Effects of Post-oxidizing Treatment on Melting Loss and Corrosion Resistance of Gas Nitrided AISI H13 Tool Steel

Shih-Hsien CHANG,1**, Tzu-Piao TANG,1 Kuo-Tsung HUANG2 and Jhewn-Kuang CHEN3

1) Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei, 10606 Taiwan, R. O. China. E-mail: changshih@ntut.edu.tw 2) Department of Auto-Mechanics, National Siluo Agricultural Industrial High School, Yunlin County, 64841 Taiwan, R. O. China.

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This study conducted gas nitriding on AISI H13 steels, followed by oxidation treatments at various temperatures (550°C, 680°C, 600°C) and soaking times (1 h, 2 h, 3 h), to investigate the melting loss and corrosion resistance of A380 aluminum alloy. The experimental results indicated that the samples of oxy-nitriding (post-oxidizing treatment after nitrided) at 680°C for 3 h, 600°C for 2 h and 600°C for 3 h have better ability to resist melting loss due to their thicker oxidized layers. The weight loss rate also showed that they are near zero after a 4 h erosion test. The increasing weight loss rate is relative to the appearance of the Fe₃AlSi₃ compound. In addition, the difference in corrosion current is closely related to the corrosion rate. A smaller corrosion current will lead to a smaller corrosion rate. As a result, increasing the temperature and soaking time of oxidation is advantageous to the corrosion resistance, and a small variation in corrosion current will result in a significant change to the polarization resistance of corrosion. Consequently, the oxide layer can enhance the polarization resistance, and quickly generate a passivation layer that increases the corrosion resistance ability.

KEY WORDS: AISI H13 steel, melting loss, corrosion resistance, A380 aluminum alloy, oxy-nitriding.

1. Introduction

The die casting process uses high pressure to inject high temperature molten material into a die cavity. During filling, solidification and die holding stages, the melting aluminum attacks the die steel surface. Corrosion and diffusion reactions occur especially near the erosion area due to the lack of an oxidation protection film. AISI H13 tool steel is normally used for Al casting dies due to its good temperature resistance, high strength, and good resistance to thermal fatigue, erosion and wear. Moreover, it adds additional erosion and corrosion resistance through surface treatments.

To extend the die-casting life, nitriding treatment is often applied to the die surface. Nitriding is a thermo-chemical treatment with nitrogen diffusion, which leads to the surface hardness of the treated dies, due to compressive internal stress within the nitrogen-enriched layer. It shows an increase of thermal fatigue characteristics due to the effects of compressive stress and the hardened surface.

In addition, oxidation treatment is one of the most economical and effective methods to improve the erosion and corrosion resistance of steels. During the oxidation process, most steels can form several kinds of oxides. Our previous study indicated that the oxide layer (Fe₃O₅) can protect and improve the aluminum erosion of H13 steel, and effectively reduce the ratio of Fe₃AlSi₃ compounds during the erosion test of the A380 solution. In the die casting process, molten aluminum alloy at temperatures ranging from 670–710°C is injected into the die cavity at a high velocity from 30 to 100 m/s. The injection pressure is 50–80 MPa. Moreover, aluminum die casting tools are exposed to erosion, corrosion and soldering, and thus, are in frequent contact with the tool surface on the casting alloy, and are subject to oxidation due to high pouring temperatures. Oxynitriding processes (post-oxidizing treatment after nitrided) use steam at the end of the nitriding stage and it is an integral part of the treatment. The principle of oxynitriding procedure is based on actually taking advantage of a small surface porosity, observed in most compound layers after nitriding. It is important, however, to control the nitrogen concentration of nitriding process in such a way that just the right proportion of the porous layer and its correct morphology are created. The control of oxide layer, as stated above, is exercised by the ability and experience to adjust the nitrogen concentration at the surface. The complex oxide layer of Fe₃O₅ and Fe₃O₄ structures are formed on the surface, improving the corrosion and erosion properties of the steel.

