Improvement of Aluminum Erosion Behavior and Corrosion Resistance of AISI H13 Tool Steel by Oxidation Treatment

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In this work, H13 tool steel was prepared with different oxidation treatments to investigate the effects of oxidation temperature and soaking time. In order to improve erosion and corrosion resistance, this study tested with oxidation temperatures of 560°C, 580°C, and 600°C, and oxidation soaking times of 1 h, 2 h, and 3 h, respectively. Experimental results showed that the oxidation treatment at 600°C and for 3 h is the optimum process. The average thickness of the oxide layer was 9.2 μm. It showed that the oxide layer (Fe₃O₄) can protect and improve the aluminum erosion of H13 steel. The specimens that underwent the oxidative procedure were proven to effectively reduce the ratio of Al–Fe–Si compounds during erosion tests of A380 alloy solution. In addition, the results showed that the oxide layer can enhance polarization resistance, and quickly generate a passivation layer to increase the ability of corrosion resistance.

KEY WORDS: H13 tool steel; erosion; corrosion; oxidation; A380 alloy.

1. Introduction

Hot work tool steels are almost exclusively used on extrusion and die-casting dies. They are characterized by high strength, ductility, good tempering resistance, and moderate cost. AISI H13 tool steel is normally used for Al casting dies, given its good temperature resistance, high hot hardness strength, and good resistance to thermal fatigue, erosion and wear. In addition, it adds additional erosion and corrosion resistance through surface treatments. Past studies mostly aimed at enhancing the surface performance of the H13 steel, and thus, focused on the development of single coatings and/or thermo-chemical treatments to protect the die surface.1,2

During hot work steel processes, the die surface is rapidly heated and then quenched, thus resulting in a decrease of surface hardness and toughness.3,4 However, thermal gradients lead to dimensional variations, and generate stress and deformation. In aluminum die casting, tools are exposed to erosion, corrosion, and soldering; they are under frequent contact of a tool surface on the casting alloy, and are subject to oxidation due to high pouring temperatures.3

Therefore, the thermal fatigue and erosion are the most important life limiting tool failures known to hot work steels.5–7

Erosion is a major cause of failure in high temperature environments. The molten alloy reacts to the iron rich surface, thereby causing intermetallic formation and dissolution of the steel surface into the melt.3,11 Furthermore, oxidation is one of the most economical and effective methods to improve erosion and corrosion resistance of steels.3,10 During the oxidative process, most steels can form several kinds of oxides, such as iron forms wustite (FeO), magnetite (FeO+Fe₂O₃ or Fe₃O₄) and hematite (Fe₂O₃). Previous studies have pointed out that Fe₃O₄ are the most beneficial to improving the erosion and corrosion resistances of steel.4,11,12

The objective of this study is to explore the possibility of surface engineering of the AISI H13 steel surface to reduce erosion and corrosion of the die surfaces.

2. Experimental

In this study, the erosion resistance of oxidation treatment was evaluated by its weight loss percentage. The weight losses of the specimens dipped in molten aluminum alloy A380 for a predetermined length of time are shown in Fig. 1(a). The experimental simulation of erosive behaviors of aluminum alloy is similar to the die casting process. The chemical composition (mass %) of the AISI H13 tool steel is as follows: 0.39% C, 0.81% Si, 0.02% P, 0.38% Mn, 0.14% Ni, 5.0% Cr, 1.15% Mo, 0.82% V and 91.29% Fe. Furthermore, the specimen sizes of the erosion test, as shown in Fig. 1(b), are AISI H13 tool steel quenched at 1 030°C, tempered at 580°C, and repeated 3 times to reach a hardness of HRC 47–48.

Oxidation treatment equipment is shown in Fig. 2. In this study, three different oxidation temperatures (560°C, 580°C, and 600°C), and three different soaking times (1 h, 2 h, and 3 h) were set as test conditions, respectively. The test specimen was dipped in the aluminum alloy A380 melt and maintained at 750°C. The rotation speed of specimen was kept at 50 rpm. The dip time was 4 h for all specimens,
in order to enhance the erosion rate and weight loss. After removing the aluminum, specimens were cleaned with NaOH to remove any oxide or other residue. The weight loss percentage of erosion test is calculated as follows:

\[ \text{Weight loss (\%)} = \frac{\text{IW} - \text{AW}}{\text{IW}} \times 100 \]

IW is the initial weight, and AW is the weight after erosion test.

