Effect of Nitrocarburizing Time on the Microstructures and Erosion Behavior of Cold-work Tool Steel

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In this study we examined the influence of nitrocarburizing holding time on the surface microstructures and erosion behavior of JIS SKD11 modified cold-work tool steel (DC11 tool steel). The steel was nitrocarburized at 570°C for varying durations of 1, 3, and 5 h. The microstructures and hardness of the nitrocarburized coatings were then analyzed. Particle erosion was examined at different impinging angles (15°-90°) and impact speeds (20.2-45.6 m/s).

The results show that a single diffusion zone is formed on the specimens at 1 h nitrocarburizing while a compound layer together with diffusion zone are formed on the specimens for the nitrocarburizing time beyond 3 h. In addition, the compound layer formed on the specimens exhibits a higher erosion resistance. The nitrocarburizing treatment not only increases the surface hardness but also improves the erosion resistance of the experimental steel. This improvement in erosion rates is more obvious at higher impact speeds and lower impinging angles. The maximum erosion rate appears at an impinging angle of 30° for all specimens. In this condition, plough grooves and cutting lips appear in the eroded surface; however, the erosion tracks are more superficial for nitrocarburized specimens than untreated specimen. The exponent in the power law $E=kV^n$ varied between 1.9-2.3 for impinging angles between 15° and 90°.

KEY WORDS: tool steel; nitrocarburizing; erosion; surface structure; microhardness.

1. Introduction

Cold work tool steels are widely used in the metal-forming and die-making industries and in many other fields due to their high hardness. In applications such as dies or tools, properties such as dimensional stability, superior mechanical strength, and high wear resistance are critical for their effective and efficient usage and long service life; such requirements demand materials possessing these properties. In order to minimize wear and rupture of tools, high quality tool steels are used. One such is JIS SKD11 modified cold-work tool steel (DC11), a tool material developed by Daido Steel, Japan. This new material is intended to replace SKD11 in use for general purposes. In addition, several surface treatments such as nitriding are employed to increase wear resistance of tools.

Different nitriding techniques have been used in the past: liquid nitriding, gas nitriding, and plasma nitriding. Although these methods are well established, gas- and plasma nitriding have some disadvantages from an engineering viewpoint; for example, they may require the use of rather complicated- and expensive apparatus. On the other hand, steel nitrocarburizing treatment (NC) is regarded as an effective, low-cost method with many advantages, such as low treatment temperature, short treatment time, high degree of shape- and dimensional stability, and reproducibility.

Liquid nitrocarburizing processes combine the absorption of more nitrogen with the absorption of less carbon to achieve surface hardness in various steels. The hardened case produced on the steel surface can be subdivided into a compound layer and a diffusion zone. The compound layer consists of iron nitrides of $\varepsilon$ (Fe$_{2-3}N$) and $\gamma'$ (Fe$_4N$), which is responsible for the superior tribological- and anticorrosive properties of the steel's surface. Wear behavior of the compound layer depends on many factors, such as composition- and thickness of the compound layer and the mode of mechanical loading. However, the diffusion zone, with N- and C-atoms interstitially dissolved in the ferrite matrix, imparts improved fatigue resistance.

Because JIS SKD11 modified cold-work tool steel is a new tool steel, little information related to its erosion behavior is available in literature. Therefore, the aim of this work was to investigate the influence of nitrocarburizing holding time on surface microstructures, and thereby to study the erosion behavior of this steel at different impinging angles (Ω) and impact speeds (V).

2. Experimental Details

2.1. Materials and Techniques

The material used in this study was a JIS SKD11 modified cold-work tool steel, which was obtained commercially in the form of a forged plate of 15-mm thickness. Its chemi-
cal composition, analyzed using a glow-discharge optical emission spectroscope (GDOS), is shown in Table 1. Square specimens of size 50 mm × 35 mm × 10 mm were cut from the plate for erosion tests. A hole with 3-mm diameter was drilled into each specimen, and a steel wire was threaded through it to facilitate loading of the specimens into the salt bath. Before nitrocarburizing treatment, the specimens were ground using #1200 silicon carbide (SiC) paper and subsequently cleaned with acetone and methanol. Finally, they were dried and loaded into the salt bath.

Before immersion into the salt bath, the specimens were preheated in an air-circulated furnace at 350°C for 1 h. The nitrocarburizing treatment was carried out at 570°C in a salt bath (mainly containing dissolved potassium and sodium cyanates and a small quantity of carbonate salt) for different durations of 1, 3, and 5 h, followed by slow cooling in air down to ambient temperature. After nitrocarburizing treatment, all the specimens were cleaned ultrasonically in acetone for 15 min. In this study, the untreated specimen and the specimens nitrocarburized for 1, 3, and 5 h were designated as NC-0, NC-1, NC-3, and NC-5, respectively.

