Sliding Wear Behavior of Salt Bath Nitrocarburized Medium Carbon Steel

P. Bala Srinivasan, C.V. Krishnakumar, and N. Krishnaraj

Salt bath nitrocarburizing is a well-known thermochemical diffusion process for enhancing the tribological and corrosion properties of ferrous components. The current work describes the role of a compound layer developed during nitrocarburizing, both in the ferritic and austenitic regimes of Fe-N-C system, on the sliding wear behavior of a medium carbon steel. The wear behavior of the nitrocarburized steel discs was assessed by the pin-on-disc tests (ASTM G 99-99) under different normal loads running against a hardened SAE52100 pin. It was observed that the compound layer on the surface not only controlled the wear rate but also resisted the adhesive wear/transfer of material from pin to disc, aside from providing low-friction coefficients.

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1. Introduction

Plain medium carbon (C) steels find extensive use in the engineering and automotive industries in view of their moderate strength and toughness. Often their properties are further enhanced by a suitable surface treatment. The surface modification, in general, is aimed at improving their mechanical and tribological properties.[1,2] Nitrocarburizing is one such surface modification treatment performed in gaseous, salt bath, or plasma medium depending on the application requirements.[3-5] This thermochemical surface modification treatment improves not only the mechanical/tribological properties[6] but also the corrosion resistance significantly,[7] owing to the development of a hard and relatively inert compound layer of carbonitride at the surface.[8]

The thickness of the compound layer and the depth of diffusion zone achievable in the treatment depend on the material, its previous heat/mechanical treatment history, and the process parameters.[9] The treatment generally is performed in the temperature range 530-570 °C, that is, within the phase field of ferrite in the iron-nitrogen-carbon system and therefore referred to as ferritic nitrocarburizing, that is, develops a compound layer comprising both epsilon and gamma prime carbonitrides. The wear resistance of nitrocarburized steels is attributed to the compound layer properties.[10]

Nitrocarburizing of C steels at temperatures higher than 593 °C in the austenitic phase field of the Fe-N-C system promotes higher compound layer growth.[9] In the current work, an attempt has been made to assess the sliding wear behavior of a medium C steel disc nitrocarburized at two different temperatures (570 °C and 700 °C in the ferritic and austenitic phase

fields, respectively) by the pin-on-disc method as per ASTM G99-99. Hardened SAE52100 material was used for the counter pin to slide against the disc.

2. Experimental

Disc specimens of 55 mm diameter and 5 mm thickness made of En8 Emergency number designation given to steels during World War II—part of British standard (EN8 designation is equivalent to AISI 1040 grade steel today) material to British Standard (BS) 970 specification (with a chemical composition given in Table 1) were used in the current investigation. The disc specimens were quenched in oil from 860 °C and tempered at 600 °C for 2 h to a final hardness of 280 HV1. The specimens were then ground to a lapping finish and nitrocarburized in a patented molten salt bath (Sursulf, Hydromecanique et Frottement [HEF], France. Salt is being manufactured by the Chemical Division of M/s Tribology India LTd., Chennai, India.), operating with the following chemistry:

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Alkali cyanates	(CNO^-)	→	$36 \pm 2\%$
Alkali carbonates	(CO_3^{2-})	→	$18 \pm 2\%$
Cyanide	(CN^-)	→	$<0.8\%$

The specimens were treated for 2 h at 570 °C and 700 °C, representing the ferritic (FNC) and austenitic (ANC) temperatures.

Optical metallographic studies were made using a Leitz microscope on polished samples etched in 2% Nital. The same specimens were also used for microhardness testing in a Leitz tester under a load of 0.5 N. Unlubricated wear studies were performed using a pin-on-disc wear-testing machine. The discs were run against stationary pins 3 mm in diameter and made of SAE52100 material hardened and tempered to 850 HV. Normal loads of 40, 60, and 80 N, and a sliding speed of 2 m·s^{-1} were used. The tests were run for different sliding distances up to a maximum of 9.6 km and the weight loss was measured in each case using an electronic balance with a measuring accuracy of 10^{-4} g. The wear tracks were also examined immediately after the tests using a high-resolution optical microscope.

