Strain Aging Behavior of Microalloyed Low Carbon Seamless Pipeline Steel

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Received on September 9, 2015; accepted on September 30, 2015

1. Introduction

Ocean oil exploitation become more and more important as oil requirement is rapidly increased and reserves in land are reduced. It is well known that pipeline is one of the most important oil transportation tools in ocean oil exploitation. Whether or not it is safe will have a direct influence on the production of petroleum industry. The vibration of pipeline is inevitable due to the action of the wave and the current in sea, resulting in the occurrence of deformation of pipeline. Meanwhile, oil pipeline has often been heated by high temperature oil from heavy oil thermal recovery technologies in ocean oil exploitation. This simply means that the strain aging phenomenon will be caused during the oil transportation. In addition, pipeline steel is also subjected to a natural aging during a long time period at room temperature, resulting in the changes on the microstructure and mechanical properties after long-term service.1,2) Therefore, the pipeline steels are critically required to have not only high strength but also excellent deformability in ocean oil exploitation. Besides the marine environment, to meet the other severe environment such as earthquake, landslide, debris flow, etc, the pipeline steels are also required to have excellent deformability.3)

The effects of strain aging on mechanical properties can include the increase of yield strength and yield ratio, and the decrease of toughness and ductility. In view of its engineering significance, strain aging has drawn more and more attention from scientists and steel industries, particularly for the strain-based design applications.4–8) Compared with welded pipe, seamless pipe has been increasingly applied for oil transportation in severe environment, for example the marine environment, due to the homogeneity of mechanical property without welded joints. At present, increasing demand for strain aging design of seamless pipe has been needed for steel industries. However, such strain aging behavior has been extensively investigated in welded pipes,3–5,9,10) but rarely in seamless pipes.

To date, only very few investigations have been performed on the effect of various microstructures on the strain aging behavior of pipe so far. Thus, the aim of this work is to understand the role of the material structure on the strain aging behavior of microalloyed low carbon steel by varied heat-treatments.

2. Experimental Procedure

A microalloyed low carbon steel was provided by Baoshan Iron & steel Co., Ltd., with the composition as listed in Table 1. The steel was melted using a vacuum furnace, casted into ingots and hot-rolled into a 10 mm thick plate. The plates were heat-treated and the methods of heat-treatment and corresponding microstructures are shown in Table 2. The plates were pre-strained at room temperature on a Schimadzu tensile testing machine to reach tensile strains of 2.5%, 5.0% and 7.5%, respectively. The amount of strain was measured by an extensometer attached to the sample. After that, all samples were unloaded and aged at 250°C for 1 h. The tensile specimens and Charpy impact
specimens were prepared in accordance with the relevant ASTM standard. Round tensile specimens with a gauge diameter of 8 mm and length of 50 mm were obtained along longitudinal direction. For Charpy impact tests, Charpy V-notch impact specimens with a size of 10 mm × 10 mm × 55 mm were cut along transverse direction. In this study,

Table 1. Chemical composition of microalloyed low carbon steel (wt%).

| Alloy  | C   | S    | P    | Mn  | Mo | Ni | Cu | V + Nb + Ti |
|-------|-----|------|------|-----|----|----|----|-------------|
| X52NS | 0.19 | ≤0.005 | ≤0.012 | 1.80 | 0.22 | 0.15 | 0.01 | 0.23 |

Table 2. Heat-treatment methods and corresponding microstructures.

| Alloy  | Heat treatment technique | Microstructure |
|-------|--------------------------|----------------|
| X52NS | 950°C normalized         | Ferritic-pearlitic |
| X65QO | 960°C water quenched + 650°C tempered | Ferritic-cementitic |

Fig. 1. Microstructures of X52NS ((a)–(d)) and X65QO ((e)–(h)) before strain aging: ((a) and (e)) optical microscopic images; ((b) and (f)) SEM micrographic images; and ((c), (d), (g) and (h)) TEM bright field images.
each value of mechanical property was obtained by the average of two tests. Vickers hardness test was performed at room temperature under 0.2 kg load.

