Effect of Oxidation Process on Surface Scale of 20Cr2Ni3 Piercing Plug Steel

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Abstract. A two-stage oxidation process compared with two conventional ones is conducted under drop-feeding atmosphere of H₂O-C₂H₅OH mixed solution for the surface treatment of the 20Cr2Ni3 steel piercing plug. The oxidation morphology and microstructure of the steel after oxidation treatment were studied by using optical microscopy and scanning electron microscopy. The results show that the investigated three oxidation processes are all appropriate from viewpoint of the steel microstructure. It is found that the two-stage oxidation process not only shows the best surface quality but also holds a moderate overall scale thickness with highest percentage of inner scale, and thus manifests the best performance. It is verified that Ni does not possess the thermodynamic conditions of oxidation under the specific atmosphere, and the mass transfer of Ni occurs in the form of elementary substance.

1. Introduction
Piercing plug generally operates at temperatures higher than 1200°C accompanied by extremely complex stress conditions, and always experiences an alternated cycling of quick heating and fast cooling [1], and therefore is one of the key deformation tool during manufacturing the seamless steel tubular product. A lot of researches have been conducted to seek for suitable ways to extend the plug service life owing to its vast quantity of consumption [2-4]. Generally speaking, the surface oxidation method is most economical and practical ones among the surface treatment methods for the piercing plug. The oxide scale formed on the piercing plug surface during oxidation treatment not only effectively isolates the heat from the hot steel billet to prevent strength softening and creeping, but also effects as lubrication under condition of the high-temperature billet piercing process. Therefore, it is very important to conduct a reasonable oxidation process to form an ideal structure of oxidation scale.
Alcohol (C\textsubscript{2}H\textsubscript{5}OH) and water (H\textsubscript{2}O) is widely employed in the method of controlled oxidation atmosphere for the plug surface treating \cite{3-4}. As for the commonly used Cr-Ni low-alloy steel plug, there are two layers of oxide scale after oxidation treatment. The outer layer is composed of Fe\textsubscript{2}O\textsubscript{3}, which is brittle and easy to fall off during billet piercing process, while the inner layer mainly consists of adhesive (Fe,\textsubscript{Cr})\textsubscript{3}O\textsubscript{4} and FeO \cite{5-8}. In our previous work, a two-stage oxidation process was designed to effectively prevent the outer layer scale falling off in the process of perforation. In the primarily stage, the thickness of the oxide scale was determined by oxidation reaction, and then the following stage was proceeded under the atmosphere of reduction reaction to transform the brittle Fe\textsubscript{2}O\textsubscript{3} to ductile FeO as the main outer layer constituent that was not easy to break up \cite{9}. In this paper, 20Cr2Ni3 steel is adopted as experimental material to characterize the influence of different oxidation processes on the surface scale quality and service life of the piercing plug.

2. Experimental methods

The chemical composition of 20Cr2Ni3 alloy steel is shown in Table 1. The piercing plugs were prepared after vacuum melting, casting, forging and machining. The cuboid samples with dimension of 6×6×36 mm were spark cut by wire cutting machine, and then polished by 600#SiC abrasive paper. The oxidation experiments of both the plugs and the cuboid samples were carried out in the furnace under atmosphere of drop-feeding H\textsubscript{2}O-C\textsubscript{2}H\textsubscript{5}OH mixed solution, and Fig.1 represents the main process parameters of different oxidation processes. Proc.1 and Proc.2 are the current processes of the concerned two factories, while Proc.3 is the specific two-stage oxidation process invented by our research group. All the three processes have a similar heating and cooling experience of four courses. Firstly, the plugs were heated to 900 ℃, and then the air in the furnace was removed by filling in nitrogen and alcohol with a flow of 3L/min and 60 drop/min, respectively. The oxidation treatment was conducted at 1020℃ in the furnace by filling in N\textsubscript{2} with a flow of 4.5L/min and furnace pressure is kept at 2Kpa. After oxidation at different drop-feeding flow and exposure time, the plugs were cooled within furnace to 850℃, followed by air cooling to room temperature.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Material & C & Si & Mn & Cr & Ni \\
\hline
20Cr2Ni3 & 0.20 & 0.70 & 1.50 & 2.00 & 2.60 \\
\hline
\end{tabular}
\caption{The chemical composition of experimental material (wt, %)}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Three different oxidation processes, in which C\textsubscript{2}H\textsubscript{5}OH is 99% pure ethanol, H\textsubscript{2}O is deionized water, and the ratio of C\textsubscript{2}H\textsubscript{5}OH to H\textsubscript{2}O is in volume}
\end{figure}