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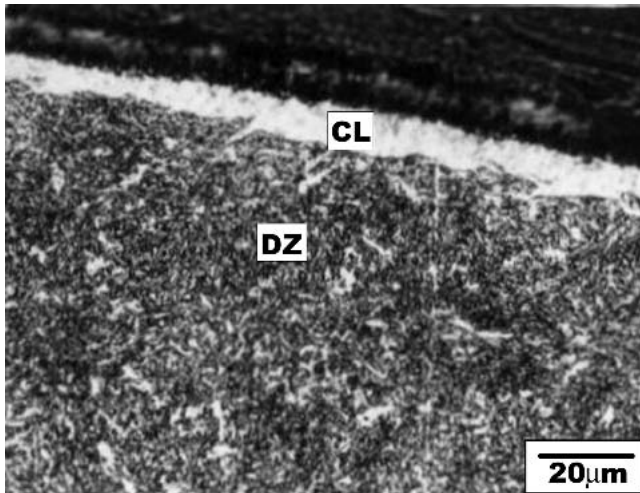
(a)
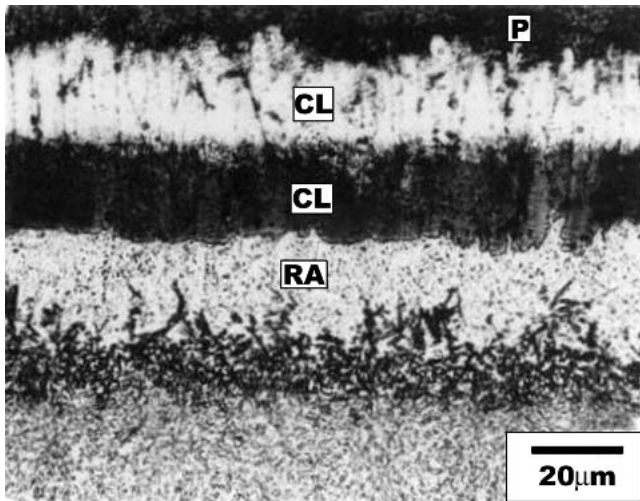
(b)

Fig. 1 Optical micrographs of nitrocarburized En8 specimens. **(a)** 570 °C; **(b)** 700 °C. CL = compound layer; RA = retained austenite; DZ = diffusion zone; P = porosity

Table 1   Chemical Composition, wt.%

Element	C	Mn	Si	S	P	Cr	Mo	V
wt.%	0.43	0.70	0.25	0.02	0.02	0.03	0.01	Trace

3. Results and Discussion

3.1 Microstructure and Hardness

Figure 1(a) and (b) shows the microstructural features of FNC and ANC specimens, respectively. The compound layer thickness can be seen to be dependent on the temperature of nitrocarburizing treatment, as is evident from the photomicrographs. Although the ANC specimen developed a compound layer of 48 μm, the FNC specimen had only a 12 μm thick layer. Porosity could be noticed at the outermost surface of the

compound layer in both the specimens, with the ANC showing a slightly higher porosity level. The diffusion zone, which develops just beneath the compound layer, could not be distinguished clearly in the FNC sample, and only the tempered martensitic structure could be seen.

The hardness profiles of the samples FNC and ANC are shown in Fig. 2. The hardness of the compound layer is marginally higher in the ANC specimen, and this is understandable because higher temperatures are known to favor the formation of epsilon carbonitride, which provides higher hardness to the compound layer.[11] The peak hardness value in both cases can be seen to occur not at the surface but at a depth slightly below, where the compound layer is compact.

The lower hardness recorded on the surface is due to the presence of pores, which causes a "sinking" effect. The practical nitrocarburized case depth as defined in Japanese Standard JIS G 0562-93,[12] that is, the "distance from the surface of the nitrocarburized layer to the point where it is harder by 50 Vickers or Knoop hardness units than the matrix," was found to be 0.175 mm and 0.200 mm for the FNC and ANC specimens, respectively.

