Effects of Thermal Fatigue on Nitriding
Hot Working Die Steel (H13)
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Abstract

X-ray stress constants of nitriding layers on a hot working die steel (AISI H13) were determined for different types of nitriding processes. Thermal fatigue behaviour was investigated by the thermal fatigue test and the heating test.

The results obtained are as follows: (1) The X-ray stress constant of nitriding specimen A (ε - Fe2,N and γ' - Fe4,N, treated at 843K for 6h) was $K_A = -648$ MPa/deg. for the $ε - Fe_2N$ 103 diffraction peak using Cr-K$_a$ radiation, and for specimen B (ε - Fe$_3$N and γ'-Fe$_4$N, treated at 833K for 30h) was $K_B = -920$ MPa/deg. for the $ε - Fe_3N$ 103 diffraction peak using Cr-K$_a$ radiation.

(2) Nitriding specimens showed a decrease of heating resistance due to decomposition of the nitriding layer during the heating test. The oxidation of the nitriding layer began at 723K (450°C) as examined by measuring weight, X-ray diffraction profiles and by microphotographic observations.

1. Introduction

Die casting dies and forging dies are considerably damaged by thermal stresses which are repetitions of heating and cooling$^1)$. One of the ways to increase the life of a die is to use a nitriding process, such as gas-nitriding, carbo-nitriding, tufftriding and plasma-nitriding. They are widely used in industrial products.

After the nitriding process is applied to a hot working die steel, it shows an increase of thermal fatigue characteristics because of the effect of compressive stress and a hardened surface$^2)$. However, during the thermal cycles, the heating temperature is about from 773K (500°C) to 873K (600°C), the nitrided layer decomposes and nitrogen gas is released from the surface. Then the
Thermal fatigue behaviour of nitriding hot working die steel had been investigated by measuring residual stress using α Fe 211 diffraction with Cr-Kα radiation including the peaks of Fe-N compounds, and by observation of diffraction profiles and crack growth. It is considered that it will be a useful method to realize the thermal fatigue phenomena of nitriding die steel by measuring residual stress using single peaks of Fe-N compounds. However, X-ray stress constants of Fe-N compound layers on the die steel have not been determined. The few data published so far concerning X-ray stress measurement of nitriding layers are carbo-nitriding layers on carbon steel and on pure iron. Furthermore, the phenomena of nitriding layers applied to die castings and hot working forging dies during operation have not been clarified.

The purposes of this study are as follows: (1) Determination of the X-ray stress and elastic constants for two types of nitriding specimen. (2) To examine the thermal fatigue phenomena in nitriding layers during the thermal fatigue test (heating-cooling cycle) by measurements of X-ray stress and X-ray diffraction profiles. (3) Investigate the decomposition and oxidation of nitriding layers in the heating test by measuring the weight, X-ray diffraction profiles and by microphotographic observations.

2. Experimental procedure

2.1 Determination of X-ray stress constants

Specimens used are shown in Table 1. The specimens were machined by means of grinding. Before the nitriding process, specimen B was heat treated at 923K(650°C) for 5 hours in argon gas for the purpose of stress release.

X-ray diffraction profiles of the specimens are shown in Fig.1. Diffraction plane analysis was employed for identification of the nitrides. For specimen A, the nitrides were ε -Fe$_{2.3}$N$^{*}$ and γ' -Fe$_{4}$N. Also, α Fe was identified. For the specimen B, the nitrides were ε -Fe$_{2.3}$N, ε -Fe$_{3}$N and γ' -Fe$_{4}$N. Fe$_{2}$O$_{3}$ was formed during the stress release heat treatment.

