Precipitation and Growth of Ni-Rich Substances in the Oxide Scale of Steel in Mixed C$_2$H$_5$OH-H$_2$O Atmosphere

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Abstract. Nickel is an iconic alloying element in the piercing plug steel. In order to study the formation mechanism of Ni-rich substances in oxide scale of steel under mixed C$_2$H$_5$OH-H$_2$O atmosphere, the high-temperature oxidation experiment was carried out by employing steels with varied Cr and Ni contents, and the oxidation characteristic was explored by using scanning electron spectroscopy (SEM), energy dispersive X-ray spectroscopy (EDS), metallographic microscope (OM) and Image-Pro Plus. Under the experimental conditions, it is found that Ni promotes the formation of denser inner oxide scale while Cr inhibits inner oxidation effectively. Congregation of Ni-rich substances is a diffusion process strongly relying on the Ni content of the steel. The total Ni-rich substances dependence of Ni content follows the parabolic law. It is proposed that the Ni-rich substances precipitate once the oxidation of Fe or Cr atoms leaves vacancies for the nearby Ni atoms to fill in to form a substitute Ni-rich crystal structure, and then the Ni-rich substances congregate and grow up as oxidation proceeds. The results are meaningful for the reasonable design of piercing plug steel.

1. Introduction
Piercing plug generally operates at temperatures higher than 1200ºC and always experiences an alternated cycling of quick heating and fast cooling, and therefore is one of the critical deformation tools during manufacturing the seamless steel tubular product [1]. Alcohol (C$_2$H$_5$OH) and water (H$_2$O) are widely employed in the method of controlled oxidation atmosphere for the plug surface treating [2-3]. The key to prolong the service life of alloy steel piercing plug requires proper implementation of oxidation treatment as well as right selection of the material. In order to realize the above target, alloying elements are usually added to the piercing plug material, in which Ni and Cr are of the most commonly used elements [1]. Cr is easy to form dense oxide of Cr$_2$O$_3$ [4-6] to increase the oxidation resistance of materials, however, it is prone to form volatile hydroxides (CrO$_2$(OH)$_2$) [7-10] and thus loses its protective ability. Meanwhile, little information can be found on the oxidation behavior of Ni element in mixed C$_2$H$_5$OH-H$_2$O atmosphere. It is mentioned that water vapour has no influence on the oxidation of nickel [5], but Ni could form through the reaction 2Fe+3NiO→3Ni+Fe$_2$O$_3$ in high temperature steam [11]. However, our former research indicates that the oxidation behavior of Cr is similar to other researches while Ni behaves differently in drop-feeding mixed C$_2$H$_5$OH-H$_2$O atmosphere, as is revealed that Ni does not possess the thermodynamic conditions of oxidation, and not involves in oxidation reaction and thus the mass transfer is carried out in a form of elementary substance [12-13]. Ni exists in the inner oxide scale as dot-like simple substance. However, the process of how they precipitate and grow up is still unknown. What is more, adjusting the content variables of such as Cr and Ni in the materials can tune up the oxidation procedure and thus regulate
the quality of the oxide scale under drop-feeding mixed H$_2$O-C$_2$H$_5$OH atmosphere. Therefore, in this paper, 30Cr3NiMo2V, 20Cr2Ni3, 20CrNi4 and 316L with varied contents of Cr and Ni were used as the experimental materials to explore the formation mechanism of Ni-rich substances. It can be seen that 20Cr2Ni3 and 20CrNi4 are the generally used piercing plug steels, while 30Cr3NiMo2V and 316L alloy are introduced for better understanding the oxidation behavior of individual elements.

2. Experimental Procedures

The detailed chemical composition of experimental materials marked as 30Cr3NiMo2V, 20Cr2Ni3, 20CrNi4 and 316L is listed in Table 1. The experimental materials were prepared subsequently by vacuum melting, casting and forging. The samples for oxidation testing with the dimension of 8×8×16 mm$^3$ were spark cut and then ground up to 600-grit SiC abrasive paper followed by ultrasonically cleaning in ethanol and acetone.

| Material          | C   | Si  | Mn  | Cr  | Ni  | Mo | V  | Fe  |
|-------------------|-----|-----|-----|-----|-----|----|----|-----|
| 30Cr3NiMo2V       | 0.30| 0.20| 0.40| 3.00| 0.90| 2.00| 0.50| Bal.|
| 20Cr2Ni3          | 0.20| 0.70| 1.50| 2.00| 2.60|-- | -- | Bal.|
| 20CrNi4           | 0.20| 0.40| 0.60|1.30 | 3.65|-- | -- | Bal.|
| 316L              | 0.03|-- | 1.40|16.0 |10.0 |2.00|-- | Bal.|