In the ANC specimen (Fig. 1b), a light-etching zone of retained austenite could be seen beneath the compound layer as a result of the treatment in the austenitic phase field of Fe-N-C system. This is due to the fact that nitrogen, being a very strong austenite stabilizer, would have depressed the M_f below the room temperature, causing retention of austenite (in the nitrogen diffused/enriched region). The presence of austenite is responsible for the minimum observed in the hardness profile in the region immediately below the compound layer (Fig. 2). The hardness value in the ANC sample increases after this sharp dip, registering a value around 600 HV, indicating the start of the diffusion zone below the retained austenite zone. This is further confirmed by having a closer look at the optical photomicrograph, Fig. 1(b), which reveals the presence of martensite needles in the interface regions between the retained austenite and the diffusion zones.

3.2 Sliding Wear Behavior

Figure 3(a) shows the wear loss of the FNC disc under three different loads and at a constant sliding speed of 2 m·s^{-1}. The corresponding pin wear loss is shown in Fig. 3(b). As can be seen from these figures that under a normal load of 80 N, the test was terminated at around 1 km, at which point the wear loss of the disc was around 30 mg. It can further be noticed that there was a small reduction in the weight loss of the disc after reaching the maximum of 30 mg. The corresponding condition for the pin, shown in Fig. 3(b), registered a sudden and steep rise in wear loss at that instant, coinciding with the inflection in the disc wear loss curve. The friction value was seen to rise suddenly at this stage of the test, indicating some drastic changes at the tribo surfaces. In fact, rapid heating of the pin causing the tip to reach red-hot conditions, drastic shortening of the pin length by wear, and material buildup at the trailing edge could be seen to occur in rapid succession during the testing.