Nitrided layers were examined using an optical microscope (OM), and X-ray diffraction (XRD) investigations of the nitrided layer were carried out using X-ray diffractometer (XRD-6000) with Cu Kα radiation. Microhardness tests of the specimens were carried out in a Vickers hardness tester, under a small load of 50 g for 15 s. An average hardness value based on six measurements was obtained from representative positions on each specimen. Finally, scanning electron microscope (SEM) was utilized to examine the eroded surface of the specimens.

2.2. Erosion Test

The erosion tests were carried out using a typical air jet erosion test rig (ASTM G76). For the erosion test, a jet of gas containing high-purity (99.6%) SiC particles of irregular shape was ejected from a nozzle of 5-mm diameter, which then impinged on the test specimen located 30 mm away from the nozzle. The hardness of the eroding particles was 2 700 HV0.025. The parameters for the erosion test are presented in Table 2. The impingement flow speed was determined using the rotating double-disk method.10) The eroded specimens were cleaned in acetone, dried and weighted to an accuracy of ±0.01 mg using an electronic balance, eroded in the test rig for 5 min and then weighted again to determine the weight loss. According to Richardson,11) when the impinging particles are harder than the tested specimen and exceed a critical size, say 120–130 μm for ductile materials and 100–125 μm for brittle materials, the intrinsic properties of impinged particles will have no obvious effect on the impingement erosion rate. Meanwhile, impinged particles with irregular shape will cause serious erosion damage12) which will shed light on the impingement erosion characteristics of the test materials. Hence, the impinged particles used in this study, 255–335 μm silicon carbide sand with irregular shape, can be considered as a controlled impingement parameter. Additionally, these impinged particles were never used more than once.

3. Results and Discussion

3.1. Microstructure and Phase Evolution Study

Figures 1(a) and 1(b) show the cross-sectional microstructure of the NC-1 and NC-3 specimens, respectively. As observed in Fig. 1(a), the microstructure consists of an internal nucleus of tempered martensite dispersed with carbide and a nitrided layer on the external surface. The corresponding X-ray diffraction (XRD) pattern of this layer is shown in Fig. 2(a). In addition, a conventional diffraction pattern of untreated specimen is shown for comparison (Fig. 2(b)). Figure 2(a) shows that the α-Fe in nitrided layers is seen to exhibit a set of broad peaks. This broadening is probably due to the gradient of nitrogen, residual stress, and possible defective structure of

### Table 1. Chemical composition of the experimental steel (wt%).

| Element | C    | Ni   | Si   | W    | Cr   | Ti   | Fe   |
|---------|------|------|------|------|------|------|------|
| (%)     | 1.55 | 0.54 | 0.26 | 0.134| 0.34 | 0.008| Bal. |

### Table 2. Parameters for the erosion test used in this study.

| Parameter                        | Value |
|----------------------------------|-------|
| Impinging angle (°)              | 15, 30, 45, 60, 75, 90 |
| Impact speed (m/s)               | 20.2, 31.5, 38.2, 45.6 |
| Erodent                          | Fresh SiC particles with irregular shape |
| Erodent feed rate (g/min)        | 15 ± 0.4 |
| Erodent size (μm)                | 255–335 |
| Impingement time (min)           | 60    |
| Test temperature (°C)            | 25    |

Fig. 1. Cross-sectional microstructure of nitrocarburized specimens: (a) NC-1, (b) NC-3.
the nitride layers. On the contrary, the microstructure of NC-3 consists of an internal nucleus of tempered martensite dispersed with the carbide and a nitrided layer on the external surface (Fig. 1(b)). The nitrided layer consists of a diffusion zone with a fine plate of precipitated nitride and a compound layer on the outer part. The XRD pattern of this specimen (Fig. 2(c)) shows that this layer consisted mainly of $\varepsilon$-nitride (Fe$_3$N) together with a small amount of $\gamma'$-nitride (Fe$_4$N), in agreement with other previous observations. The XRD data also show the existence of low-intensity peaks, labeled “$\theta$” in Fig. 2(c). These peaks are identified as those of cementite, Fe$_3$C.

### 3.2. Microhardness

The microhardness profiles of specimens nitrocarburized for 1, 3, and 5 h durations are shown in Fig. 3. The maximum surface hardnesses in the profiles are in the range of 970–1 110 HV$_{0.05}$. This clearly shows that the hardness of nitrocarburized specimens is higher by a factor of approximately 1.3 to 1.5 in comparison to that of substrate material. The profiles of the NC-3 and NC-5 specimens show a plateau shape. This is because the hardening- and trapping effects of the $\varepsilon$-phase (Fe$_3$N) and $\gamma'$-phase (Fe$_4$N) in both the compound- and the diffusion layers reduce progressively with distance from the surface. However, the hardness of NC-1 decreases gradually with increasing distance from the surface. The depth of the hardened layers is nearly 50, 90, and 100 $\mu$m from the surface for NC-1, NC-3, and NC-5, respectively.