An electronic balance (Sartorius) with a sensitivity of 0.001g was used to measure the mass gain before and after oxidation of the cuboid samples. The cross-section specimens of the treated cuboid were prepared and polished for further observation. The average value of the scale thickness was
counted by measuring the equidistantly 20 points along the cross section of the oxidation specimen. A Quanta450 scanning electron spectroscop (SEM) incorporated with an energy dispersive X-ray spectrometer (EDS) was employed for characterization of the oxide morphology. A DM6000M metallographic microscope (OM) was employed to observe the microstructure of specimens after etching with 4% nitric acid alcohol. Each group of 13 plugs randomly selected from three different oxidation processes was applied to the billet piercing of a P110 steel grade casing in a seamless steel pipe factory, and the number of produced pipes per a piercing plug is recorded for comparison.

3. Results and Discussion

3.1. Mass gain of different oxidation processes

Fig. 2 shows the mass gain dependent different processes under oxidation at 1020°C. The mass gain of the three processes is about 450g/m² for Proc.1, 300g/m² for Proc.2, 390g/m² for Proc.3, respectively. It can be seen that the mass gain of Proc.1 is the largest because of the highest content of water (C₂H₅OH: H₂O =1:7). Although the exposure time of Proc.2 at 1020°C is prolonged to 4h, higher than that Proc.1 (3h), the mass gain is only 2/3 that Proc.1. The mass gain of Proc.3 lies between Proc.1 and Proc.2, about 86% that Proc.1, and 1.3 times that Proc.2.

![Figure 2. Oxidation mass gain dependent different processes](image1)

![Figure 3. Metallographic microstructure dependent different processes](image2)

3.2. Metallographic structure

Fig. 3 shows the metallographic structure of the cross-sectional specimens under three oxidation processes. It can be seen that all the specimens underwent the three processes consist of a large amount of bainite matrix dispersed with ferrite and there exhibits no obvious decarbonization layer. The decarburization layer can result in local softening of matrix and premature failure of the plug, therefore it can be inferred that the present three oxidation processes for the 20Cr2Ni3 plug steel are all appropriate from viewpoint of decarburization.

No significant difference is found to exist in the matrix steel, however, the oxide scale distinctly exhibits two layers. Fig. 4 emphasis the oxidation scale morphology, showing clearly two layers, which is consistent with the previous reports [5-6]. The outer oxide scales of both Proc.1 and Proc.2 are damaged to different degrees (Fig.4a-b), while that of Proc.3 (Fig.4c) is much integrated. For all the three processes, there exist large quantity of white dots in the inner oxide scale.
Figure 4. Cross section oxidation morphology of different processes (a) Proc.1, (b) Proc.2, (c) Proc.3

Fig.5a represents the variation tendency of the overall scale thickness under different processes, and which thickness of the inner layer is also presented for a comparison. The overall scale thickness of the three processes is about 400μm for Proc.1, 280μm for Proc.2, 350μm for Proc.3, respectively, and can be sequenced as Proc.1 > Proc.3 > Proc.2, which is consistent with the trend of oxidation weight gain curve (Fig.2). However, the inner oxide scale thickness sights differently and can be sequenced as Proc.1 ≈ Proc.3 > Proc.2 (Fig.4, Fig.5a). The oxidation exposure of Proc.3 is the same as that of Proc.2, but the oxide scale thickness of Proc.3 is much thicker than that of Proc.2. This indicates that the reduction reaction in the secondary stage of Proc.3 is accompanied by the oxidation reaction of H2O through the outer oxide scale into the inner layer, resulting in an increase in the inner oxide scale thickness. Fig. 5b represents the percentage of inner layer to total oxide scale, and it can be seen that the two-stage oxidation process holds the highest percentage of inner scale.