Microstructural evaluations of test samples were carried out using EVO MA25 scanning electron microscopy (SEM) and JEM 2100F transmission electron microscopy (TEM) equipped with energy-dispersive X-ray spectroscopy (EDX). The TEM thin foils of 3 mm diameter were prepared by the twin-jet polishing technique with a solution containing 4% perchloric and 96% ethanol at −30°C.

3. Results

3.1. Microstructure

The microstructures of X52NS and X65QO before strain aging are shown in Fig. 1. The microstructure of X52NS consists of the pre-eutectoid ferrite and pearlite and no apparent particles are observed in the microstructure (see Figs. 1(a)–1(b)). Details of microstructure of X52NS are further examined by TEM, as shown in Figs. 1(c)–1(d). It can be seen that there are two types of particles in the pre-eutectoid ferrite, one is square-shaped with sizes ranging in 50–200 nm and another is spherical nano-particles. Microanalysis has been performed on these two types of particles and the results reveal that the first type is (Ti, Nb)C and the second is V-rich carbide, as shown in Fig. 2. For pearlite, no particles are seen in eutectoid ferrite and the typical lamellar cementite is shown clearly.

Unlike X52NS, the microstructure of X65QO consists of polygonal ferrite, lath ferrite and particulate precipitates distributed within the grain and at the grain boundary (see Figs. 1(e)–1(f)). EDX microanalysis shows that the particles

![Fig. 2. EDS spectrum of particles: (a) ferrite phase for comparison; (b) square-shaped particles; (c) spherical nanoparticles; (d) large particles in Fig. 1(g).](image)

![Fig. 3. TEM micrographs of X52NS (a)–(b)) and X65QO (c)–(d) with 7.5% pre-strain after strain aging: (a) pre-eutectoid ferrite; (b) pearlite; (c) polygonal ferrite; (d) lath ferrite.](image)
precipitated more or less uniformly dispersed are particulate cementite. Details of microstructure are further examined by TEM, as shown in Figs. 1(g)–1(h). Further TEM observations confirm the presence of particulate cementite with the sizes ranging from 50 to 300 nm, as shown in Figs. 1(g) and 2(d). In addition, square-shaped (Ti, Nb)C and spherical nano-particles V-rich carbides are also revealed (Figs. 1(g)–1(h)).

SEM images do not exhibit any visible changes before and after strain aging. However, significant changes in the microstructure are revealed in TEM images. Bowing of dislocations resulting from pinning effect of nanoparticles (shown by arrows) is clearly seen in Figs. 3(a) and 3(c). The density of dislocations in steels after strain aging increases significantly in comparison with that of steels before strain aging, as shown in Figs. 1 and 3. It is noted that the serve bowing and breaking of lamellar cementite in pearlite for X52NS can be observed due to the large pre-strain, as shown in Fig. 3(b).

3.2. Mechanical Properties

The mechanical properties of all the samples are shown in Fig. 4 and Table 3. As seen in Figs. 4(a)–4(b), with the increase of pre-strain, the strength increases remarkably while the elongation and impact toughness decreases slightly. It is worth noting that the elongation of X65QO with 7.5% pre-strain dramatically decreases and reaches about 1% due to the occurrence of brittle fracture, as shown in Fig. 4(b). The yield ratios of X65QO with pre-strains of 2.5%, 5.0% and 7.5% are 0.963, 1.0 and 1.0, respectively and corresponding that of X52NS were 0.879, 0.947 and 0.970, respectively. Clearly, the yield ratios of X65QO with different pre-strains are significantly higher than that of X52NS. It is well known that the yield ratio of sample is a key factor for the strain-based design applications, so strain aging resistance of X52NS is, to a great extent, bet-
Table 3. Effect of strain aging on mechanical properties of samples.