Corrosion potential analysis adopted three electrodes method. Reference electrode was saturated with silver–silver chloride electrode, auxiliary electrode was a Platinum electrode, and working electrode was connected to the testing specimens. The contact area of specimen was 2.01 cm². Meanwhile, the corrosive solvent used 3.5 wt% NaCl, and was kept at room temperature. The main parameters of corrosion testing included: scanning speed of 0.5 mV s⁻¹, initial potential of −1.5 V, and the final potential of 0.5 V. The polarization curve was obtained by Corr-View software for analysis, and compared with different oxidation parameters of the corrosion potential \( E_{\text{corr}} \) and corrosion current \( I_{\text{corr}} \). Finally, the polarization resistances \( R_p \) of different oxidation treatments for AISI H13 tool steel were compared.

3. Results and Discussion

Figure 3 shows the XRD patterns of H13 tool steel after 560°C oxidation treatment for AISI H13 tool steel after different soaking time. Obviously, at the same temperature and different soaking times of oxidation treatment, XRD analysis indicated that two different kinds of oxide layers were provided after oxidation treatments, which are the crystal structures of Fe₃O₄ and Fe₂O₃. The intensity of the original \( \alpha \)-Fe gradually decreased as the soaking time of oxidation increased, indicating that increasing the soaking time of oxidation would reduce the proportion of the \( \alpha \)-Fe structure. On the contrary, Fe₃O₄ and Fe₂O₃ diffraction peaks gradually increased as the soaking time of oxidation increased. These results are the same as those of oxidation processes at 580°C and 600°C, with soaking times of 1 h, 2 h and 3 h.

In order to discuss the melting loss of A380 aluminum alloy by different oxidative parameters for AISI H13 tool steel, the weight loss percentage of un-treated and oxidation treated AISI H13 tool steel after 4h erosion tests were compared, as shown in Fig. 4. At the same temperature of oxidation treatment, increasing the soaking time (1 h→2 h→3 h) could help to reduce the rate of melting loss. However, there was only a minor improvement for the treatment process at 560°C with soaking times of 1 h, 2 h, and 3 h.
indicating that an oxidation temperature above 580°C would have better anti-damage effects of aluminum melt. In addition, when the oxidation temperature reached 600°C, the erosion rate rapidly decreased to obtain the best improvement. The test results revealed that the oxidation temperature and soaking time would directly affect the erosion rate of the specimens. Therefore, increasing the oxidation temperature (560°C→580°C→600°C) or the soaking time (1 h→2 h→3 h) is beneficial to improving the melting loss of aluminum alloy for AISI H13 tool steel.

**Figure 5** shows the thickness of the oxide layer of AISI H13 tool steel after oxidation treatments at different temperatures and soaking times. The results show that the thickness of the oxide layer was not significantly increased after treatment at 560°C, even when the soaking time was increased to 3 h. However, the thickness rapidly increased after treatment at 580°C and 600°C with soaking time of 2 h. Both indicate a significant change in the thickness of the oxide layer. The greatest thickness of the oxide layer (9.2 μm) appeared after treatment at 600°C with soaking time of 3 h. In this study, extending the soaking time increased the thickness of the oxide layer after treatment at 580°C. When the oxidation temperature was greater than 560°C, an increase of the oxidation temperature would result in a higher oxide thickness.

Normally, the oxide formed on the alloy surface consists of an outer layer of porous magnetic (Fe₃O₄) and an inner layer of iron chromium oxide, (Fe, Cr)₃O₄ with spinel structure. Moreover, increasing the oxide temperature would effectively enhance the diffusion speed of oxygen elements, and increase the heat-activation of iron substrate. The relative agreement between the activate energies for oxidation and that of grain boundary diffusion of oxygen supports an activation of melting leads to a substrate material loss of the iron element, the high temperature molten aluminum would enter the substrate by diffusion. As a result, A380 alloy would produce inter-metallic compounds with the iron, and thus, appear in the boundaries of the steel. The EDS analysis on areas A and B for un-treated H13 tool steel, as listed in Table 1, found that areas A and B contained similar elements, mainly iron, aluminum, and silicon elements. It was proven the previous metallographic observation was the Fe–Al–Si intermetallic compounds. Due to the high temperatures involve (above 750°C), chemical reaction and diffusion play an important role at the cast metal–die steel interface. Die steel dissolves in the aluminum alloy melt forming complex aluminum–iron–silicon intermetallics. Furthermore, previous study has proposed intermetallic layers (AlₓFe₇Si₃) form at the cast metal–die steel interface when the liquid metal is brought in intimate contact with the die steel. Their morphology depends on the composition of the cast metal and die steel. Consequently, it is reasonable to suggest that the intermetallic layers (AlₓFe₇Si₃) in this study should be the AlₓFe₇Si₃, AlₓFe₇Si₃, and AlₓFe₇Si₃ after H13 steel is immersed in molten A380 alloy.