3.3. SEM morphology

Fig.6 shows the surface morphologies under different processes, and cracks are found in all the specimens, as remarked by the arrows in the figure. The cracks of Proc.1 (Fig.6a) are relatively wide and deep, and that of Proc.2 (Fig.6b) seem thin and shallow, while that Proc.3 (Fig.6c) become hardly identifying. The local morphologies at high magnification are put at the upper right corner of each figure, appearing similar small pores on the surface. The Proc.1 (Fig.6a) and Proc.2 (Fig.6b) have a large number of deep holes in the surface oxide scale, which makes the surface very rough, while the holes of Proc.3 (Fig.6c) is relatively shallow, and thus the surface is relatively smooth.

In the process of high temperature oxidation, a lot of H2 and CO2 are produced, sometimes accompanied by CrO2(OH)2, Fe(OH)2 and other volatile substances\textsuperscript{10-12}. These gases escape through the oxide scale, leaving small holes in the surface of the oxide scale that resemble pores through which the gas travels outward. Similarly, a large number of vacancies are produced in the mass transfer process, and the vacancies aggregate to form the pores in the oxide scale\textsuperscript{13}. These small holes (Fig.6)
result in different smoothness of the outer surface.

![Figure 6. Surface morphologies of the samples oxidized in different processes. Images with different magnifications are presented. (a) Proc.1, (b) Proc.2 and (c) Proc.3](image)

Cracks occurred on the surface of the outer oxide scale. The internal stress produced by oxide layer is the driving force of oxide scale cracking \[^{[14-15]}\]. The coefficients of thermal expansion of Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\) and FeO vary with temperatures, and the higher the temperature, the greater the coefficient of thermal expansion \[^{[16]}\]. After the oxidation treatment, the temperature decreases continuously, and the internal stress of the oxide scale is produced, which leads to the surface cracking of the oxide scale.

The advantages of Proc.3 is that the secondary stage is designed to be of reduction reaction so that the outer brittle oxide scale is reduced to FeO. Fe\(_2\)O\(_3\) or Fe\(_3\)O\(_4\) forms again by the reaction of FeO in the outer scale with air after that furnace cooling to 850°C when the furnace is opened. The newly formed oxide in the crack expands and fills the crack, and the pores can also be filled to improve the surface quality and make it relatively smooth.

![Figure 7. SEM analysis of the specimen under Proc.3 (a) Morphology of the inner oxide scale (b) The EDS pattern corresponding to the white dot](image)

It was reported that Ni can wedge the oxide film into the substrate and enhance the adhesion between the oxide film and the matrix \[^{[17]}\]. Fig.7a shows the SEM morphology of the inner oxide scale. The oxide is wedge-shaped into the matrix, and a large number of white dots appears in the inner oxide scale, which is in accordance with Fig.4. The white dot analyzed by EDS(Fig.7b) is mainly of Fe, rich in Ni and Cr.