From the results of identification for specimen A, ε -Fe$_{2.3}$N 103 diffraction by Cr-Kα radiation was used. The peak position was about 134deg. Also, for specimen B, ε-Fe$_{3}$N 103 and 200 diffraction with the same radiation was used. The apparatus for X-ray stress measurement was a RIGAKU MSF-2M which has a parallel beam system and ψ -goniometer. It was used for...
measurements of the $\varepsilon$-Fe$_{23}$N 103 diffraction and the $\varepsilon$-Fe$_3$N 103 diffraction. Also, an $\Omega$-goniometer was used for the $\varepsilon$-Fe$_3$N 200 diffraction. In the measurement of X-ray stress constants, the specimens were bent by a four-point-bending device with a strain gauge. X-ray stress and elastic constants were obtained from change of slope of $2\theta$ -sin$^2\psi$ diagrams. A strain gauge was attached to the tension side which is the opposite one to the X-ray diffraction. Strains applied to the specimens were from 0 to 600x10$^{-6}$ with an interval of 100x10$^{-6}$, and 800x10$^{-6}$ was added. Especially, in case of the 103 diffraction for the specimen A and the 200 diffraction for the specimen B, a strain value of 1000x10$^{-6}$ was added. The stress measurements for each specimen were repeated five times. Applied stresses in this experiment were calculated using the Young's modulus for H13 (208.8 GPa). The values of sin$^2\psi$ in the diagram were from 0 to 0.6 with an interval of 0.1.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Hot working die steel (AISI H13, JIS SKD61)</td>
<td></td>
</tr>
<tr>
<td>Width-length-thickness, mm</td>
<td>10-100 -3</td>
<td>843K(570°C), 6h</td>
</tr>
<tr>
<td>Heat treatment and hardness</td>
<td>Quenching and tempering, 45HRC</td>
<td>833K(560°C), 30h</td>
</tr>
<tr>
<td>Nitriding condition</td>
<td></td>
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Fig. 1 X-ray diffraction profiles of the specimens

2.2 Thermal fatigue test

Specimens in the form of cylinders (58mm diameter and 20mm thickness) were prepared from hot working die steel (AISI H13, JIS SKD61) which was heat treated and hardness of 48HRC was obtained. The nitriding process was performed under a gas atmosphere at 793K (520°C) for 20
In the thermal fatigue test, the specimen was heated up to 843K (570°C) for 160sec. by contact to a heating block, and was cooled to 373K (100°C) in a water bath. Heating temperatures are representative of aluminum die casting operation. The thermal fatigue test was carried out up to 1000 cycles (repetition of heating and cooling). During the thermal fatigue test, residual stresses on the surface were measured step by step using the X-ray stress constant value obtained from the results mentioned in the paragraph below.

An X-ray diffraction profile of the specimen for the thermal fatigue test is shown in Fig.2. Diffraction from the ε-Fe₂₃N₁₀₃ for which the stress constant was -648MPa/deg. with Cr-Kα radiation was used. Also, the peak at about 156deg. which was diffracted from both the ε-Fe₂₃N and the α-Fe 211 was used with the X-ray stress constant (-297MPa/deg.) of the hot die steel.

2.3 Phenomena of oxidation during heating

Specimens were heat treated to 45HRC and prepared by wire EDM (15mm width, 25mm length and 0.5mm thickness). After removal of the eroded layer by emery paper, nitriding was performed at 843K (560°C) for 30 hours, same as for specimen B.

Specimens were heated from 673K to 973K, for each 50K, they were kept 6 hours then cooled in the furnace. Specimens were evaluated by observation of sectional area, measurement of weight ratio, Vickers Hardness and X-ray diffraction profiles. The weight ratio $\Delta W_T$ for specimens heated at temperature $T$ was obtained from the equation (1)

$$\Delta W_T = \frac{W_T - W_0}{W_0} \times 100 \text{ (%) } \quad (1)$$

where $W_0$ and $W_T$ are the weight of the specimen before and after heating.
3. Results and discussion

3.1 Determination of X-ray stress constants

Fig. 3 shows the $\sigma_x$-$M$ and $\sigma_x$-$2\theta_{\psi=0}$ diagrams obtained from each specimen, where $M$ is the slope of the $2\theta$-$\sin^2\psi$ diagram, $2\theta_{\psi=0}$ is the intercept, and $\sigma_x$ is the applied stress. The plots in the diagram of specimen B for the $\varepsilon$-$Fe_2N$ 103 diffraction were somewhat scattered. However, the other results: $\varepsilon$-$Fe_2N$ 103 diffraction for specimen A and $\varepsilon$-$Fe_3N$ 200 diffraction for specimen B indicated good linearity.