| Sample     | Yield strength (MPa) | Tensile strength (MPa) | Yield ratio | Elongation (%) | −20°C Impact toughness (J) |
|------------|----------------------|------------------------|-------------|----------------|----------------------------|
| X52NS      | 374                  | 517                    | 0.723       | 19.0           | 166.0                      |
| 2.5%PS, 250°C/1 h | 479                  | 545                    | 0.879       | 16.3           | 151.0                      |
| 5.0%PS, 250°C/1 h | 536                  | 566                    | 0.947       | 14.8           | 147.0                      |
| 7.5%PS, 250°C/1 h | 571                  | 589                    | 0.970       | 13.3           | 133.3                      |
| X65QO      | 565                  | 583                    | 0.969       | 15.0           | 267.3                      |
| 2.5%PS, 250°C/1 h | 596                  | 619                    | 0.963       | 15.3           | 264.3                      |
| 5.0%PS, 250°C/1 h | 638                  | 648                    | 1.0         | 13.5           | 257.6                      |
| 7.5%PS, 250°C/1 h | 687                  | 687                    | 1.0         | 0              | 263.3                      |

Fig. 5. Effect of various amounts of pre-strain on the age harden-
ing response at 250°C in samples.

Fig. 6. Calculated dislocation density with various amount of pre-
strain for samples.

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The age hardening response of samples with varying amounts of pre-strains is shown in Fig. 5. It can be seen that the hardness of two samples gradually increases with the increase of the pre-strain and the hardness of X65QO is higher than that of X52NS at different pre-strains. The increase of hardness can mainly be attributed to an increase in the dislocation density in ferrite during strain aging process. The dislocation density in a pre-strain material can be evaluated from: 11)

\[
\rho = 8\pi (1 - \nu) \left( \frac{\sigma}{Gb} \right)^2 \tag{1}
\]

Where \( \rho \) is the dislocation density, \( G \) is the shear modulus, \( \nu \) is the Poisson’s ratio, \( \sigma \) is the pre-strain stress and \( b \) is the Burgers vector. The value of \( \sigma \) can be determined from the microhardness indentations using the following equation: 12)

\[
\sigma = \frac{2F}{3d^2} \tag{2}
\]

Where \( F \) and \( d \) are, respectively, the load and indentation diameter during the microhardness test. The dislocation density determined with the help of Eqs. (1) and (2) has been plotted against the amount of pre-strain in Fig. 6. The following constants have been used for the calculations: \( \nu = 0.33; G = 8 \times 10^{10} \text{ Nm}^2; b = 2.03 \times 10^{-10} \text{ m}. \)

Figure 6 reveals that the dislocation density of X65QO is higher than that of X52NS at different pre-strains. Several factors contribute to the observed change in hardness during aging of a pre-strain material. These include the amount of pre-strain (dislocation density), recovery and precipitation. In this case, recovery is insignificant due to low aging temperature (250°C) and small pre-strain (≤7.5%) 12) and no precipitation is observed in microstructure after strain aging. Therefore, the change of hardness can mainly be attributed to the pre-strain during strain aging process. In other word, the increase of hardness can mainly be attributed to an increase in the dislocation density in ferrite during strain aging process. Clearly, it seems appropriate to employ the Eqs. (1) and (2) in estimating the dislocation density during strain aging process.

In addition, it can be seen from Fig. 1 that the amounts of particles in X65QO is remarkably larger than that in X52NS. Clearly, an interaction between particles and dislocation is stronger for X65QO during the deformation process in comparison with that for X52NS. Therefore, the strain aging response of X65QO is stronger than that of X52NS at different pre-strains, indicating that the yield
ratios of X65QO with different pre-strains are significantly higher than that of X52NS. The dislocation density will increase with the increase in pre-strain from 2.5%, 5.0% to 7.5%. It is therefore concluded that the strength and yield ratio gradually increase with the increase of the pre-strain.