### 3.3. Erosion Behavior

#### 3.3.1. Cumulative Weight Loss

Figures 4(a) and 4(b) show the cumulative weight losses of untreated and nitrocarburized specimens versus erosion time at impact speed of 20.2 m/s and impinging angles of 30° and 90°, respectively. The cumulative weight losses versus erosion time at other impinging angles show a variation tendency similar to those in Figs. 4(a) and 4(b) and are hence omitted here. As shown in Figs. 4(a) and 4(b), for the NC-0 and NC-1 specimens, the cumulative weight losses are found to increase linearly with increasing erosion time. This indicates that the erosion mechanism does not change noticeably, implying a steady erosion damage during the impingement processes, regardless of the variation in the impinging angle. However, the NC-1 specimen exhibits a lower weight loss than the NC-0 specimen. It is strongly believed that the diffusion zone extends the erosion incubation period. On the other hand, for the NC-3 and NC-5 specimens, the weight loss increases linearly at a moderate slope until a turning point found at 25 and 30 min for NC-3 and NC-5, respectively. This feature is ascribed to the hardening effect of compound layer which provides a moderate resistance to erosion wear. After erosion at the time of turning point, the compound layer is impinged off and the diffusion zone is exposed; hence, the erosion rate is similar to that of NC-1. The cumulative weight losses versus erosion time at impact speed of 45.6 m/s are shown in Figs. 4(c) and 4(d). Which shows a variation tendency similar to those in Figs. 4(a) and 4(b); however, the slope of curves is increased and the time of turning point is shorter. This can be reasonably expected because that higher impact force is acted on the impinged surface at higher impact speed. The higher impact force will induce more severe damage during impingement erosion. Hence, the weight loss should be higher at higher impact speed.
It is quite clear that irrespective of impinging angles and impact speeds, the cumulative weight losses are significantly improved with the formation of nitried layers on the nitrocarburized specimen surface. However, the wear loss of nitrocarburized specimens changes only slightly with nitrocarburizing holding time, especially for the NC-3 and NC-5 specimens, in which the compound layer is formed on the top of nitried layer. In Fig. 4, the ratio of the weight loss in the initial part of the curve to the weight of the eroding particles causing the loss (i.e. testing time $\times$ particles feed rate) was then computed as the dimensionless erosion rate.

### 3.3.2. Influence of Impinging Angle on Erosion Rates

Figures 5(a)–5(d) show the erosion rates of untreated and nitrocarburized specimens as a function of impinging angle for various impact speeds. The erosion rates for all specimens show a similar variation tendency, in which the erosion rate first increases and then decreases with impinging angles increasing from $15^\circ$ to $90^\circ$ and reaches a maximum at about $30^\circ$. It shows a typical ductile erosion behavior. For ductile materials, impingement at low impinging angles will increase material removal by microcutting because of the oblique shear force, thus increasing the erosion rate. At high impinging angles, the resolved normal stress will produce the accumulated damage mainly from fatigue, microforging, and extrusion processes. These processes can only produce slighter erosion damage than that caused by cutting removal at low impinging angles. Hence, there appears a maximum erosion rate at around $30^\circ$. 

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**Fig. 4.** Variation of cumulative weight losses of untreated and nitrocarburized specimens as a function of erosion time at different impinging angles ($30^\circ$ and $90^\circ$) and impact speeds (20.2 m/s and 45.6 m/s).

**Fig. 5.** Influence of impinging angle on erosion rate of untreated and nitrocarburized specimens at different impact speeds: (a) 20.2 m/s, (b) 31.5 m/s, (c) 38.2 m/s, (d) 45.6 m/s.
As shown in Fig. 5, the nitrocarburized specimens have lower erosion rates than the untreated specimen. Their difference in erosion rates is more obvious at lower impinging angles. This indicates that nitrocarburizing treatment improves the erosion resistance of the experimental steel, especially at lower impinging angles. For the NC-3 and NC-5 specimens, the compound layer exhibits a higher erosion resistance; hence their erosion rates are lower than that of NC-1.

3.3.3. Influence of Impact Speed on Erosion Rates

Figures 6(a)–6(f) show the erosion rates of untreated and nitrocarburized specimens as a function of impact speeds at various impinging angles. The erosion rate is almost 3–6 times higher when impact speed has been increased from 20.2–45.6 m/s. The least square fit to the data points were obtained by the power law \( E=KV^n \), where \( E \) is the erosion rate, \( V \) is the impact speed, \( k \) is a constant and \( n \) is the exponent. The fitting parameters have been summarized in Table 3. The speed exponents are in the range of 1.9–2.3 at different impinging angles. These values confirm ductile erosion behavior. In general, materials behaving in ductile manner are typically 2\(<n<3\) while materials behaving in brittle fashion are typically 3\(<n<5\). In Figs. 6(a)–6(f), nitrocarburized specimens are also found to have lower erosion rates than the NC-0 specimen. Their difference in erosion rates is more obvious at higher impact speeds.