The peak from the $\varepsilon$-$Fe_2N$ 103 diffraction plane is about one deg. higher than the peak used and might influence determination of the peak position. Stress measurement for specimen B, using the $\varepsilon$-$Fe_3N$ 200 diffraction is more accurate than that from 103 diffraction. In case of the determination of the X-ray stress constant of the $\varepsilon$-$Fe_3N$ where the 103 diffraction peak overlaps the $\varepsilon$-$Fe_2N$ 103 diffraction as in specimen B, it is necessary to separate the peaks.

(a) Specimen A for the $\varepsilon$-$Fe_2N$ 103

(b) Specimen B for the $\varepsilon$-$Fe_3N$ 103 peak

(c) Specimen B for the $\varepsilon$-$Fe_3N$ 200 peak
The values of X-ray stress and elastic constants obtained from these figures and the residual stresses are shown in Table 2. The confidence limit shown in the table is 50%. It is found that compressive stresses were accumulated in specimen A. Also in specimen B, tensile stress were obtained.

Table 2  X-ray stress constants of nitriding specimen A for Fe₂₃N 103 and specimen B for Fe₃N 103 and the 200 diffraction peaks

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Diffraction plane</th>
<th>Stress constant K, MPa/deg.</th>
<th>Residual stress ( \sigma_R, \text{MPa} )</th>
<th>Elastic constants ( S_1 ), ( S_2 ), TPa⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(103)</td>
<td>-648 ± 33</td>
<td>-358 ± 14</td>
<td>2.0 ± 0.1, 5.50 ± 0.06</td>
</tr>
<tr>
<td>B</td>
<td>(103)</td>
<td>-920 ± 40</td>
<td>342 ± 24</td>
<td>1.30 ± 0.3, 4.03 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>-365 ± 9</td>
<td>188 ± 9</td>
<td>-0.71 ± 0.05, 3.67 ± 0.01</td>
</tr>
</tbody>
</table>

\[
S_1 = -\frac{\nu}{E} - \frac{1}{2} \cdot \frac{\partial^2 \theta}{\partial \sigma_x^2} \cdot \frac{\pi}{180} \cdot \cot \theta_0 \quad S_2 = -\frac{2(1+\nu)}{E} \cdot \frac{\partial M}{\partial \sigma_x} \cdot \frac{\pi}{180} \cdot \cot \theta_0
\]

3.2 Thermal Fatigue Test

Fig.4 and Fig.5 show the change of residual stress and peak intensity during the thermal fatigue test. The confidence limit shown in Fig.4 is 50%.

Before the test, a compressive stress of -300MPa was observed from the \( \varepsilon \)-Fe₂₃N 103 diffraction peak. The residual stress profile measured from the \( \varepsilon \)-Fe₂₃N 103 diffraction had a convex shape. The intensity of this diffraction peak began to decrease at 50 cycles and disappeared at 500 cycles.

On the other hand, before 20 cycles, the residual stresses obtained from the peak at 156 deg. namely the \( \varepsilon \)-Fe₂₃N 200 diffraction with the \( \alpha \) Fe 211 showed the same results as the \( \varepsilon \)-Fe₂₃N 103 diffraction. At 50 cycles and 100 cycles, it was observed that the residual stress tended to decrease and was scattered widely. After 200 cycles, the residual stress fell in the range of about -200 to -400MPa. The value of the peak intensity increased 2 times at 1000 cycles, however, that of the \( \varepsilon \)-Fe₂₃N 103 diffraction decreased between 20 and 100 cycles, that of the overlapped peak didn’t change up to 100 cycles.

