Improving the Erosion and Erosion–Corrosion Properties of Precipitation Hardening Mold Steel by Plasma Nitriding

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In this study plasma nitriding of precipitation hardening mold steel has been carried out at 470, 500 and 530°C for 12 h in order to achieve good erosion and erosion–corrosion resistance. The microstructure, phase present and microhardness profiles of unnitrided and nitrided layers were examined. The influence of plasma nitriding on the erosion and erosion–corrosion resistance of the tested steel was investigated using a jet solid particle erosion tester and a rotated slurry erosion–corrosion tester.

The results indicate that the surface properties of the plasma nitrided layers in terms of hardness, erosion wear, and erosion–corrosion resistance are highly dependent on nitriding temperature, and all three plasma surface treatments can significantly improve the surface hardness and effectively enhance their erosion resistance under dry erosion. The erosion–corrosion resistance in 20 mass% SiC particles/3.5% NaCl slurry can be effectively improved 48, 65 and 68% by plasma nitrided at 470, 500 and 530°C, respectively. The erosion rate decreases with increasing surface hardness and obeys a power function ($\dot{E} \propto H^{-n}$) with exponent of 1.047. However, the correlation between erosion–corrosion rate and hardness does not obey any power functions of the exponent in the range of 1–1.5 due to the complexity of the interaction between erosion and corrosion. [doi:10.2320/matertrans.M2012083]

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1. Introduction

The precipitation hardening tool steels have been used for fabricating plastic injection molds. One example is NAK80 mold steel developed by Daido Steel, Japan. This steel is usually supplied in the solution-treated condition, and its hardness ranges from 30 to 32 HRC. On aging at 470–530°C for 5 h, the hardness ranges from 39 to 41 HRC.¹⁾

Wear and corrosion are the common problems in plastic injection molds, especially in high production molds. Erosion wear is induced by the reinforced resins flow and corrosion attack from acids and chloride formed by the decomposition of thermoplastic (e.g., PVC) due to overheating.²⁾ As a result of the combined effects of erosion and corrosion, the overall wear rate of material can be greater than the sum of the rates of material loss from either of the two processes, erosion and corrosion, acting separately. The additional part in material loss is defined in terms of synergistic effect.^{3–5)} Under this background, it is required to try to take advantage of a certain surface engineering technique to address the problem in order to improve the erosion and erosion–corrosion resistance of the plastic injection molds.

Nitriding is a surface treatment technique used to introduce nitrogen into metallic materials to improve their surface hardness, mechanical properties, as well as wear and corrosion resistance.^{6–8)} Conventional gas and liquid nitriding processes are not suitable for precipitation hardening steels because the high temperature of over 550°C employed in these processes exceeds the aging temperature of such steels and could result in the overaging of the core. However, plasma nitriding can be carried out at temperatures lower than the aging temperature.

In the plasma nitriding process, by means of a glow discharge in a gas mixture of N₂ and H₂, with the temperature of the steel at the vicinity of 500°C, nitrogen can penetrate

the surface and diffuse into the steel.⁹⁾ Under such conditions, the structure of the nitrided layers produced on the steel surface can be subdivided into a compound layer and a diffusion layer. The compound layer consists of ϵ -nitride (Fe_{2–3}N) and γ' -nitride (Fe₄N) as well as nitrides with alloying elements, while the diffusion layer consists mainly of interstitial atoms in solid solution and fine, coherent nitride precipitates when the solubility limit is reached. The diffusion layer determines the strength of the nitrided layer, as well as its fatigue strength,^{10,11)} while the compound layer determines the tribological characteristics and corrosion resistance.^{12–14)}

Several works have been published reporting a better performance of plasma nitrided precipitation hardening stainless steel in corrosion and wear conditions.^{15,16)} In another work, Öztürk *et al.*¹⁷⁾ reported an effectiveness of plasma nitriding conditions in improving the tribological and corrosion properties of X36CrMo17 injection mold steel. Oliveira *et al.*¹⁸⁾ indicated the nitriding and aging of precipitation hardening plastic mold steel can be achieved simultaneously in the same treatment cycle and found that the corrosion resistance was enhanced after nitriding. However, for a deeper understanding of precipitation hardening tool steels the effects of plasma nitriding on erosion by solid particle and erosion–corrosion by slurry are essential, but very little work has been done on these aspects.

In the present investigation, NAK80 mold steel was DC-pulsed plasma nitrided at 470, 500 and 530°C for 12 h. The metallurgical structures as well as microhardness profiles, erosion and erosion–corrosion resistance of the surface nitrided layer were evaluated, analyzed and discussed.

2. Experimental Details

Specimens were made out of NAK80 mold tool steel, (C 0.12, Si 0.26, Mn 1.43, Ni 3.18, Al 1.02, Cu 0.95, Mo 0.22, Fe balanced all, in mass%) and machined to

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Fig. 1 Aging curves of the specimens aged at various temperatures.

