Surface Microstructure and Its Growth Behavior by Nitrocarburizing with Lithium Added Molten Salt in Fe–0.4 mass% C Alloy*

Haruna Ishizuka¹, Youichi Watanabe¹ and Masao Takeyama²

¹Nihon Parkerizing Co., Ltd., Hiratsuka 245-0027, Japan
²Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, Tokyo 152-8552, Japan

The surface microstructure and growth behavior of an Fe–0.4 mass% C alloy formed by lithium-added salt-bath nitrocarburizing were investigated. The Fe–0.4 mass% C alloy was prepared by arc melting and nitrocarburized by a salt-bath containing Li⁺, Na⁺, K⁺, CNO⁻, and CN⁻ at 823 K from 0.1 h up to 10 h. A compound layer forms on the surface at the beginning of nitrocarburizing, and then an oxide layer forms on the compound layer after nitrocarburizing for 1.0 h. Afterwards, the thickness of both layers increase. A grain boundary oxide forms at the interfaces of columnar crystals in the compound layer. The oxide consists of Li₂Fe₁₋ₓO with an NaCl-type structure, and the growth of the oxide layer is controlled by the outward diffusion of iron in the oxide layer. Meanwhile, the compound layer consists mainly of an ε-Fe₂(N,C)₁₋ₓ phase and a slight γ'-Fe₄(N,C)₁₋ₓ phase near the substrate. [doi:10.2320/matertrans.H-M2020865]

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1. Introduction

Salt-bath nitrocarburizing is a thermochemical treatment of a surface that diffuses nitrogen and carbon from the surface into steel at temperatures below the austenitizing temperature. Through this treatment, a nitrocarburized layer forms on the surface that improves wear resistance and fatigue strength. The benefits of nitrocarburizing using a salt-bath are easier removal of a surface passive film and simpler pre-cleaning than other nitrocarburizing methods such as using gas and plasma. Therefore, this treatment has been applied to plain carbon steel and low alloy steel as well as stainless steel and heat-resistance steel, which are difficult to nitrocarburize. The nitrocarburizing reaction in the salt-bath is as follows,

$$
4\text{MCNO} \rightarrow 2\text{MCN} + \text{M}_2\text{CO}_3 + \text{CO} + 2\text{[N]} \tag{1}
$$

$$
2\text{CO} \rightleftharpoons [\text{C}] + \text{CO}_2 \tag{2}
$$

$$
2\text{MCNO} + 3/2\text{O}_2 \rightarrow \text{M}_2\text{CO}_3 + \text{CO}_2 + 2\text{[N]} \tag{3}
$$

where M is sodium or potassium. Equation (1) is the decomposition reaction of cyanate and eq. (3) is the oxidation reaction of cyanate.

A novel nitrocarburizing salt-bath containing lithium has recently been developed and applied to mass production. The novel nitrocarburizing salt-bath can form a lithium-containing oxide layer on the surface of steel in concurrence with a nitride layer because it is oxidizable due to having a lower cyanide concentration than the conventional salt-bath. The oxide layer dramatically improves seizure resistance and aluminum erosion resistance.¹,² Thus, it is expected to extend the durability of a die such as an aluminum die-casting die or a hot forging die.

Die steel contains many alloying elements for improving wear resistance and resistance to temper softening. These alloying elements affect nitrocarburizing and oxidation reactions. Furthermore, the microstructure formed by the novel nitrocarburizing is complex, particularly the oxide layer, and its formation mechanism during the nitrocarburizing have not been fully investigated.

Many researchers¹–⁷ have reported the nitrocarburized microstructure and its formation mechanism. At the beginning of nitrocarburizing in pure iron, a nitrogen and carbon diffusion layer is formed from the diffusion of nitrogen and carbon. The diffusion rates of nitrogen and carbon are almost the same, but carbon in the α-Fe is less soluble than nitrogen over 773 K. Therefore, δ-Fe₃C precipitates on the surface. The δ gradually converts into ε-Fe₂(N,C)₁₋ₓ, and the iron nitrogen compound layer (hereafter referred to as the compound layer) is formed by continued nitrocarburizing. After that, the γ'-Fe₄(N,C)₁₋ₓ phase is induced near the substrate interface, and the compound layer that consists of the ε and γ' phases grows due to the diffusion of nitrogen and the redistribution of carbon. While the oxidation behavior of nitrided pure iron has been investigated,⁸–¹¹ there is little research on oxidation layers used practically such as over a few hundred nm. Oxynitriding which cause both nitriding and oxidation reactions at the same time, are not yet fully understood.¹²–¹⁴ Thus, in this study, we focus on the oxide layer and investigate the microstructure formed by the novel nitrocarburizing and its growth behavior.