Fig.6 shows the half-value breath of both of the peaks during the thermal fatigue test. The half-value breath of the \( \varepsilon \)-Fe₂₃N 103 diffraction decreased slightly, that of the overlapped peak around 156 deg. fell off to nearly 3.3 deg. which is the value for quenched and tempered die steel.

From the results of residual stress, peak intensity and half-value breath measurements, at
103 and the overlapped peaks. In the range from 100 to 500 cycles, major inflection points exist in each case. In this experiment, because the heating temperature in the thermal fatigue test was close to the nitriding temperature, these phenomena correspond to decomposition of nitrides in the 5 to 10 µm depth of X-ray penetration. The existence of unstable crystals due to decomposition might cause the change of the values and the wide scatter. For the overlapped peak, more crystallization of the α-Fe 211 diffraction might stabilize the values in the range over 500 cycles. In case of nitriding processes applied to dies, during thermal cycling (heating-cooling), it is hard to check with the eye what the condition of the nitriding layer is. It became clear that X-ray stress measurement using the peak from the ε-Fe₂₃N 103 diffraction and the α-Fe 211 with the ε-Fe₂₃N 200 diffraction would be one of the useful methods of quality control. However, when the overlapped peak is used, it needs to be separated. Also, the peak separation and the influence on residual stress of the decomposition of the nitride layer should be considered.

Fig. 4 Residual stress during the thermal fatigue test

Fig. 5 Peak intensity of the specimen during the thermal fatigue test

Fig. 6 Changes in half-value breath during the thermal fatigue test
3.3 High temperature oxidation behaviour

Microphotographic observations of cross sectional area near the layers produced by the nitriding process and after heating are shown in Fig.7(a), (b) and (c). Also, the X-ray diffraction profiles are shown in Fig.8.

The nitride layer shown as a white color was observed at the surface of the specimen, as produced. The thickness of the layer was about 5 to 10 μm. Below the layer, deposition which is referenced§ as iron carbide (it is called snake like carbide) was observed at grain boundaries. This deposition existed along grain boundaries up to about 50 μm underneath the nitrided layer, at more than 50 μm it was parallel to the surface. From the results of X-ray diffraction, ε-Fe₃N, γ’-Fe₄N| a few a Fe and Fe₂O₃ peaks were observed.

After heating at 723K(450°C), brittle and porous oxide layers were formed at the surface of the nitride, whose thicknesses were about 5 μm. The appearance of Fe₂O₃ peaks was observed in the X-ray diffraction profiles.

After heating at 823K(550°C), the oxide layers were not observed in microphotographs Fe₂O₃ peaks were evidenced by X-ray diffraction measurement. Also, changes in surface color of the specimen were observed. These results coincide with the result of reference7 on the oxidization of nitrided (γ’-Fe₄N) prepared from pure iron.

After heating at 673K(400°C), analysis of the X-ray diffraction peaks, ε-Fe₃N, γ’-Fe₄N, Fe₂O₃ and new a Fe peaks were identified. Around this temperature, the nitride layer decomposed and nitrogen gas was released from the surface. On the other hand, due to low activity of oxygen, the decomposed nitride layer was observed as a Fe. In this experiment, the penetration depth of Cr-Kα radiation in a Fe is about 5 to 10 μm for the 110 diffraction peak (2 θ=69deg.), it does not diffract through the layer. These results coincide with the results of the previous section.

(a) Before heating (b) Heating at 723K(450°C) (c) Heating at 823K(550°C)

Fig.7 Microphotographic observation of cross sectional areas
Hardness distribution curves for the various nitriding specimens are shown in Fig. 9. In this figure, the result for the specimen before heating is shown with “○” mark.

Hardness did not change at heating temperature less than 773K (500°C), however, it decreased about 20HV at 823K (550°C) due to formation of oxides after decomposition of nitrides on the surface. Also, the decrease below the nitride layer was due to the effect of tempering and diffusion of solute nitrogen.