The high temperature oxidation of the samples was conducted in the furnace under the atmosphere of drop-feeding mixed C$_2$H$_5$OH-H$_2$O solution. Firstly, the air in the furnace was removed by filling in alcohol and nitrogen with a flow of 50 drops·min$^{-1}$ and 2.5 L·min$^{-1}$, respectively. Secondly, the isothermal oxidation was carried out at 1020°C in the furnace for 4 hours by filling in mixed C$_2$H$_5$OH-H$_2$O solution with a flow of 2.5 L·h$^{-1}$ (Water is deionized, the alcohol is ethanol with the purity of 99%, and the volume ratio of alcohol to water is 1:4). Finally, the samples were cooled to 850°C in furnace, followed by air cooling to room temperature.

The cross-section oxidized samples were prepared and polished. A DM6000M microscope (OM) and a Quanta450 scanning electron spectroscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) were employed to characterize the cross-sectional morphology and the distribution of the chemical composition of oxide scale. The size and number of Ni-rich substances were counted by Image-Pro Plus. The oxide scales of 30Cr3NiMo2V, 20Cr2Ni3 and 20CrNi4 are thick, and the measured area can be selected by OM pictures. However, the 316L oxide scale is very thin and must be by means of SEM picture. To eliminate the influence of the size of the measured area on the statistical results, the percentage of a single Ni-rich substance in the measured area is firstly calculated, and the dimensionless value is used to characterize its size. Then, in order to compare the size of Ni-rich substance more clearly, it is divided into 6 grades (A: 0-0.2‰, B: 0.2-0.4‰, C: 0.4-0.6‰, D: 0.6-0.8‰, E: 0.8-1.0‰, F: more than 1.0‰) according to the Ni-rich substance size. Subsequently, the percentage of the number of Ni-rich substances in different grades in the measured area is tallied, and the value is used to compare the number of Ni-rich substances in different grades. The formulas are as follows:

$$P_s = \frac{S'}{S}$$  \hspace{1cm} (1)

$$P = \frac{X_i}{X} = A\cdots F$$  \hspace{1cm} (2)

Where $S'$ is the area of a single Ni-rich substance, $S$ is the measured area, $P_s$ is the percentage of the area of a single Ni-rich substance, $A\cdots F$ is the six grades according to the Ni-rich substance size, $X_i$ is the number of each grade, $X$ is the total number of Ni substances in the measured area, and $P$ is the percentage of the number of Ni-rich substances in different grades.
3. Results and Discussion

Fig.1 presents the cross-sectional oxidation morphologies of the four materials, showing obviously two layers. Inner oxidation can be found along grain boundaries in the matrix near the inner oxide scale, and the severity of inner oxidation ranks in order of 316L (Cr 16%)<30Cr3NiMo2V (Cr 3%)<20Cr2Ni3 (Cr 2%)<20CrNi4 (Cr 1.3%). It is known that Cr makes the oxide scale dense and reduces the oxidation rate [4-6]. Among the materials, inner oxidation of 20CrNi4 is the most serious, but the inner oxide scale is denser than that of 30Cr3NiMo2V and 20Cr2Ni3, for which the chemical composition is responsible, i.e., the Ni content of 20CrNi4 is relatively high while the Cr content is the lowest. As shown by the points 1-4 in Fig.1a-d, a large amount of varied size of dot-like substances can be found in the inner oxide scale. The density of dot-like substances ranks 30Cr3NiMo2V (Ni 0.90%)<20Cr2Ni3 (Ni 2.60%)<20CrNi4 (Ni 3.65%)<316L (Ni 10%) and the compactness of the inner oxide scale also follows the order above. It can be seen that under such experimental conditions, Cr can effectively inhibit inner oxidation, while Ni promotes the formation of dense inner oxide scale. The constituents and quality of the oxide scale is fundamental to improve the service life of the piercing plug during the process of pipe piercing, therefore, reasonable alloying of Cr and Ni in the piercing plug steel is especially important. Based on the results of 20CrNi4, Adding Cr appropriately can reduce certain degree of inner oxidation, and thus can improve the service life of the piercing plug as a whole.