2. Experimental Procedures

The ingot of Fe–0.4 mass% C alloy, approximately 20 to 30 mm in diameter and 30 g in weight, was prepared by a vacuum arc melting furnace in an inert Ar atmosphere. The ingot was annealed at 1123 K for 1.0 h and air cooled. The ingot was then reheated at 1303 K, quenched in oil at 373–383 K, and double tempered at 873 K for 1.0 h, similar to the heat treatments applied to hot-die steels. The alloy surface was polished using # 800 emery paper. Specimens were cut and nitrocarburized at 823 K for 0.1–10 h, followed by air cooling. A salt-bath containing lithium carbonate, sodium carbonate and potassium carbonate, and the concentration

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of CN– and CNO– were below 0.1 and 13–17 mass%, respectively.

Microstructures on the surface and cross-sectional surface layer of the specimens were observed using an optical microscope and field emission scanning electron microscope (FE-SEM). Crystal structures were identified by an X-ray diffractometer (XRD) using monochromatic Co Kα radiation. The distribution of phases was analyzed by electron back scattered diffraction pattern (EBSD). The distribution of elements was analyzed by glow discharge optical emission spectrometry (GD-OES), energy dispersive X-ray spectroscopy (EDS), and wavelength dispersive X-ray spectroscopy (WDS). Six standard specimens were used to create a calibration curve for carbon (0–3.2 mass%) and nitrogen (0–1.1 mass%). The distribution of hardness was measured using a micro-Vickers hardness tester.

3. Results

3.1 Nitrocarburized microstructure

Figure 1 shows optical microscopy images of the cross-section of the specimens nitrocarburized at 823 K for 0.1, 1.0, and 10 h. A compound layer was formed after 0.1 h and was covered by an oxide layer for 1.0 h, and finally both layers were grown for 10 h. Vertically aligned oxides, formed by conventional nitrocarburizing, were observed near the surface in the compound layer instead of voids. Hereafter, an oxide layer formed on the surface and a compound layer formed underneath the oxide layer continuously are referred to as the oxide layer and compound layer, respectively. An oxide formed into a compound layer is referred to as an internal oxide.

The specimen nitrocarburized for 10 h was used for analyses because each surface layer had sufficiently grown. SEM images and the results of EDS analysis focused on the oxide layer are shown in Fig. 2 and Table 1. The interface between the oxide and nitride was clear. The void was observed at the interface and inside of the oxide. It is not clear whether the void is formed during the formation of the surface layers or the removal of the oxide when the cross-sectional microstructure is polished. The analysis of the oxide in the oxide layer and internal oxide revealed the presence of oxygen, carbon, and iron, as shown in Table 1. Focusing on the concentration of oxygen and iron, that of iron is slightly higher inside. Figure 3 shows the distribution of lithium, oxygen, and iron on the surface obtained by GD-OES. The concentrations of lithium and oxygen were higher on the surface and decreased as depth increased. The opposite was observed for iron. This may indicate that the oxide layer is

![Fig. 1 Optical micrographs of cross-sectional surface layer of Fe-0.4 mass% C alloy specimen nitrocarburized at 823 K for (a) 0.1 h, (b) 1.0 h and (c) 10 h. The arrows show internal oxide.](image)

![Fig. 2 SEM images of cross-sectional surface layer of the specimen nitrocarburized for 10 h.](image)

![Table 1 EDS analysis of oxide and nitride from points a-d in Fig. 2.](table)
formed by the inward diffusion of lithium and oxygen from the salt-bath and the outward diffusion of iron from the substrate. Figure 4 shows an XRD profile of the surface microstructure. The peaks of Fe₃N, Fe₄N, and α-Fe were identified in the specimen nitrocarburized for 0.1 h, and peaks from the fcc structure that could be oxides were detected in the specimen nitrocarburized for more than 0.5 h. The peaks did not shift with nitrocarburizing time. As shown in Figs. 2 and 3, the oxide mainly consists of lithium, iron, and oxygen. The ionic radiuses of Li⁺, Fe²⁺, Fe³⁺, and O²⁻ are 0.090, 0.075, 0.069, and 0.126 nm, respectively. The ratio of the radius of cation (r_cation) to anion (r_anion), r_cation/r_anion is 0.55–0.71. Thus, the oxide is a NaCl-type structure with a coordinate number of 6. The ratio of cation to anion is 1:1 in a NaCl-type structure, so the oxide formed by the nitrocarburizing can be described as (Li, Fe)O, as shown in Fig. 5.