Figure 4 shows the appearance of the pin tip after the test. The material buildup at the trailing edge can be noticed. Furthermore, to ascertain the extent of softening of the pin as a
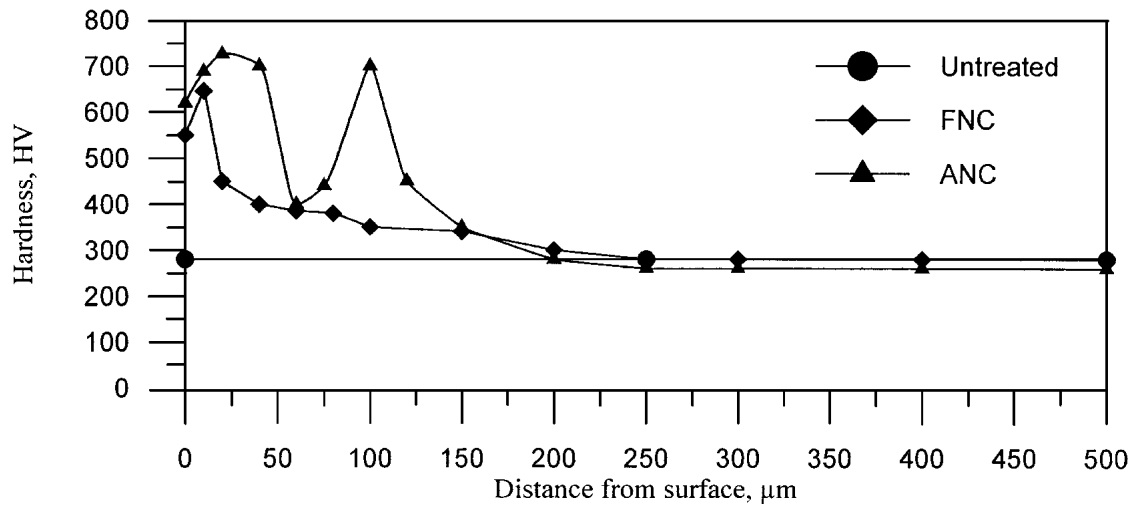
Fig. 2 Microhardness profiles of nitrocarburized En8 specimens
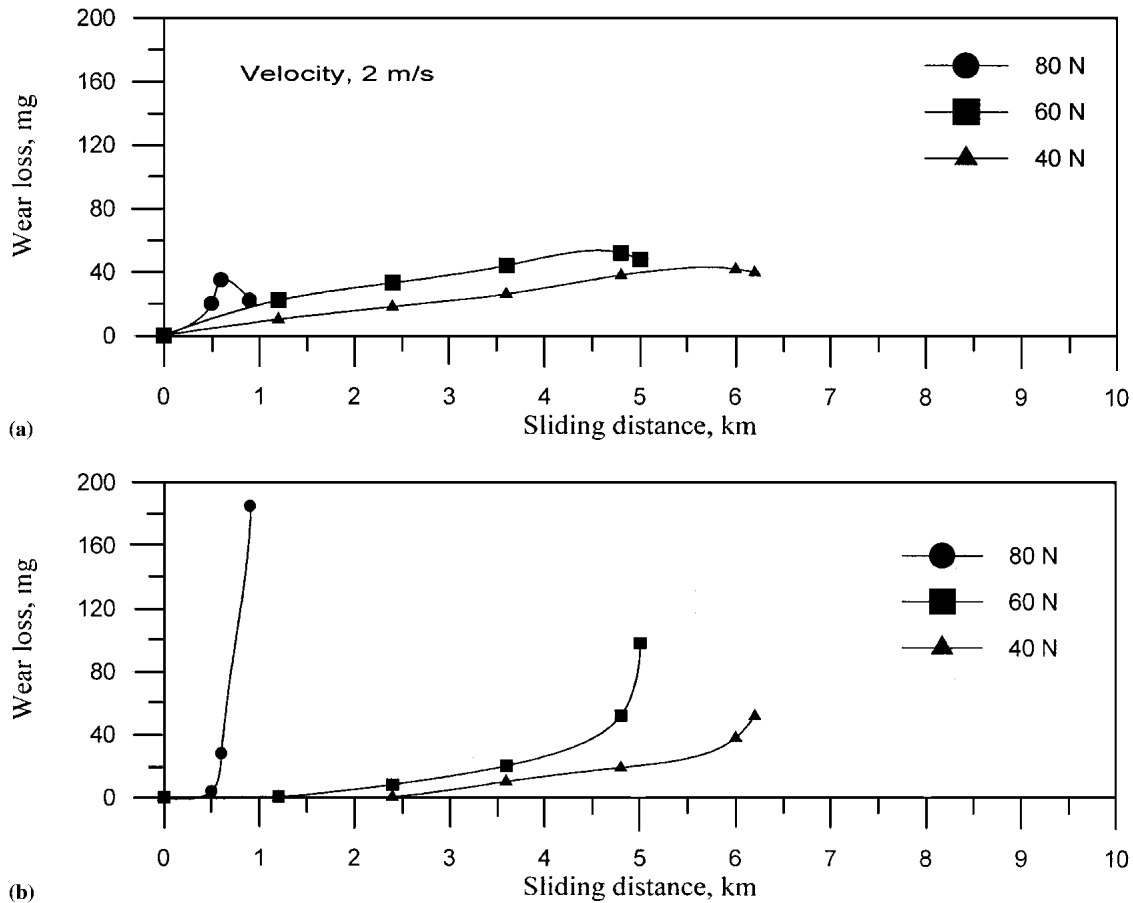

Fig. 3 Pin-on-disc wear data of nitrocarburized (FNC-570 °C) specimen. (a) Disc; (b) Counter pin

result of the intense frictional heat generated at the interface, hardness traverse was taken along the length of the pin after the test was over, and it was observed that the pin had softened up to a length of 10 mm from the worn-out tip. The hardness of the pin, which was 850 HV before wear testing, was found to have reduced to as low as 320 HV at the worn tip, which obviously reflects the effect of heat, resulting in a tempering effect to the pin.