$80 \times 25 \times 3 \text{ mm}^3$ in size. The material was received in the solution and aging at 500°C for 5 h with a hardness of 40.7 HRC. This received material was left unnitrided intentionally for the purpose of comparison. These specimens were initially solubilized at 900°C and then aged at temperatures of 470, 500 and 530°C for periods ranging from 1 to 20 h in order to draw up their aging curves, and guide the nitriding treatments. Figure 1 shows that a high hardness level was reached between 4 and 12 h of aging, and no signs of overaging were detected for treatment durations less than 15 h. Therefore, the nitriding time was settled on 12 h. Prior to the nitriding process, the specimens were polished to the same surface roughness ($R_a = 0.04 \mu\text{m}$) and cleaned in an ultrasonic bath with acetone. Plasma nitriding was carried out in an industrial nitriding facility (DC-pulsed). The specimens were sputter cleaned in an atmosphere of 80% Ar + 20% H_2 at about 250°C for 1 h, to remove the oxide layers formed on their surfaces. They were then plasma nitrided in an atmosphere of 25% N_2 + 75% H_2 at temperatures of 470, 500 and 530°C for 12 h, with the chamber pressure maintained at 600 Pa.

The microstructures of nitrided layers were observed by optical microscopy. The phases formed on the nitrided surface were characterized by X-ray diffraction with Cu $K\alpha$ radiation using a Shimadzu X-ray diffractometer (LabX XRD-6000). The microhardness of the nitrided layers was measured using a Future-Tech FM-7 automatic tester with a small load of 50 g for 15 s. The erosion tests were carried out by using a typical air jet erosion test rig (ASTM G76). A jet of gas containing irregular SiC particles with the sizes of 255–335 μm was ejected from a nozzle of 5 mm diameter, which then impinged on the test specimen located 30 mm away from the nozzle. The impingement flow speed was adjusted by air pressure and it was determined using the rotating double-disk method.¹⁹⁾ The eroded specimens were cleaned in acetone, dried and weighted to an accuracy of $\pm 0.01 \text{ mg}$, eroded in the test rig for 5 min and then weighted again to determine the weight loss. Additionally, these impinging particles were never used more than once.

The erosion–corrosion tests were carried out with a rotated slurry wear tester as shown in Fig. 2 of the Ref. 5) with the same electrolyte as that in corrosion test plus 20 mass% of

irregular SiC particles. The rotation diameter of the specimens was 100 mm. The bolts fixed in the holder could adjust the impact angles of solid particles. The erosion–corrosion rate ($\dot{E}_C$) was calculated by measuring the weight loss of specimens. The parameters employed for erosion and erosion–corrosion tests are presented in Table 1. The worn surface morphology was observed in the scanning electron microscope of JEOL JSM-5600 to study the mechanisms of erosion and erosion–corrosion wear of NAK80 mold steel.

3. Results and Discussion

3.1 Microstructure

Optical micrographs of the unnitrided and nitrided specimens are shown in Fig. 2. These micrographs show a case hardened nitrided layer and an internal nucleus of bainite plus martensite. The nitrided surface consisted of two layers: a compound layer at the top and a nitrogen diffusion layer beneath. The thickness of the nitrided layer increased with an increase in nitriding temperature due to greater diffusivity at higher temperatures. The corresponding XRD patterns obtained from the surface of these specimens are shown in Fig. 3. The unnitrided specimen showed only $\alpha\text{-Fe}$, whereas the nitrided specimens exhibited additional peaks due to different nitrides. In the specimen treated at 470°C , some $\epsilon\text{-nitride}$ and $\gamma'\text{-nitride}$ peaks accompanied the $\alpha\text{-Fe}$ peaks. In nitriding at 500°C , the nitrided surface layer was dominantly $\epsilon\text{-nitride}$ along with $\gamma'\text{-nitride}$, and the amount of $\alpha\text{-Fe}$ phase was much less than that in the nitriding at 470°C . The amount of $\epsilon\text{-nitride}$ and $\gamma'\text{-nitride}$ in 530°C nitrided surface layer was further increased, and the amount of $\alpha\text{-Fe}$ phase was decreased apparently. Therefore, the peaks of $\alpha\text{-Fe}$ phase almost disappeared. Optical microscopy and XRD analysis show that the microstructure of the nitrided case is temperature depended. The intensity of the $\alpha\text{-Fe}$ peaks progressively decreased, and the intensity of the nitride peaks progressively increased with increasing nitriding temperature indicating an increase in volume fraction of the nitride phase at the expense of parent $\alpha\text{-Fe}$. Our early study has been confirmed that the presence of a dense nitride layer rich in $\epsilon\text{-nitride}$ on the surface could enhance corrosion resistance. As nitride is a noble phase, formation of more nitride helps to protect the surface from corrosion attack and corrosion resistance improves with increase in nitriding temperature.²⁰⁾

3.2 Microhardness

Figure 4 shows that the microhardness of the nitrided specimens is greater than that of the substrate material by a factor of approximately 1.6 to 1.8. The depth of the hardened layers extends nearly 45, 140 and 200 μm below the surface for the specimens nitrided at 470, 500 and 530°C , respectively. In addition, the microhardness is in graded distribution from the surface to the core of the specimens, which is beneficial to the surface mechanical properties of the specimens.