The lattice spacing d_hkl which is the diffraction of (h,k,l) in a cubic system, is related to the lattice parameter a, as follows.

\[
\frac{1}{d_{hkl}} = \sqrt{h^2 + k^2 + l^2} / a
\]  

(4)

The lattice parameter of the oxide is approximately 0.421 nm according to the calculation of the peaks based on a Bragg equation \(2d \sin \theta = n \lambda\). Thus, we investigated the lattice parameter of the oxide consisting of iron, oxygen, and/or lithium of a NaCl-type structure in the database of ICDD (International Centre for Diffraction Data). Li₂O was excluded because it is an antifluorite-type structure. Figure 6 shows the relationship between the composition of the oxides and the lattice parameter. A proportional relationship was found between the mole ratio and the lattice parameter of the oxide layer. Vegard’s law was established for the concentration of solute atoms replaced by iron atoms in an oxide solid solution with a NaCl-type structure such as Fe₁₋ₓO. Therefore, the composition of the oxide with a lattice parameter of 0.421 nm can be Li₀.₆⁷Fe₁.₃₃O₂. However, the oxide should be described as LiₓFe₁₋ₓO (x < 1) since the oxide in this study has a concentration gradient as shown in Table 1 and Fig. 3. Lithium is less electronegative than iron. The ratio of the ionic bonds in the crystal structure increases as lithium increases. The radius of the ionic bonds is smaller than that of the covalent bond, so the lattice parameter of LiₓFe₁₋ₓO becomes smaller than that of Fe₁₋ₓO as the ratio of lithium increases.

The surface layers of the specimen nitrocarburized for 0.1, 1.0, and 10 h were analyzed by EBSD to clarify the change in the phase distribution with time. The results of this analysis are shown in Fig. 7. The oxide layer mainly consisted of an fcc structure with a small amount of bcc structure.
regardless of nitrocarburizing time. The compound layer mainly consisted of a hcp structure, and an fcc structure was observed near the substrate. Considering the result in Fig. 5, the compound layer formed in this study mainly consisted of a $\gamma'$ phase and, to a lesser extent, a $\varepsilon$ phase. The internal oxide had an fcc structure, which is the same as the oxide layer on the surface, and it formed along the grain boundary of the columnar crystal of the $\varepsilon$ phase.

Figure 8 shows the distribution of nitrogen and carbon from the surface of the specimens nitrocarburized for 0.1, 1.0 and 10 h using WDS. The concentration of nitrogen in the compound layer was highest, 6.0–6.4 mass% underneath the oxide layer, and it decreased toward the inside regardless of nitrocarburizing time. Furthermore, the concentration of nitrogen near the internal oxide in the compound layer was over 5 mass%. On the other hand, the concentration gradient of carbon is the opposite of nitrogen and is not a continuous gradient. The concentration of carbon increased toward the substrate in the $\varepsilon$ phase and it decreased in the $\gamma'$ phase. This concentration gradient of nitrogen and carbon in the compound layer was similar to that found in past research. At 823 K, the solubility of carbon in the $\gamma'$ phase is very low (<0.1 mass%), whereas the solubility in the $\varepsilon$ phase is high (<3.8 mass%). The diffusion coefficient of carbon in the $\varepsilon$ phase is also small. Therefore, the phase structure of the compound layer in this study that consists of the $\varepsilon$ phase near the surface and the $\gamma'$ phase near the substrate corresponds to that formed by conventional nitrocarburizing. Therefore, the compound layer formed by nitrocarburizing using the lithium-added salt-bath has the same microstructure as that formed by conventional nitrocarburizing.

### 3.2 Growth behavior of surface layers

Figure 9 shows (a) the change in thickness of the surface layers formed by nitrocarburizing over time, and (b) its log-log graph. The thickness of the internal oxide region is the depth of the observed internal oxide region. The thickness of the surface layers varies according to measurement location, so the thickness is the average of four points, and maximum and minimum thicknesses are plotted as error bars.

The compound layer was formed in 0.1 h and grew to approximately 23.3 $\mu$m in 10 h. The oxide layer started to form from 0.5 h and reached approximately 4.2 $\mu$m in 10 h. The internal oxide region was observed after 0.5 h and grew over time. The slope of the growth behavior of the compound layer is close to $1/2$ in Fig. 9(b), indicating a parabolic rate law. The growth behavior of the internal oxide region also follows a parabolic rate law after an initial incubation time. On the other hand, the growth behavior of the oxide layer does not follow a sequential law. However, the growth of the oxide layer might be considered to follow a linear rate law up to 1.0 h and a parabolic rate law after 1.0 h based on the slope. This indicates that the rate-limiting process transfers a surface reaction to diffusion once the oxide is formed uniformly on the surface.