Hardness decreased in all of the region at 873K (600°C), furthermore, it decreased in the range from the surface to a depth of about 50 μm. At 973K (700°C), the hardness fell about 500 to 550 HV in all of the range, because of the influences of vigorous decomposition and diffusion. The X-ray microanalyzer (XMA) results are shown in Fig. 10. Nitrogen content of the nitride layer was about 16%. Because of this the nitride is similar to the one formed by the tufftriding process.

Before heating, the high nitrogen content area was observed to be about 40 μm. Below this area, it decreased with the distance from the surface, and became equal to the matrix at about 250 μm. After heating at 873K (600°C), a high oxygen content area with formation of oxide was observed in the region near the surface. On the other hand, the distribution curve of nitrogen content had a convex shape. This curve corresponded to that of nitrogen.
Also, after heating at 873K(600°C), oxidation progressed at the surface by decomposition of nitrides, hardness was maintained by solute nitrogen in the diffusion layer.

The relationship between heating temperature and weight ratio calculated from equation (1) is shown in Fig. 11.

An increase of weight was observed at more than 923K(650°C), because of the surface oxides on the die steel specimen. This specimen (H13) is the hot working steel which shows inactivity at high temperature by forming chromium oxides. Due to the protection effect on forming of oxide on the surface, an increase of the weight ratio for the die steel specimen was not observed and, an increase of the weight ratio for the nitride specimen...
was observed for $T > 723\text{K}(450^\circ\text{C})$. In the nitriding process, chromium binds to nitrogen in preference to other elements due to its high affinity for nitrogen. Because of the reduction in the content of chromium, the heating resistance of the specimen is decreased. At high temperature, nitrides such as $\text{Me(Fe, Cr)}$, decompose and are released from the surface, nitrogen atoms are rediffused in the diffusion layer, and at the same time imperfections, i.e., pores are formed at surface and grain boundaries. It is considered that as oxidation progresses, the weight ratio increases due to enlargement of surface area by the formation of imperfections. Therefore, a nitriding process, as in this experiment, applied to a die casting die, is able to be one of the useful methods of increasing die life such as the reduction of the maximum temperature at the die surface.

4. Conclusion

Determination of X-ray stress constants of the nitriding layer on hot working die steel for different types of nitriding processes were carried out and thermal fatigue behaviour has been investigated by thermal fatigue tests and the heating tests. The results obtained were as follows:

(1) X-ray stress constant of nitriding specimen A ($\varepsilon$-Fe$_{2.3}$N and $\gamma'$-Fe$_4$N, treated at 843K for 6h) was $K_A = -648\text{MPa/deg.}$ with the $\varepsilon$-Fe$_{2.3}$N 103 diffraction peak of Cr-K$_\alpha$, and specimen B ($\varepsilon$-Fe$_{3}$N and $\gamma'$-Fe$_4$N, treated at 833K for 30h) was $K_B = -920 \text{MPa/deg.}$ with the $\varepsilon$-Fe$_{3}$N 103 diffraction peak of Cr-K$_\alpha$.

(2) In the thermal fatigue test, however, peak intensity from the $\varepsilon$-Fe$_{2.3}$N diffraction decreased with the number of the thermal cycles and disappeared at 500 cycles, while that from the $\varepsilon$-Fe$_{2.3}$N with the $\alpha$ Fe around 156 deg. increased with the number of the cycles.

(3) Nitriding specimens showed a decrease of heating resistance due to decomposition of the nitriding layer during the heating test. The oxidation of the nitriding layer began at 723K ($450^\circ\text{C}$) as examined by measuring weight, X-ray diffraction profiles and by microphotographic observations.

Acknowledgments

We are indebted to K. Kiyoyama of Nichiei Corporation for preparing specimens. We thank M. Sano of Yamanashi Industrial Technology Center and M. Egawa of Polytechnic University for X-ray stress measurement.
References