**Figure 6** shows the SEM observation of AISI H13 tool steel after treatment at 600°C with soaking times of 1 h, 2 h, and 3 h, before and after erosion tests. All oxidation treatments clearly indicated the location of the oxide layer and the structure of the matrix, and remained the standard Martensite structure, as shown in Figs. 7(a), 7(c), and 7(e). After 4-h erosion tests, it was found that the Fe–Al–Si compounds were generated after treatment at 600°C with soaking time of 1 h, as shown Fig. 7(b). When the oxide time was increased to 2 h, there was no significant compound appeared in the boundaries, as shown in Fig. 7(d). However, there were almost no compounds after treatment at 600°C with soaking time of 3 h, as show in Fig. 7(f). Particularly, the oxide layer was appeared obviously and exited in the un-treated H13 tool steel material was obviously eroded by the A380 aluminum alloy. Because the dynamic behavior of melting leads to a substrate material loss of the iron element, the high temperature molten aluminum would enter the substrate by diffusion. As a result, A380 alloy would produce inter-metallic compounds with the iron, and thus, appear in the boundaries of the steel. The EDS analysis on areas A and B for un-treated H13 tool steel, as listed in Table 1, found that areas A and B contained similar elements, mainly iron, aluminum, and silicon elements. It was proven the previous metallographic observation was the Fe–Al–Si intermetallic compounds. Due to the high temperatures involve (above 750°C), chemical reaction and diffusion play an important role at the cast metal–die steel interface. Die steel dissolves in the aluminum alloy melt forming complex aluminum–iron–silicon intermetallics. Furthermore, previous study has proposed intermetallic layers (AlₓFe₇Si₃) form at the cast metal–die steel interface when the liquid metal is brought in intimate contact with the die steel. Their morphology depends on the composition of the cast metal and die steel. Consequently, it is reasonable to suggest that the intermetallic layers (AlₓFe₇Si₃) in this study should be the AlₓFe₇Si₃, AlₓFe₇Si₃, and AlₓFe₇Si₃ after H13 steel is immersed in molten A380 alloy.

**Figure 7** shows the SEM observation of AISI H13 tool steel after treatment at 600°C with soaking times of 1 h, 2 h, and 3 h, before and after erosion tests. All oxidation treatments clearly indicated the location of the oxide layer and the structure of the matrix, and remained the standard Martensite structure, as shown in Figs. 7(a), 7(c), and 7(e). After 4-h erosion tests, it was found that the Fe–Al–Si compounds were generated after treatment at 600°C with soaking time of 1 h, as shown Fig. 7(b). When the oxide time was increased to 2 h, there was no significant compound appeared in the boundaries, as shown in Fig. 7(d). However, there were almost no compounds after treatment at 600°C with soaking time of 3 h, as show in Fig. 7(f). Particularly, the oxide layer was appeared obviously and exited in the
boundary after 4-h melting tests. These results were further compared with the weight loss percentage, as shown in Fig. 4. It is reasonable to suggest that the oxide layer plays an important role in reducing melt loss for AISI H13 tool steel.

**Figure 8(a)** shows the SEM observation and line-scan of Fe, Al, Si, and O elements after treatment at 600°C with soaking time of 3 h, after 4-h erosion tests. As seen in Fig. 8(e), the obvious oxygen elements still exited between the Fe–Al–Si compound and H13 substrate. It is suitable to
Table 2. Comparison of the un-treated and different oxidation treatments for AISI H13 tool steel after 3.5 wt% NaCl corrosion tests.