Here, the growth rate constant of the layers, when a parabolic rate law holds, is calculated using eq. (5),

$$L = k \cdot t^{1/2}$$  \hspace{1cm} (5)

where $L$ is the thickness of all layers and $t$ is nitrocarburizing time. The growth rate constant is $5.2 \times 10^{-4} \mu$m$^2$/s for the oxide layer ($k_{OL}$), $1.6 \times 10^{-2} \mu$m$^2$/s for the compound layer.

Fig. 8 Distribution of concentration of (a) nitrogen and (b) carbon in the specimen nitrocarburized for various times.
4. Discussion

4.1 Formation mechanism of nitrocarburized microstructure

The formation process of the microstructure initially formed by nitrocarburizing was discussed. At 0.1 h, the compound layer was formed but no oxide was present on the surface. This might indicate that the compound layer is formed at the initial stage because of the large solubility of nitrogen and carbon in the substrate. In the salt-bath, Li\(x\)Fe\(1-x\)O is formed stably at low temperatures because of the reaction between the Fe\(1-x\)O that formed on the surface and the lithium from the salt-bath. It has been reported that \(\alpha\)-LiFeO\(_2\) forms on the surface when iron is dipped in a molten carbonate such as the salt mixture of Li\(_2\)CO\(_3\) and K\(_2\)CO\(_3\). This is because \(\alpha\)-LiFeO\(_2\) is more stable thermodynamically than Fe\(_2\)O\(_3\) or FeO in the molten salt. Therefore, in this study, Li\(x\)Fe\(1-x\)O forms on the \(\varepsilon\) phase when the concentration of nitrogen in the \(\varepsilon\) phase becomes high, e.g., over approximately 5 mass\%. The initial behavior of the oxide layer formation appears to follow a linear rate law in Fig. 9 because the reaction of the formation of the oxide on the compound layer is rate-limiting. Meanwhile, the internal oxide is formed along the grain boundary of columnar crystal of \(\varepsilon\) nitride. The diffusion rate of atoms in the grain boundary is faster than that in the lattice, and there is a larger nucleation site in the grain boundary than in the lattice. Thus, oxygen from the salt-bath diffuses preferentially into the grain boundary so that the oxide is nucleated at the grain boundary of \(\varepsilon\) nitride.

4.2 Growth mechanism of nitrocarburized microstructure

The growth behavior of all layers followed a parabolic rate law except that of the oxide layer up to 1.0 h (Fig. 9). In other words, the growth of each layer is controlled by diffusion. \(L_{\text{NCL}}\) can be expressed as the following equation, assuming the growth of the thickness of the compound layer \(L_{\text{NCL}}\) is controlled by the diffusion of nitrogen in the compound layer.

\[
(k_{\text{NCL}}) - 1.0 \times 10^{-2} \text{ m}^2/\text{s}
\]

The reported growth rate constant is \(1.8 \times 10^{-4} - 9.1 \times 10^{-4} \text{ m}^2/\text{s}\) for an oxide layer on steel and iron nitride, and \(1.3 \times 10^{-2} - 1.9 \times 10^{-2} \text{ m}^2/\text{s}\) for a compound layer. These reported values correspond to the values in this study. \(k_{\text{IO}}\) is close to \(k_{\text{NCL}}\), so the growth of the internal oxide region is related to that of the compound layer.

\[
\frac{\partial}{\partial t} \left( \frac{\partial L}{\partial t} \right) = D \frac{\partial^2 L}{\partial x^2}
\]

where \(D\) is the diffusion coefficient of nitrogen in the oxide layer.

\[
L = \frac{k}{D}
\]

Thus, the formation of the oxide can be presented by the following equation.

\[
\text{Fe}^3+ + \text{Li}^+ + 2\text{O}^{2-} \rightarrow \text{LiFeO}_2
\]

Sodium and potassium ions do not contribute to the formation of oxide because their radii are larger than those of lithium and iron ions. Two phases of \(\alpha\)-Fe and Fe\(_2\)O\(_4\) are stable but Fe\(_1-x\)O is unstable under 843 K at normal atmospheric pressure, as illustrated by an Fe-O phase diagram. However, based on the result in this study, it is considered that Fe\(_1-x\)O is stable phase in a Fe–N–O phase diagram. Past studies reported that Fe\(_1-x\)O forms when an iron nitride is oxidized below 843 K. Graat et al. clarified that the following relation between the crystallographic orientation of the Fe\(_1-x\)O grains and the orientation of the underlying \(\varepsilon\)-Fe\(_2\)N\(_{1-x}\) grain was established after the stabilization of Fe\(_1-x\)O because of a favorable value of the Fe\(_1-x\)O and \(\varepsilon\)-Fe\(_2\)N\(_{1-x}\) interfacial energy and the occurrence of a preferred orientation relation.