Figure 1. Cross-sectional oxidation morphologies of the experimental materials (a) 30Cr3NiMo2V (b) 20Cr2Ni3 (c) 20CrNi4 (d) 316L and the lower left quarter are the enlarged interface between matrix and inner oxide scale

Figure 2. EDS analyses of point 3 in Fig.1c
Fig. 2 presents the result of EDS analysis of dot-like substance at point 3 in Fig. 1c. It can be seen that it is mainly of Fe, rich in Ni and Cr. According to the thermodynamic principles, the formation and growth of the oxide scale on the alloy surface is closely related to the Gibbs free energy of oxides. At the present case, the following reactions surely take place:

\[
3\text{NiO}(s) + 2\text{Fe}(s) \rightarrow 3\text{Ni}(s) + \text{Fe}_2\text{O}_4(s) \quad \Delta G^\theta = -156423 \text{ J/mol} \tag{3}
\]

\[
\text{NiO}(s) + 3\text{FeO}(s) \rightarrow \text{Ni}(s) + \text{Fe}_3\text{O}_4(s) \quad \Delta G^\theta = -30012 \text{ J/mol} \tag{4}
\]

However, NiO hardly forms, because

\[
\text{Ni}(s) + \text{H}_2\text{O}(g) \rightarrow \text{NiO}(s) + \text{H}_2(g) \quad \Delta G^\theta = 61917 \text{ J/mol} \tag{5}
\]

The standard Gibbs free energy (\(\Delta G^\theta = 61917 \text{ J/mol}\)) is higher than zero, so Ni does not possess the thermodynamic conditions of oxidation. Therefore, the existence of Ni is in elementary substance under the specific oxidation atmosphere [13].

Fig. 3 represents the distribution characteristic of Ni-rich substances of the four materials. Obviously, the size distribution is closely related to the Ni content of the steel. The Ni content of 30Cr3NiMo2V is the lowest and then most of the Ni-rich substances remain in the lowest A level (Fig. 3a), which accounts for about 69%, while all the other size grades occupy the rest, of which F level (the biggest level of size) only accounts for about 1%. With the increase of the Ni content from 20Cr2Ni3 to 20CrNi4 and then to 316L, the proportion of Ni-rich substances in grade A decreases to 29% in Fig. 3b, to 27% in Fig. 3c and then to 20% in Fig. 3d, respectively. On the other hand, the proportion of other grades increases, especially of grade F, and the proportion increases to about 11% and to 23% and then to 39%, respectively. It is clear the more Ni source supplies, the bigger size the Ni-rich substance grows.

Figure 3. Distribution of Ni-rich substances of (a) 30Cr3NiMo2V, (b) 20Cr2Ni3, (c) 20CrNi4 and (d) 316L, where I shows the morphology of the oxide scale, II shows the measured area, and III shows the histogram of Ni-rich substances distribution.
As discussed above, the materials with varied Ni content exhibit different influences on the formation of Ni-rich substances during the identical oxidation conditions. Let $P_{Ni}$ be the percentage of total Ni-rich substances area to the measured area. Fig.4 represents the variation curve of $P_{Ni}$ with the Ni content of the material $W_{Ni}$. It can be seen that with the increase of Ni content, Ni-rich substances increase at first and then tend to slow down. $P_{Ni}$ dependence of $W_{Ni}$ follows the parabolic law, and has the form:

$$P_{Ni} = -0.38W_{Ni}^2 + 8.0W_{Ni}$$

(6)

**Figure 4.** The total Ni-rich substances proportion dependence of Ni content

Such variation tendency reflects that precipitation of Ni-rich substances is a diffusion process of nucleation and growth which strongly relies on the Ni content of the steel.

According to Fig.1-3, we summarize a schematic diagram for the process of Ni-rich substances precipitation and growth at 1020°C in C$_2$H$_5$OH-H$_2$O atmosphere, as shown in Fig.5. At the initial oxidation process, the active elements such as Mn, Si, Cr and V oxidize firstly along austenite grain boundaries (dark grey dots in Fig.5a), and inner oxidation occurs accompanied by decarbonization [12], and then FeO oxide forms to replace the steel matrix along grain boundaries, meanwhile Ni at the oxidation area begins to nucleate and then gradually congregates into white dot particles (Fig.5b). As oxidation proceeds, diffusion process accelerates accompanied by the disappearance of the prior austenite grain, meanwhile the adjacent Ni-rich substances begin to merge and grow to lower its surface energy and make it more stable (Fig.5c). Finally, Ni-rich substances grow up by engulfing small particles around it, and present a macroscopic appearance shown in Fig.5d.