However, the effects of oxynitriding treatment on the erosion behavior and corrosion resistance of H13 steel remain unclear. In this study, oxynitriding process is applied to AISI H13 tool steel to explore the possibility of surface engineering of the die steel. This study aims to clarify the effects of oxide layer at the end of the nitriding stage on AISI H13 steel through analyses of XRD, microstructural features, melting loss and corrosion resistance.
2. Experimental

AISI H13 tool steel was chosen as the substrate material to achieve a homogeneous heat treatment (quenched at 1030°C and tempered at 580°C, and repeated 3 times to reach a hardness of HRC 47-48), all specimens were subjected to gas nitriding (570°C, 1 h), and then various oxidation treatments (oxidation temperatures: 560°C, 580°C and 600°C; soaking times: 1 h, 2 h and 3 h, respectively). The chemical compositions of AISI H13 tool steel are listed in Table 1. In this study, the untreated and only nitride treated H13 specimens are designated as “H13” (base metal) and “NH13” (nitriding treatment) in this paper, and the oxidizing treated specimens is designated as “O-NH13”.

In this experiment, an A380 aluminum alloy was used as a cast material, and the composition is listed in Table 2. The erosion resistance of oxy-nitriding was evaluated by its weight loss percentage: weight loss of the specimens dipped in molten aluminum alloy for a predetermined length of time, as shown in Fig. 1(a). The specimen size of the erosion test is shown in Fig. 1(b). The specimens were dipped in A380 alloy for the melting solution and maintained at 750°C. The rotational speeds of the specimens were maintained at 50 rpm, and the dip time was 4 hours in order to evaluate erosion resistance and weight loss. After removal from the molten Al alloy, the specimens were cleaned with NaOH to remove oxide or other residues. The weight loss percentage of the erosion test was calculated as follows: Weight loss (%)= (IW-AW) / IW × 100 where, IW is the initial weight and AW is the weight after erosion test.

Corrosion potential analysis uses three electrodes method: the reference electrode is a saturated of silver-silver chloride electrode, auxiliary electrode is a Platinum electrode, and the working electrode is connected to the test specimens. The contact area of the specimen was 2.0 cm². The corrosive solvent used 3.5 wt% NaCl and was maintained at room temperature. A scanning speed of 0.5 mvs⁻¹, initial potential of -1.5 V, and the final potential of 0.5 V were controlled. The polarization curve was obtained by Corr-View software to analyze and compare the corrosion potential (Ecorr) and corrosion current (Icorr) of different oxidation parameters. Finally, a comparison was conducted for the polarization resistance (Rp) of different oxy-nitriding treatments of AISI H13 tool steel.

3. Results and Discussion

3.1. X-ray Diffraction Line Profile and Optical Microstructure Observation

The X-ray diffraction line profiles of various O-NH13 specimens are shown in Fig. 2. The results indicate that the diffraction peak of α-Fe decreases as the soaking time of oxidation is increased. Figure 2 also shows that the diffraction line peaks of the O-NH13 samples at 600°C oxidation treatments are α-Fe, Fe₃O₄ and Fe₃O₅. All the O-NH13 specimens have a similar feature and shape of diffraction line peaks. Although a slight difference is observed to confirm the effects of different oxidation treatments on the shape of the diffraction line peaks among the three O-NH13 specimens, the difference in diffraction line peaks of the specimens can be easily proven by comparing the results, as also shown in Fig. 2. The total phase (100%) is equal to the sum of the α-Fe, Fe₃O₄ and Fe₃O₅ phases. A decrease of the α-Fe phase resulted from increasing the Fe₃O₄ and Fe₃O₅ phases. It is reasonable to suggest that the Fe₃O₄ and Fe₃O₅ phases increase as the soaking time of oxidation is increased.

The microstructure of the H13 steel substrate obtained after quenching and tempering processes is shown in Fig. 3. The typical microstructure is obtained through commercial heat treatment, which comprises the structure of tempered martensite and proeutectoid carbides. In order to improve the erosion resistance of the steel surface, a nitriding process is normally used to restrain the surface in producing the intermetallic compound layer. In addition, both carbon content and alloying additions can raise surface hardness, thereby enhancing the wear resistance. On the other hand, previous study pointed out that formed the Fe₃Al, Si, intermetallic compound on the surface of the sample was disadvantageous to the erosion tests. To further examine the

![Fig. 1. Schematic illustration of the (a) erosion test setup, (b) specimen dimension of AISI H13 tool steel.](image)

![Fig. 2. X-ray diffraction line profiles of the O-NH13 specimens (600°C and different soaking time of oxidation treatment).](image)
intermetallic compound. Fig. 4 shows the SEM images and Mapping results of the H13 specimens. It is difficult to judge whether the H13 samples suffer thermal cycles after 4 h erosion tests, but these results confirm that the shape of the microstructure is an obviously change.