| Process       | $\beta_1$ (mV) | $\beta_2$ (mV) | $I_{\text{corr}}$ (Amp/cm$^2$) | $E_{\text{corr}}$ (Volts) | $R_p$ (Ω·cm$^2$) |
|---------------|----------------|----------------|-------------------------------|---------------------------|------------------|
| Un-treated    | 405.52         | 262.36         | 0.00053134                    | -0.0619                   | 130              |
| 560°C, 1 h    | 378.29         | 258.4          | 0.00029557                    | -1.2665                   | 226              |
| 560°C, 2 h    | 439.6          | 281.7          | 0.00025306                    | -1.255                    | 295              |
| 560°C, 3 h    | 337.87         | 238.84         | 0.00016423                    | -1.2579                   | 370              |
| 580°C, 1 h    | 393.12         | 278.59         | 0.0002126                      | -1.2578                   | 333              |
| 580°C, 2 h    | 430.84         | 296.83         | 0.00013954                    | -1.239                    | 547              |
| 580°C, 3 h    | 396.13         | 249.97         | 0.00015647                    | -1.257                    | 425              |
| 600°C, 1 h    | 475.5          | 258.71         | 0.00016776                    | -1.2718                   | 434              |
| 600°C, 2 h    | 517.68         | 296.17         | 0.0001559                     | -1.23                    | 525              |
| 600°C, 3 h    | 429.34         | 262.83         | 0.00011322                    | -1.252                    | 625              |

suggest that the oxide layer has not completely disappeared. Figs. 8(b), 8(c), 8(d) show the line-scan of Fe, Al and Si elements overlap on the surface of AISI H13 steel. Moreover, the Fe–Al–Si compound was distributed on the surface of steel, and the contents of the Fe element were decreased as closed to the interface, as shown in Fig. 8(b). Obviously, oxidation treatment at 600°C with soaking time of 3 h could effectively increase the thickness of the oxide layer and provide better erosion resistance for H13 tool steel.

Table 2 shows the corrosive results of un-treated and oxidation treated AISI H13 tool steel after the 3.5 wt% NaCl corrosion test. $\beta_1$ and $\beta_2$ were the cathode and anode of Tafel slope. In addition, $I_{\text{corr}}$, $E_{\text{corr}}$ and $R_p$ were the current, potential, and polarization resistance of corrosion, respectively. The corrosion potential of un-treated AISI H13 tool steel specimens was higher than other oxidation treated specimens, as the treated specimens would form a passive film on the surface, which is normally a Fe$_3$O$_4$ structure. It shows the passivation probability of the −0.4−1.0 V across a large potential range. The passive film was mainly due to the oxide layer, which results from the oxidation process, and thus, can decrease the effects of corrosion behavior in the NaCl solution.

In this study, no obvious change was observed in the corrosion potential of AISI H13 tool steel after oxidation treatment, however, the corrosion current varied through the different oxidation parameters after corrosion tests. The oxidation treatments with higher temperature and longer soaking time would result in a smaller corrosion current. The difference of the corrosion current is closely related with the corrosion rate. Therefore, smaller corrosion current would lead to smaller corrosion rate, which is advantageous to the corrosion resistance of the materials. The lowest $I_{\text{corr}}$ (1.1322×10$^{-4}$ Amp cm$^{-2}$) and highest polarization resistance (625 Ω·cm$^2$) appeared after treatment at 600°C with soaking time of 3 h. As a result, oxidation treatment with higher temperature (600°C) and longer soaking time (3 h) can produce better anti-corrosion properties, which are in agreement with the findings.

4. Conclusions

(1) The XRD analysis found that the Fe$_2$O$_3$ and Fe$_3$O$_4$ oxide layers are generated after oxidation treatment for AISI H13 tool steel. The content of these two oxide layers would increase with higher oxidation temperature and longer soaking time.

(2) Fe–Al–Si compounds can accelerate the erosion rate of aluminum alloy, and obviously appear in the boundary of A380 alloy and AISI H13 tool steel. Increasing the thickness of the oxide layer for oxidation treatment is effective in decreasing the melting loss of AISI H13 tool steel under aluminum erosion test. The experimental results showed that the oxidation treatment at 600°C with soaking time of 3 h can produce the optimal erosion resistance.

(3) All oxidation treatments of AISI H13 tool steel would form a passive film, which contributed to a better anti-corrosion property during the corrosion test. The lowest $I_{\text{corr}}$ and highest $R_p$ appeared after treatment at 600°C with soaking time of 3 h, in order for the specimens to acquire an optimal ability of anti-corrosion.

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