To understand these sudden changes in behavior, the wear track was examined by optical microscopy. Figure 5 shows the
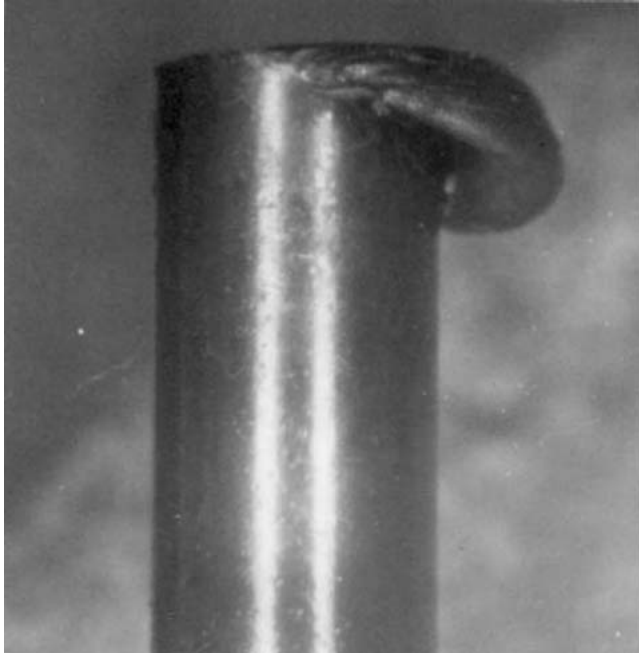
Fig. 4 Photograph showing the worn pin tip-trailing edge formed in AISI 52 100 counter pin slid against nitrocarburized (FNC-570 °C) En8 disc specimen
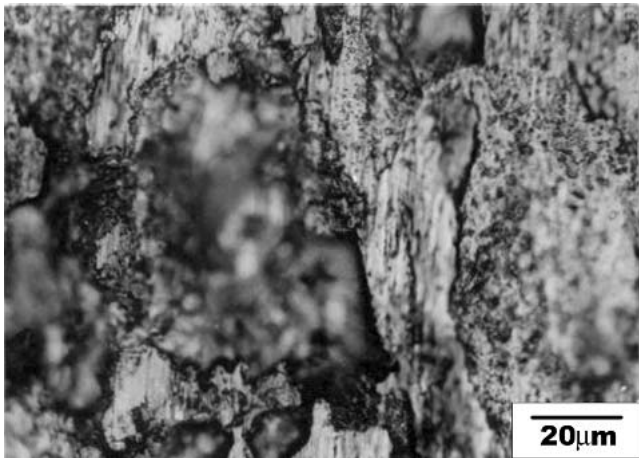

Fig. 5 Optical micrograph of the wear track of FNC-570 °C specimen

optical micrograph of the wear track after the test, wherein "mounds" of material, referred to as "prows" in the literature,[13] can be seen in relief over the track. Metallographic examination/observation of a cross-section of the wear track taken along the tangential direction, shown in Fig. 6, revealed tiny and rounded white-etching particles in the mound region. These particles are presumably primary chromium (Cr) carbides, considering that the pin material is SAE52100 (1% carbon–1.5% Cr) steel, and were getting transferred by the adhesive wear mechanism to the disc.

Based on the density of the iron nitride (6.35 g·cm^{-3}),[14] the calculated wear loss of 30 mg corresponded to a removal of
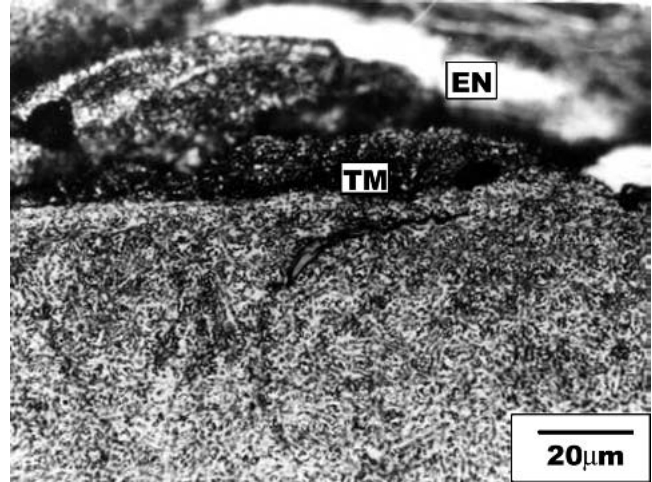

Fig. 6 Optical micrograph of the cross section of FNC-570 °C wear track. EN = electroless Ni coat for edge retention; TM = transferred material. (Note white Cr carbide particles)

12 μm thick material. This was exactly the compound layer thickness achieved in the FNC specimen and therefore the behavioral changes such as overheating of the pin and the transfer of material to the disc had taken place only upon wearing out of the compound layer. The observation that as long as the compound layer was present the pin did not develop high temperature clearly points to the beneficial effect of the compound layer, particularly its low-friction property in resisting adhesive wear. This effect itself is attributable to the hexagonal close-packed structure of the epsilon carbonitride. The superiority of epsilon carbonitride over gamma prime carbonitride from the tribological point of view has been highlighted in an earlier research work.[15]

It can be noticed from Fig. 3(a) that the wear tests lasted for longer sliding distances of 4.8 km and 6.0 km when the normal load was reduced from 80 N to 60 N and 40 N, respectively. The corresponding wear loss of the discs was found to be 58 mg and 50 mg, respectively, under these loads. The corresponding pin wear loss was 95 mg and 70 mg, respectively, with the catastrophic wear occurring towards the end as has been noticed under 80-N test.