Due to the diffusion of Fe and Al atoms, which are located between the H13 and the A380 alloy that result in the intermetallic compound to be formed after 4 h erosion test. It should be possible for the diffusion of aluminum and iron atoms to form Fe$_2$Al$_3$Si$_2$ intermetallic across the interface that showed in the vicinity of A and B areas, as shown in Fig. 4(b). The EDS analysis on the areas of A and B for H13 tool steel, as listed in Table 3. It can be found that the areas of A and B contained the similar elements, which mainly are iron, aluminum, and silicon elements. It was proven the previous metallographic observation was the Fe$_2$Al$_3$Si$_2$ intermetallic compounds. Meanwhile, the mapping results of A and B areas, which both show the homogeneous distributions of Fe, Al and Si elements after 4 h erosion test. It is also agree with the above mentioned results (Fe$_2$Al$_3$Si$_2$ compound), as shown in Fig. 4(c). Compared the Fig. 4 with the Table 3, the EDS analysis of the A and B areas (Fig. 4(b)) indicate that they have a similar composition, which are almost the Fe, Al and Si elements. As a result, the distributions of Fe, Al and Si elements formed the Fe$_2$Al$_3$Si$_2$ intermetallic compound are verified, which agrees with the previous study. The previous study indicates that the complex intermetallic layers of Fe$_2$Al$_3$Si$_2$ formed on the surface of the H13 metal normally are Fe$_3$Al$_2$Si, Fe$_5$Al$_3$Si and Fe$_3$Al$_2$Si.$^{16}$

Micro-photographic observations of cross sections of O-NH13 specimens, both before and after 4 h erosion tests, are shown in Fig. 5. Obviously, the oxide layer and nitriding layer is easily recognized for the O-NH13 specimens before erosion test, as shown in Figs. 5(a), 5(c), 5(e). Further

![Fig. 3. Microstructure of the H13 specimen after quenching and tempering treatment.](image)

![Fig. 4. SEM observations and Mapping results of untreated H13 tool steel (a) (b) SEM images before and after 4 h erosion test, respectively. (c) Mapping results.](image)

![Fig. 5. OM images of O-NH13 specimens (600°C for (a) (b) 1 h, (c) (d) 2 h, (e) (f) 3 h oxidation treatments, respectively), where (a) (c) (e) before, (b) (d) (f) after 4 hours erosion test.](image)

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area A</td>
<td>31.34</td>
<td>60.35</td>
<td>6.24</td>
<td>2.07</td>
</tr>
<tr>
<td>Area B</td>
<td>21.47</td>
<td>64.00</td>
<td>13.26</td>
<td>1.27</td>
</tr>
</tbody>
</table>
thermore, the etched O-NH13 specimens reveal that the microstructure has significant differences after 4 h erosion tests, as illustrated in Figs. 5(b), 5(d), 5(f). These results can be further compared with the macrostructure of the untreated samples, as shown in Fig. 4(b). The intermetallic compound between the matrix and Al alloy tends to decrease as the time of oxidation treatments is increased.

3.2. Effect of Oxy-nitriding Treatment on Weight Loss after Erosion Tests

The weight loss of the tested samples could be ascribed to two factors. One is the diffusion of aluminum entering the base matrix, and then, forming a FeAl2Si intermetallic compound in the base matrix. Another factor is the Fe element that escapes from base matrix, while combined with aluminum and silicon elements to generate the FeAl2Si compound at the interface during the erosion test processes.\(^{(4)}\) Figure 6 shows the weight loss rate of the NH13 and different O-NH13 specimens after 4 h erosion tests. The nitriding treated specimens (NH13) show significant erosion (4.37%) by the 750°C molten A380 solution. Conversely, there is only slight erosion appearing in the oxy-nitriding treated specimens (O-NH13). The O-NH13 specimens reveal almost no melting phenomenon when the temperature of oxidation treatment is over 580°C. Figure 6 also shows that the weight loss rate of O-NH13 specimens tends to decrease as the oxidation temperature is increased.