3.3 Erosion by solid particles

Figure 5 shows the cumulative weight losses of unnitrided and nitrided specimens versus erosion time. The unnitrided specimen exhibits the highest value of weight loss and that

Fig. 2 Optical microscopy images of (a) unnitrided specimen, (b) nitrided at 470°C for 12 h, (c) nitrided at 500°C for 12 h and (d) nitrided at 530°C for 12 h.

Table 1 Parameters for the erosion and erosion–corrosion tests used in this study.

Parameter	Erosion	Erosion–corrosion
Erodent	SiC, feed rate: $15 \pm 0.4 \text{ g min}^{-1}$	20 mass% SiC + 3.5% NaCl solution
Impact velocity, $v/\text{m s}^{-1}$	30	7.3
Impact angle	30°	30°
Test duration, t/min	30	60

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. However, the cumulative weight losses are significantly improves with the formation of nitrided layers on the nitrided specimen surface. It is strongly believed that the diffusion zone extends the erosion process incubation period. For 470°C nitrided specimen, the weight loss increases linearly at a moderate slope until a turning point found at 20 min. This feature is ascribed to the hardening effect of diffusion zone which provides a moderate resistance to erosion wear. After erosion at the time of turning point, the diffusion zone is impinged off and the base material is exposed; hence, the erosion rate is similar to that of unnitrided specimen. For 500 and 530°C nitrided specimens, the depth of erosion tracks are still within the diffusion zone. Consequently, steady erosion damage with lower weight losses than 470°C nitrided specimen is found. In

Fig. 3 XRD diffraction patterns of the unnitrided and nitrided specimens.

Fig. 5, the ratio of the weight loss in 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 ($\bar{E}$). The erosion rates are 0.205, 0.138, 0.119 and 0.108 mg g^{-1} for the unnitrided and 470, 500 and 530°C nitrided specimens, respectively.

Fig. 4 Microhardness depth profiles for NAK80 mold steel nitrided for 12 h.

Fig. 5 Cumulative weight losses of unnitrided and nitrided specimens versus erosion time.

Fig. 6 Solid particle erosion morphologies of the specimens after 30 min impingement: (a) unnitrided, (b) 470 °C nitrided, (c) 500 °C nitrided and (d) 530 °C nitrided.

Figure 6 shows the typical SEM micrographs of the eroded surfaces for the unnitrided and nitrided specimens after 30 min impingement erosion. Due to the relatively low hardness, the surface of the unnitrided specimen is severely deformed during erosion test. Obvious plough grooves and cutting lips appear in the eroded surface, and wider and deeper erosion trace could be seen in Fig. 6(a). This ploughing mechanism will have a significant material removal rate, and hence exhibit a high erosion rate. On the other hand, all the nitrided specimens exhibit considerably less erosion damage. The erosion tracks on the eroded

surfaces of the nitrided specimens are found to be shallow and superficial. This is attributed to the formation of nitrided layer on the surface of the nitrided steel. However, the difference of erosion tracks between the 500 and 530 °C nitrided specimens is not significantly confirming the change of their erosion rate only slightly. Compared with the unnitrided specimen, all the nitrided specimens exhibit milder erosion damage and lower erosion rate. The improvement of the erosion resistance for plasma nitrided NAK80 mold steel is considered as a result of combined effects of the microstructure and the high surface hardness in the nitrided

layer. The high surface hardness can resist the plastic deformation, and reduce the plough grooves and cutting damages impacted by particles. As the nitriding temperature increases, both the surface hardness and the hardness–profile depth increase. Consequently, the erosion resistance improves with nitriding temperature.

3.4 Erosion–corrosion behavior of slurry

The erosion–corrosion rate for the unnitrided and nitrided specimens is compared in Fig. 7. It can be seen that the erosion–corrosion resistance in 20 mass% SiC particles/3.5% NaCl slurry can be improved 48, 65, and 68%, respectively

Fig. 7 The erosion–corrosion rate of the unnitrided and nitrided specimens after 60 min.

by nitriding at 470, 500 and 530°C. The nitrided specimens have higher surface hardness, better solid particle erosion resistance and undamaged passivating film, which guaranteed their better property in erosion–corrosion resistance than that of the unnitrided specimen.