Table 3. Values of the \( n \) exponents for the experimental steel impinged at various angles.

| Specimens | Impinging angle (°) |
|-----------|---------------------|
|           | 15      | 30      | 45      | 60      | 75      | 90      |
| NC-0      | 2.26    | 2.28    | 2.34    | 2.20    | 2.02    | 1.90    |
| NC-1      | 1.95    | 2.10    | 2.03    | 1.91    | 2.04    | 1.96    |
| NC-3      | 2.19    | 2.24    | 2.06    | 2.07    | 1.85    | 2.00    |
| NC-5      | 1.93    | 2.06    | 1.96    | 2.05    | 1.96    | 2.21    |

3.4. Morphologies of the Eroded Surfaces

Figures 7(a)–7(f) show the typical SEM micrographs of the eroded surfaces for the NC-0, NC-1, and NC-3 specimens subjected to impingement erosion of 15 min at 30° and 90° impinging angles and 45.6 m/s impact speed. The erosion tracks of the NC-0, NC-1, and NC-3 specimens are reasonably representative of the wear mechanisms of substrate, diffusion zone, and compound layer, respectively. Two distinct morphologies can be found for these specimens impinged at various angles. As shown in Figs. 7(a)–7(c) for an impinging angle of 30°, the surface morphologies show numerous long furrows and ridges, which are ploughed out by the impinging particles. This ploughing mechanism will have a significant material removal rate, and hence exhibit a high erosion rate, as shown in Fig. 5. At impinging angle of 90°, the surface morphologies exhibit profuse overlapping and irregular concavities (Figs.
This is because the impact force of particle at high impinging angle is largely utilized to induce plastic deformation. The combined deformation of microforging and extrusion produces indented concavities and protruding thin platelets. These platelets are then partially impinged by the subsequent impinging particles or attach themselves onto nearby surfaces.

In Fig. 7, it also can be found that the erosion tracks on the eroded surfaces are wider and deeper for NC-0 than NC-1 and NC-3. Due to the relatively low hardness, the surface of the NC-0 specimen is severely deformed during erosion test. Obvious erosion tracks appear in the eroded surface. On the other hand, the erosion tracks on the eroded surfaces of NC-1 are found to be shallow and superficial indicating that the erosion damages are less than that of NC-0. This is attributed the formation of diffusion zone on the surface of the NC-1 specimen. Furthermore, the erosion tracks are more superficial for the NC-3 specimen because the compound layer provides a much better erosion resistance. On the basis of these results, it can be concluded that the erosion resistance can be improved by nitrocarburizing treatment, as evidenced by the experimental results shown in Figs. 4–6.

4. Conclusions

The erosion behavior of JIS SKD11 modified cold-work tool steel (DC11) has been studied as a function of holding time used during nitrocarburizing. The main conclusions from these investigations can be summarized as follows:

(1) During nitrocarburizing treatment, a single diffusion zone is formed on the specimens at 1 h nitrocarburizing while a compound layer together with diffusion zone are formed on the specimens for the nitrocarburizing time beyond 3 h. The microhardness profiles of nitrocarburized specimens show surface hardnesses in the range of 970–1 110 HV0.05, which is increased by a factor of approximately 1.3 to 1.5 in comparison to that of substrate material. As the nitrocarburizing holding time increases, both the surface hardness and the hardness-profile depth increase.

(2) The nitrocarburized specimens show a much better erosion resistance than that of untreated specimen. This improvement in erosion rates is more obvious at higher impact speeds and lower impinging angles. In addition, the erosion resistance is higher for the specimens having compound layer than the specimens having a single diffusion zone. Nevertheless, as the compound layer is formed on the top of the nitrided layer, the erosion properties including ero-
sion rate and erosion mechanism do not change significantly with nitrocarburizing holding time.

(3) The maximum erosion rate appears at an impinging angle of 30° for substrates both with and without nitrocarburizing treatment. In this condition, obvious plough grooves and cutting lips appear in the eroded surface, but the erosion traces on the untreated specimens are wider and deeper. As the nitrocarburizing holding time increases, the erosion traces of the specimen become more superficial. This feature leads to the decrease of erosion rate.

(4) The impact speed has a pronounced effect on the erosion wear of the experimental steel. The steady state erosion rate ($\dot{E}$) has been related to the impact speed ($V$) as $\dot{E}=kV^n$. The speed exponents at different impinging angles (15–90°) and impact speeds (20.2–45.6 m/s) are in the range of 1.9–2.3.

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