To further compare the Fig. 6 with the Fig. 5. It can be clearly found that the weight loss rate of 600°C 3 hours oxidation treatment, which is very close to zero after 4 h erosion test. In addition, according to the literature\(^{(5)}\) indicates that nitriding treatments alone do not significantly improve the general erosion resistance of alloy steels. When an oxidation post-treatment is applied, the erosion rate decreases by an important factor: the thickness of the oxide layer, which produces the greater improvement. Due to the oxide layer of oxy-nitriding treatment is enhanced as temperature and soaking time increased. As a result, the maximum thickness of the oxide layer (6.17 μm) appears in the 600°C, 3 h oxy-nitriding treatment, as shown in Fig. 5(c). Consequently, it is suitable to suggest that the thickness of oxide layer is a main factor in improving the erosion resistance of AISI H13 tool steel through different oxy-nitriding treatments.

Furthermore, Fig. 6 shows that the weight loss rate of O-NH13 specimen decreases as the soaking time of oxidation is increased. It is possible to suggest that the increased temperature and soaking time of oxidation plays an important part in decreasing the weight loss rate. It can be further compared with the SEM images, as shown in Fig. 7. The diffusion of aluminum and iron atoms across the interface occurs to form FeAl2Si intermetallic compounds at the interface after the 4 h erosion test, as shown in Fig. 7(b). Moreover, during 4 h erosion tests, the cyclic process of dissolution continues, while the steel surface continuously loses iron to the melt.

When comparing the Fig. 6 with Fig. 7, it is seems that the increasing weight loss rate is relative to the appearance of the FeAl2Si compound. In an earlier study, Chang et al. pointed out\(^{(6)}\) that the FeAl2Si compound formed results

Fig. 6. Weight loss rate of the NH13 specimen and the different oxidation treated O-NH13 specimen.

Fig. 7. SEM images of O-NH13 specimens (600°C for (a) (b) 1 h, (c) (d) 2 h, (e) (f) 3 h oxidation treatments, respectively), where (a) (c) (e) before, (b) (d) (f) after 4 hours erosion test.
from a reaction of diffusion between the A380 alloy and iron matrix at a high temperature (750°C). The Fe elements escape from the parent matrix, while combined with aluminum and silicon elements at the interface to generate the Fe₉Al₅Si₂ compound that results in weight loss. As a result, the weight loss correlates closely with the Fe₉Al₅Si₂ compound. In order to further examine the existence of an intermetallic compound in the O-NH13 specimen, in which the weight loss rate is very close to zero, a line-scan is performed, as shown in Fig. 8(a). The results indicate that there is no Al element appearing in the line scan, and therefore, it is suitable to suggest that the A380 alloy cannot adhere to the O-NH13 specimen (600°C, 3 h oxidation treatment) during 4 h erosion tests. Consequently, a weight loss rate close to zero can be verified, and the thicker oxide layer of the O-NH13 specimens is advantageous to erosion resistance. During the post oxidation of oxy-nitrizing cycle, the nitriding sequence is followed by a surface oxidation step, leading to the formation of porous, black-colored magnetite (Fe₃O₄) layer. For the anti-corrosion reasons, this oxide layer will further act as a corrosion barrier. In our study, there are two different crystal structures, Fe₃O₄ and Fe₂O₃. They are the typical magnetite and hematite type crystal structures of Fe₃O₄ and Fe₂O₃, respectively. Complex oxide layers of Fe₂O₃ and Fe₃O₄ structures are formed on the matrix surface after oxidation treatment, which can significantly decrease the weight loss rate of the O-NH13 specimens after 4 h erosion tests.

Figs. 8(b), 8(c), 8(d) show that the line-scan of the Fe, O and Cr elements overlap on the surface of the AISI H13 steel. The EDS analysis in the A area (Fig. 8(a)) confirms that the interface is only a complicated oxide layer, as shown in Table 4. Our previous study found that the oxidation treatments with steam processes is the least oxidative step of the oxidized treatment for the formation of a porous oxide layer, which is composed of a mixture of Fe₂O₃ and Fe₃O₄ oxides. Fe₂O₃ and Fe₃O₄ structures tend to increase as the oxidation temperatures and soaking times are increased (Fig. 2). The complex oxide layer of Fe₂O₃ and Fe₃O₄ structures are formed on the surface of the O-NH13 specimens, improving the erosion resistance with minimal effect on its tribological properties. This oxide layer can eventually be sealed with an unpregnation fluid to increase corrosion resistance.  