3.4. Standard Gibbs free energy

The oxidation process in piercing plug steel is controlled by the heat and mass transfer through the reaction product of alloy elements with H\(_2\)O or FeO \[^{[7]}\]. According to the thermodynamic principle \[^{[18]}\], the standard Gibbs free energy required for the reaction of different alloy elements with 1 mol H\(_2\)O or FeO to form the certain oxides is calculated and listed in Table 2. For example, the standard Gibbs free energy for the reaction of C with 1 mol H\(_2\)O to form CO is -54322 J, and while that for reaction with 1
mol FeO to form CO is -39158 J. From the calculation results it can easily be concluded that the reactivity order is as follows: Si-Mn-Cr-C-Fe-Ni. It should be pointed out that the standard Gibbs free energy of Ni is greater than 0 at 1020 ℃, while the white spots in the inner oxide scale are mainly of Fe, and rich in Ni and Cr (Fig. 7), therefore, it is inferred that Ni does not undergo oxidation reaction under this condition, and mass transfer occurs in the form of simple substance. It had been reported that Ni could form through the reaction 3FeO+NiO → Ni+Fe3O4 [6], however according to the experiment, \( \Delta G = \Delta G^0 + RT \ln k_p \geq 55308 \text{J·mol} > 0 \) (C2H5OH:H2O =1:4), \( \Delta G = \Delta G^0 + RT \ln k_p \geq 48655 \text{J·mol} > 0 \) (C2H5OH:H2O =1:7), the reaction cannot proceed.

Table 2. Standard Gibbs free energy of different element oxides (J / mol)

| Reactant | Si→SiO2 | Mn→MnO | Cr→Cr2O3 | C→CO | Fe→FeO | Ni→NiO |
|----------|---------|---------|----------|-------|--------|--------|
| H2O      | -165591 | -109953 | -92099   | -54322| -15164 | 61917  |
| FeO      | -150428 | -94789  | -76935   | -39158| ---    | 77081  |

3.5 Performance of piercing plug under different oxidation processes

Fig.8 shows the macrophotographs of the piercing plugs under different oxidation processes. There are obvious differences in their surface appearance, which is a straight reflection of surface cracks and holes in the oxide scale. The color of Proc.1 is dark, and that of Proc.2 is very bright, while the color of Proc.3 looks glittering and translucent. The surface smoothness of the oxidation scale on piercing plug influences the quality of the inner surface of seamless steel tubular product, while the thickness and structure of the oxide scale directly affects the service life of the piercing plug, thereby affecting the production efficiency and expense.

These plugs were applied to the same batch of billet piercing during mass manufacturing the Φ139.7×9.19 mm specification of a P110 steel grade casing, and the number of produced pipes per a piercing plug is represented in Fig.9. The number of pipes produced by Proc.3 is about 1.3 times that of Proc.1 and about 1.6 times that Proc.2, and the concerned two-stage oxidation process possesses obvious advantages than the conventional processes.

4. Conclusions

The two-stage oxidation process compared with two conventional ones is conducted for processing the 20Cr2Ni3 steel piercing plug, the main results are as following:
(1) The matrix of 20Cr2Ni3 steel piercing plugs underwent the three processes consist of bainite and dispersive ferrite, and all exhibit no obvious decarbonization layer. The presented three oxidation processes for the 20Cr2Ni3 plug steel are all appropriate from viewpoint of microstructure.

(2) All the three processes exhibit two layers of oxide scale, where the inner oxide scales are wedge-shaped into the matrix. A large quantity of white dots with the composition of mainly Fe, rich in Ni and Cr appears in the inner oxide scale. It is verified that Ni does not possess the thermodynamic conditions of oxidation under the specific oxidation atmosphere at 1020°C, the mass transfer of Ni occurs in the form of simple substance.

(3) The two-stage oxidation process obtains a medium mass gain of 390g/m², about 86% and 1.3 times that other two processes, and holds a moderate overall scale thickness of about 350μm with highest percentage of inner scale, and subsequently manifests the service life about 1.3 to 1.6 times that of the conventional two processes.

(4) Many cracks and a large number of deep holes are found in the oxide surface of the conventional two processes, as for the two-stage oxidation process, there exists hardly identified cracks and relatively shallow holes which makes the surface appearance of processed piercing plug look glittering and translucent.

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