The surface morphologies of the unnitrided and nitrided specimens after 60 min erosion–corrosion test are shown in Fig. 8. The unnitrided specimen corrodes most severely, and some large and deep circular pits as well as several erosion tracks can be seen on the surface (Fig. 8(a)). This can be attributed to its low hardness and hence mediocre resistance to erosion (Fig. 6(a)) combined with poor corrosion resistance leads the highest total weight loss. Both corrosion pits and erosion tracks could also be seen on the erosion–corrosion surface of the 470 and 500°C nitrided specimens, but the amount of erosion tracks and the size and dimension of pits were less than those of the unnitrided specimen. For the 530°C nitrided specimen, only mild cutting grooves are observed on the surface and there is no corrosion pits. Although the corrosion resistance of all three plasma-nitriding specimens is enhanced but the depth of the nitrided layer for the 470°C nitrided specimen is thinner than that for high temperature (500 and 530°C) nitrided specimens. During the erosion–corrosion test, the thinner nitride layer could be penetrated more quickly and the protection by nitride from corrosion attack failed. Therefore, the erosion–corrosion surface of the 470°C nitrided specimen showed much more corrosion pits (Fig. 8(b)) while the 530°C nitrided specimen showed no corrosion pits (Fig. 8(d)).

Fig. 8 Erosion–corrosion morphologies of the specimens (a) unnitrided, (b) 470°C nitrided, (c) 500°C nitrided and (d) 530°C nitrided.

Fig. 9 Effect of surface hardness on the erosion and erosion–corrosion of unnitrided and nitrided NAK80 mold steel.

3.5 Hardness effect

Erosion by impact of solid particles is a mechanical process and is thus dependent on mechanical properties of the surface. For solid particle erosion, material removal occurs by two mechanisms, namely by: plastic deformation and brittle fracture. The former is surface hardness dependent whilst the latter is fracture toughness dependent.²¹⁾ In general, the softer the specimen surface, the deeper and larger are the cutting grooves. In our cases, the hardness of the impacted particles is much higher than that of the tested materials, these particles will indent the tested samples, and the relative motion will lead to the formation of groove as shown in Fig. 6. Although abrasion and erosion depend not only on hardness, but also on toughness and elastic modulus of the materials, as reported by Zum Gahr,²²⁾ however, our test conditions were in the high wear region according to the hardness model of Rabinowicz,²³⁾ the volume of the worn groove is proportional to the contact area of the hard particle on the soft surface. Therefore, the volume of the removed materials is equal to the volume of the groove and then the wear rate can be expressed as a function of hardness of the tested samples according to Tabor's relation.²⁴⁾ Figure 9 depicts the correlation between the erosion rate and surface hardness of the tested specimens. As can be seen from Fig. 9, the erosion rate falls exponentially with the surface hardness of NAK80 mold steel. In erosion theory,²⁵⁾ the relationship between the erosion rate and the hardness (H) of the surface can be expressed approximately by: $\dot{E} \propto H^{-n}$. The exponent n depends mainly on the impact angle and material removal mechanism. For oblique angles of incidence, material is removal by individual particles in a cutting action and $n = 1$; at high impact angles debris becomes detached only after repeat deformation under cyclic plastic deformation and $n = 1.5$. In Fig. 9, the erosion rate of NAK80 mold steel obeyed the above power function ($R^2 = 0.9661$) with the exponent $n = 1.047$ confirming that the material removal during erosion is most probably via cutting.

It can be seen from Fig. 9 that the erosion–corrosion rate of NAK80 mold steel also decreases with increasing surface hardness; however, its correlation does not obey any power functions for the exponent of 1–1.5. Because the erosion–corrosion rate depends on pure corrosion, pure erosion and more importantly the synergistic effects between erosion and

corrosion. The complexity of the interaction between erosion and corrosion could possibly cause that the correlation between erosion–corrosion rate and hardness does not obey the power function.

4. Conclusions

- (1) Plasma nitriding can be used to produce a variety of surface layer structure in NAK80 precipitation hardening mold steel, and the surface properties of the layers in terms of hardness, erosion wear and erosion–corrosion resistance are highly dependent on nitriding temperature.
- (2) The erosion–corrosion resistance of NAK80 mold steel in a 20 mass% SiC particles/3.5% NaCl slurry can be improved 48, 65 and 68%, respectively by plasma nitrided at 470, 500 and 530°C.
- (3) The erosion rate of NAK80 mold steel decreases with increasing surface hardness and obeys a power function ($\dot{E} \propto H^{-n}$). The exponent is about 1.047 for the erosion confirming that the material removal is most probably via cutting. However, the correlation between erosion–corrosion rate and hardness does not obey the power function because the interactions between erosion and corrosion are complex.

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