\[
(100)_{\text{Fe}_1-x\text{O}} // (001)_{\varepsilon}\text{Fe}_2\text{N}_{1-x}, \quad [010]_{\text{Fe}_1-x\text{O}} // [-110]_{\varepsilon}\text{Fe}_2\text{N}_{1-x},
\]

In the salt-bath, Li\(x\)Fe\(_1-x\)O is formed stably at low temperatures because of the reaction between the Fe\(_1-x\)O that formed on the surface and the lithium from the salt-bath. The reaction of the formation of the oxide on the compound layer is rate-limiting. Meanwhile, the internal oxide is formed along the grain boundary of columnar crystal of \(\varepsilon\) nitride. The diffusion rate of atoms in the grain boundary is faster than that in the lattice, and there is a larger nucleation site in the grain boundary than in the lattice. Thus, oxygen from the salt-bath diffuses preferentially into the grain boundary so that the oxide is nucleated at the grain boundary of \(\varepsilon\) nitride.
$L_{NCL} = k_N \cdot t^{1/2} = 2K_N(D_N \cdot t)^{1/2}$ \hspace{1cm} (10)

where $k_N$ is a constant growth rate, $t$ is nitrocarburizing time, $K_N$ is constant, and $D_N$ is the diffusion coefficient of nitrogen in the compound layer. It is assumed that the compound layer consists of the $\varepsilon$ phase, and the effect of carbon is ignored because the concentration of carbon is lower than that of nitrogen. The $K_N$ is determined by the following equation, which is solved as a diffusion equation. \cite{20,21}

\[
C_{NCL/a} - C_{a/NCL} = \frac{(C_a - C_{NCL/a}) \exp(-K_N^2)}{\sqrt{\pi K_N \operatorname{erf}(K_N)}} - \frac{(C_{a/NCL} - C_0) \exp(-K_N^2)}{\sqrt{\pi \phi K_N [1 - \operatorname{erf}(K_N \sqrt{\phi})]}} \hspace{1cm} (11)
\]

where $C_{NCL/a}$ is the concentration of nitrogen in the compound layer in equilibrium with the substrate ($\alpha$-Fe), $C_{a/NCL}$ is the concentration of nitrogen in the substrate in equilibrium with the $\varepsilon$ phase, $C_a$ is the concentration of nitrogen just under the oxide layer, $C_0$ is the concentration of nitrogen in the core of the substrate, $\phi$ is the ratio of the diffusion coefficient of nitrogen in the compound layer to that in the substrate $D_0/D_m$, and $D_p$ is the diffusion coefficient of nitrogen in the substrate. In this study, $C_{NCL/a}$, $C_0$, and $D_0$ were acquired in the experiment, and $C_{a/NCL}$ is 0.1 mass\% \cite{22,23} $D_N$ and $D_p$ are 2.44 \times 10^{-14} \text{ cm}^2/\text{s}$ and 9.68 \times 10^{-12} \text{ cm}^2/\text{s}$, respectively. The calculated constant growth rate $k_N$ was 0.0161, and the $K_{NCL}$ of the experimental value was 0.0156. Both values are almost the same, suggesting that the inward diffusion of nitrogen in the core of the substrate is not inhibited by the oxide layer. The growth of the compound layer was not affected by the inward diffusion of nitrogen, so the growth of the oxide layer consisting of Li$_x$Fe$_{1-x}$O.

## 5. Conclusion

We investigated the microstructure and its growth behavior in Fe-0.4 mass\%C alloy nitrocarburized by a salt-bath, and clarified as follows.

1. The oxide nitrocarburized by the salt-bath in both the oxide layer and the grain boundary of the compound layer consists of NaCl-type Li$_x$Fe$_{1-x}$O, and the growth of oxide layer on the surface is controlled by the outward diffusion of iron.

2. The oxide which is formed by the bond of iron, oxygen and lithium is nucleated at the surface and the grain boundary of columnar $\varepsilon$-Fe$_2$(N,C)$_{1-x}$ phase when the concentration of nitrogen increases in the $\varepsilon$ phase.

3. The compound layer consists of $\varepsilon$-Fe$_2$(N,C)$_{1-x}$ and $\gamma'$-Fe$_2$(N,C)$_{1-x}$ phases, and its growth is controlled by the inward diffusion of nitrogen.

## REFERENCES


