

2.2. Morphology observation

Prior to the corrosion tests, the specimens were ground gradually with 400- 1500-grit SiC abrasive papers and polished to a mirror surface with 1 µm diamond paste. The inclusions on the specimens were observed using a tungsten filament scanning electron microscope (TFSEM, JEOL, JSM-6390A) and the chemical compositions were confirmed using energy-dispersive X-ray spectroscopy (EDS, JEOL, JSM-6390A). The secondary electron (SE) mode was selected for morphology observation. The accelerating voltage was 15 kV for both SE and EDS scanning.

Several groups of immersion tests were performed to investigate the correlation between inclusions and the initiation of pitting corrosion. The specimens were immersed into 3.5 wt.% NaCl solution for 1 min, 7 min and 20 min, respectively. After immersion, the specimens were removed from the electrolyte, cleaned with alcohol and dried in air. The corrosion morphologies were observed by SEM and EDS (JEOL, JSM-6390A).

To obtain more direct evidence of pitting initiation from inclusions, one group of SEM tests was conducted according to the following procedure. Firstly, a mark was made on the surface of specimen using a Vickers hardness tester (Wolpert, 401MVD). Then, the inclusions around the mark were found under SEM and their chemical compositions were confirmed using EDS. The specimen was then immersed into 3.5 wt.% NaCl solution for 7 min. Finally, the corrosion morphologies around the above inclusions were observed. Following the same procedure, two more groups of tests were conducted using a field emission scanning electron microscope (FESEM, Zeiss Gemini500) to study the effects of electron irradiation in SEM. Different acceleration voltages (5 kV and 10 kV) were used to study the effects.

3. Results and discussion

3.1. Characterization of inclusions

First of all, to investigate the chemical compositions of inclusions, the polished specimens were observed using SEM and EDS (Fig. 1). The inclusions are typically spherical, with the general chemical composition of Al-Mg-O-Ca-S. The chemical compositions of the spherical inclusions were further studied using the line-scan EDS method, and three typical inclusions are shown in Fig. 2. It is seen that the distribution of elements is inhomogeneous. For the inclusions in Fig. 2a and b, Al and Mg are located in the center; Ca is located at the boundaries. For the inclusion in Fig. 2c, Ca is more uniformly distributed on the surface of inclusion with a very low content of Mg. For all these three inclusions, the simultaneous appearance of the peaks of Ca and S is observed; while it is observed that the peaks of Ca and Mg do not appear together at the same time. These findings are consistent with the chemical compositions of Al_2O_3-MgO-CaO-CaS inclusions. The formation mechanism of the inclusions is discussed in the following sections.

3.2. Formation mechanism of spherical inclusions

The MgO-Al_2O_3 spinel inclusions are formed during the production of steels [36–39]. Due to their high melting point and high hardness, the MgO-Al_2O_3 spinel inclusions have been considered detrimental to the castability of steel and the quality of products. Thus, control of the MgO-Al_2O_3 spinel inclusions has been a widely discussed topic in the field of metallurgy [40–42]. Calcium treatment is a common practice for modification of solid alumina inclusions to liquid/partially liquid calcium aluminates in the production of Al-killed steels [43–48]. The spherical Al_2O_3-MgO-CaO-CaS inclusions can be generated during the calcium treatment process, as illustrated in Fig. 3.

There are many examples of spherical Al_2O_3-MgO-based inclusions after calcium treatment, which have been reviewed by Yang et al. [44]. Before calcium treatment, the MgO-Al_2O_3 spinel inclusions are typically irregular. During the calcium treatment, the irregular MgO-Al_2O_3 spinel inclusions react with dissolved calcium. The magnesium in the inclusion is replaced by the dissolved calcium; and then dissolved magnesium is produced and enters the molten steel. A thin layer of CaO-Al_2O_3 is generated on the outside of the spinel inclusion. The outside CaO-Al_2O_3 layer may cover the original spinel and become a spherical shape due to the surface tension of the liquid CaO-Al_2O_3 phase. Finally, a spherical Al_2O_3-MgO-CaO inclusion is formed after calcium treatment.

According to the replacement reaction, Mg and Ca cannot coexist at the same location, which agrees well with the chemical compositions shown in Fig. 2. Usually the calcium treatment cannot fully modify the