During controlled rolling process of TMCP (Thermo-Mechanical Control Process) for welded pipe, carbon and nitrogen should be solubilized supersaturately in the ferrite phase because of rapid cooling after controlled rolling. Aging of pre-strain material allows the interstitial solute atoms to diffuse to the existing dislocations, forming Cottrell atmospheres and pinning them, which causes strain aging phenomenon. In this case, during the heat-treatment process of X65QO (quenched/tempered) and X52NS (normalized), all carbon has been precipitated with the form of cementite, (Ti, Nb)C and V-rich carbides according to Fe–C binary phase diagram. This indicates that few free carbon atoms exist in ferrite for X65QO and X52NS. Therefore, unlike welded pipe, few carbon atoms in supersaturated solid solution diffuse to the mobile dislocations, forming Cottrell atmospheres and producing strain aging phenomenon in seamless pipe. This difference is attributed to the different pipe making technique: TMCP for welded pipe and traditional heat-treatment for seamless pipe.

The impact toughness can be related the formation and propagation of microcrack in the matrix. For X52NS, the continuous lamellar cementite in pearlite will provide fast-propagation paths which decrease significantly the impact toughness. On the contrary, many particles with high hardness, such as cementite, (Ti, Nb)C and V-rich carbides, uniformly dispersed in the soft ferrite matrix will act as an effective obstacle for the crack propagation. The means that the impact toughness is higher for X65QO than for X52NS.

For X52NS, the strain aging can take place in ferrite which generally leads to a decrease in impact toughness. In addition, continuous lamellar cementite in pearlite was damaged due to the large pre-strain, producing the serve bowing and breaking of lamellar cementite in pearlite which may decrease the fast-propagation paths of crack in the matrix, resulting in an increase in impact toughness. Consequently, the impact toughness of X52NS can be either decreased or increased during strain aging process, depending on the dominant events. The impact toughness decreases slightly by the strain aging, because continuous lamellar cementite in pearlite was damaged, leading to increase impact toughness.

After strain aging, the hardness of X65QO (222 HV) with pre-strains of 2.5%, 5.0% and 7.5% were increased and reached 235 HV, 250 HV and 281 HV, respectively. The increase of hardness can mainly be attributed to an increase in the dislocation density in ferrite, thus obtaining ferrite matrix with high hardness. However, the increase in hardness of ferrite matrix after strain aging can be ignored in comparison with the hardness of particles in ferrite, cementite (950–1 050 HV), (Ti, Nb)C (3 200 HV) and V-rich carbides (2 100 HV). Therefore, the microstructure after strain aging consists of many particles with high hardness dispersed in the soft ferrite matrix which is similar to that of X65QO without strain aging. Clearly, if the error bars were taken into account, impact toughness of X65QO does not experience obvious change for pre-strains of 2.5%, 5.0% and 7.5% after strain aging.

5. Conclusions

Static strain aging tests with different amounts of pre-strains were performed on a microalloyed low carbon steel with different microstructures. According to the changes of the microstructure and mechanical properties of steel after strain aging, the main results can be summarized as follows:

1. The yield ratios of steels with ferritic-pearlitic microstructure at different pre-strains are significantly higher than that with ferritic-cementitic microstructure, so strain aging resistance of normalized steel is, to a great extent, better than that of quenched-and-tempered steel.

2. An interaction between particles and dislocation is stronger for quenched-and-tempered steel in comparison with that for normalized steel. Therefore, the strain aging response of quenched-and-tempered steel is stronger than that of normalized steel at different pre-strains.

3. Unlike welded pipe, few carbon atoms in supersaturated solid solution diffuse to the mobile dislocations, forming Cottrell atmospheres and producing strain aging phenomenon in seamless pipe. This different is attributed to the different pipe making technique: TMCP for welded pipe and traditional heat-treatment for seamless pipe.

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