<table>
<thead>
<tr>
<th>Area</th>
<th>Fe</th>
<th>O</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>46.60</td>
<td>46.30</td>
<td>7.10</td>
</tr>
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</table>

3.3. Effect of Oxy-nitriding Treatment on Corrosion Resistance

Past studies pointed out that polarization resistance is increased with an erosive current decrease. Table 5 lists the corrosive results of the NH13 and different O-NH13 specimens, after the 3.5 wt% NaCl corrosion test. βₛ and β₅ are the cathode and anode of Tafel slope, respectively. I≈, Icorr and Rₛ are the current, potential, and polarization resistance of corrosion, respectively. Table 4 also shows that the corrosible potential of the NH13 specimens is higher than the other O-NH13 specimens.

The O-NH13 specimens are able to form a passive film on the surface during the oxynitriding process, which normally are Fe₂O₃ and Fe₃O₄ structures. Our previous study showed that the passivation probability in the −0.4 ~ −1.0 V crosses a potentially large range. Figure 9 shows the samples that underwent oxynitriding treatments, while produced
Table 5. Corrosion results of the NH3 and O-NH3 specimens at the 3.5 wt% NaCl solution.

<table>
<thead>
<tr>
<th>Process</th>
<th>$\beta_1$ (mV)</th>
<th>$\beta_2$ (mV)</th>
<th>$\eta_{corr}$ (10^-7 Amp cm^-2)</th>
<th>$E_{corr}$ (Volts)</th>
<th>$R_p$ (Ohm cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3</td>
<td>971.74</td>
<td>334.46</td>
<td>42.39</td>
<td>-1.111</td>
<td>255</td>
</tr>
<tr>
<td>560°C, 1 h</td>
<td>519.73</td>
<td>544.21</td>
<td>40.84</td>
<td>-1.210</td>
<td>287</td>
</tr>
<tr>
<td>560°C, 2 h</td>
<td>421.31</td>
<td>253.61</td>
<td>21.66</td>
<td>-1.245</td>
<td>317</td>
</tr>
<tr>
<td>560°C, 3 h</td>
<td>408.29</td>
<td>242.44</td>
<td>20.78</td>
<td>-1.262</td>
<td>333</td>
</tr>
<tr>
<td>580°C, 1 h</td>
<td>465.82</td>
<td>228.13</td>
<td>22.15</td>
<td>-1.278</td>
<td>300</td>
</tr>
<tr>
<td>580°C, 2 h</td>
<td>340.27</td>
<td>268.70</td>
<td>17.86</td>
<td>-1.261</td>
<td>365</td>
</tr>
<tr>
<td>580°C, 3 h</td>
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<td>374.18</td>
<td>12.24</td>
<td>-1.238</td>
<td>391</td>
</tr>
<tr>
<td>600°C, 1 h</td>
<td>503.22</td>
<td>294.30</td>
<td>25.66</td>
<td>-1.240</td>
<td>314</td>
</tr>
<tr>
<td>600°C, 2 h</td>
<td>495.43</td>
<td>447.52</td>
<td>16.06</td>
<td>-1.216</td>
<td>636</td>
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<tr>
<td>600°C, 3 h</td>
<td>183.39</td>
<td>155.17</td>
<td>0.66</td>
<td>-1.269</td>
<td>556</td>
</tr>
</tbody>
</table>

4. Conclusions

(1) Significant Fe$_2$O$_3$ and Fe$_3$O$_4$ oxide layers are formed on the surface of O-NH3 specimens. Furthermore, the Fe$_2$O$_3$ and Fe$_3$O$_4$ phases increase as the soaking time of oxidation increases.

(2) For the O-NH3 specimens, Fe$_x$Al$_{1-x}$Si$_x$ compounds are obviously decreased after 4 h erosion tests, as the temperature and soaking time of the oxidation treatments is increased, which are closely related to the melting loss. Moreover, Fe$_x$Al$_{1-x}$Si$_x$ compounds can accelerate the erosion rate of O-NH3 specimens, the weight loss rate is close to zero when the oxidation temperature is up to 580°C, and soaking time is over 3 hours.

(3) All the O-NH3 specimens would form a passive film, which contributes to better anti-corrosion properties during the corrosion tests. The lower $I_{corr}$ and higher $R_p$ appear after the 3 h oxidation treatment at 600°C, which is effective in improving corrosion resistance.

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