**Figure 5.** Macro schematic diagram of Ni-rich substances precipitation and growth, where dark grey dot refers to the inner oxidation particle of Mn, Si, Cr and V, white dot to Ni-rich substance, gray area to oxide and white area to steel matrix. (a) formation of inner oxidation particles, (b) nucleation of Ni-rich substances, (c) precipitation and (d) growth of Ni-rich substances
The particular aggregation behavior of Ni may be related to Fe which content is the highest in the steel. Ni and Fe have similar physical parameters. The atomic radii of \( \gamma \)-Fe and Ni are 0.1288 nm and 0.1246 nm, respectively, while the corresponding lattice constants are 0.36468 nm and 0.35236 nm. Moreover, the maximum solubility of Ni in \( \gamma \)-Fe is 100\% [14]. Under the experimental conditions, the crystal structure of steel is of face-centered cubic (FCC) type (Fig.6a), and Ni or Cr and other atoms replace the position of Fe atoms in \( \gamma \)-Fe to form a substitutional solid solution. The vacancy formation energy of Fe is 1.03 eV [15], while the diffusion activation energy of Ni in Fe is 2.26 eV [16]. At the initial inner oxidation stage, the reactions occur:

\[
Fe(s) + H_2O(g) \rightarrow FeO(s) + H_2(g) \quad \Delta G^0 = -15164 J/mol (0.157eV)
\]

\[
2Cr(s) + 3H_2O(g) \rightarrow Cr_2O_3(s) + 3H_2(g) \quad \Delta G^0 = -276296 J/mol (2.865eV)
\]

These reactions provide not only the formation possibility of vacancies but also simultaneously the energy for diffusion that might be from reaction heat.

Based on these facts, Fig.6 further illustrates the precipitation of Ni-rich substances from the atomic point of view. Fe or Cr atoms leave their original position and combine with O atoms to form FeO or Cr\(_2\)O\(_3\), leaving a large number of vacancies as diffusion channels (Fig.6b). The Ni atoms near the vacancies fill into the vacancy position to keep system energy minimum, causing the Ni atoms to come together to form a substitute Ni-rich crystal structure (Fig.6c-d).

\[\text{Figure 6. Microscopic schematic diagram of Ni-rich substances precipitation and growth. (a) FCC crystal structure of steel, (b) Fe or Cr atoms leaving their original position to form vacancies, (b) Ni atoms diffusing into the vacancies, (d) the formation of Ni-rich crystal structure precipitation.}\]

4. Conclusions

Four materials with varied contents of Cr and Ni were employed to explore the formation mechanism of Ni-rich substances in the oxide scale at 1020°C in C\(_2\)H\(_5\)OH-H\(_2\)O atmosphere.

1) Reasonable composition of Cr and Ni in the piercing plug steel is especially important. Sufficient Ni content promotes the formation of denser inner oxide scale while insufficient Cr content increases the inner oxidation severity. Appropriate design of the Cr and Ni contents can improve the service life of the piercing plug effectively.

2) The distribution characteristic of the Ni-rich substances is distinctly different for the materials containing varied Ni content under the same oxidation conditions. The more Ni source supplies, the bigger size the Ni-rich substance grows. The total Ni-rich substances dependence of Ni content follows the parabolic law: \( P_{ni} = -0.38W_{ni}^2 + 8.0W_{ni} \).

3) Congregation of Ni-rich substances is a diffusion process strongly relying on the Ni content of the steel. During the high temperature oxidation process, inner oxidation occurs firstly followed by the formation of iron oxide. Ni-rich substances precipitate once Ni atoms diffuse into the vacancies of former Fe or Cr position to form a substitute Ni-rich crystal structure, and then the Ni-rich substances nucleate and grow up as oxidation proceeds.
5. References

[1] Zheng C M, Yuan H P and Tian Q C 2018 Steel Pipe 47 14
[2] Ohnuki A, Hamauzu S, Kawanami T and Nakajima K 1986 Tetsu-to-Hagane 72 450
[3] Yang Z D 1998 J. Sichuan Univ. : Eng. Sci. Ed. 2 45
[4] Trindade V, Christ H J and Krupp U 2010 Oxid. Met. 73 551
[5] Saunders S R J, Monteiro M and Rizzo F 2008 Prog. Mater. Sci. 53 775
[6] Wright I G and Dooley R B 2010 Int. Mater. Rev. 55 129
[7] Berthod P, Aranda L, Mathieu S and Vilasi M 2013 Oxid. Met. 79 517
[8] Peng X, Yan J, Zhou Y and Wang F 2005 Acta Mater. 53 5079
[9] Yamauchi A, Kurokawa K and Takahashi H 2003 Oxid. Met. 59 517
[10] Asteman H, Svensson J E and Johansson L G 2002 Oxid. Met. 57 193
[11] Wang Z W, Gong X T and Jiang Z 2017 Min. Metall. Eng. 37 119
[12] Zheng C M and Tian Q C 2019 Acta Metall. Sin. 55 427
[13] Zheng C M and Tian Q C 2019 IOP Conf. Series: Mater. Sci. Eng. 490 413
[14] Hu GX Cai X and Rong YH 2000 Fundamentals of materials science (Shanghai: Shanghai Jiao Tong University Press ) p 32
[15] Wang Y J 1959 Acta Phys. Sin-ch Ed. 15 469
[16] Shu X L and Wang C Y 2004 Physica B 344 413