It can be seen that for the 60-N load, the initial wear rate was marginally higher up to a distance of 1.2 km. This could be observed more clearly in Fig. 7, drawn to an enlarged scale, which provides information not only on the wear of pin and disc but also the co-efficient of friction values during the test. The above observation is due to the running-in phase, when a large number of asperity interactions take place leading to interlocking and even formation of micro-welds.[16] These junctions resist the relative movement, which manifests as rise in friction at the tribo-surfaces and a steep rise in friction co-efficient is seen during this running-in period. The frictional value settled down to a more or less steady state once the compliance of the sliding surfaces took place, which is also apparent from this figure. Furthermore, the wear rate of the disc was also, in turn, lower during this steady state.

Also, it can be noticed that the running-in phase observed in the wear test with 60-N load was not evident with either 80- or
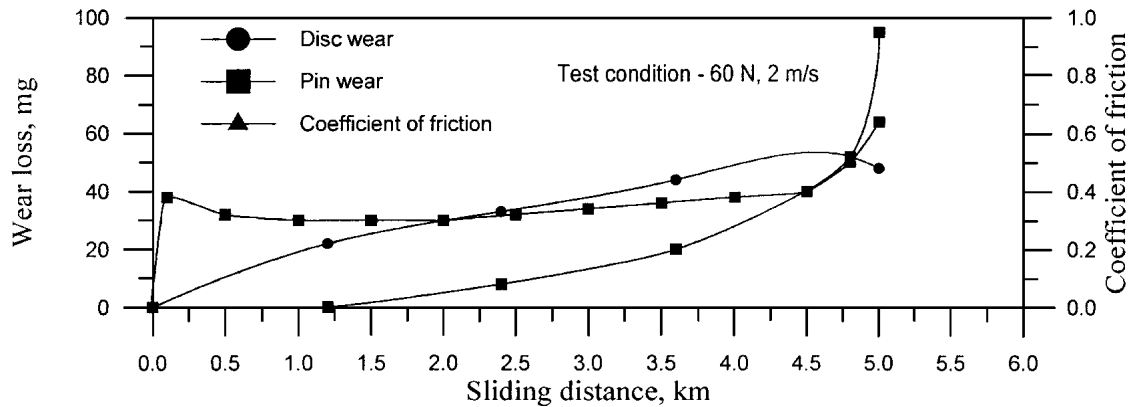
Fig. 7 Pin-on-disc wear data of nitrocarburized (FNC-570 °C) specimen under 60-N load (indicating the coefficient of friction and wear loss under 2 m/s condition)

40-N load. This is plausible because under 80 N, the test duration was so short that the failure took place even before reaching the steady state; with 40-N load, however, it could be because of lower stress levels, making the transition from running-in to steady state very gradual.

The end of the test under these lower loads was also marked by the phenomena of rapid heating and material transfer, similar to the one noticed with the 80-N test. However, the weight loss of the discs in these cases, viz., 58 mg and 50 mg when calculated in terms of thickness, indicated that the surfaces had been worn away much beyond the compound layer thickness of 12 μm. This observation points to the fact that the condition of the material transfer from pin to disc (along the wear track) did not take place immediately upon wearing out of the compound layer, but only after some more sliding in the diffusion zone below. The reason for this can be traced to lower tangential forces resulting from lower normal loads applied and hence frictional heat necessary to heat the pin to red hot condition could develop only after considerably longer distances of sliding. The gradual heating of the tribo-surfaces also caused mild oxidation of the wear track (disc), which further helped to delay the onset of material transfer from the pins.

Figure 8 shows the oxidized patches observed in the wear track of the FNC sample tested under 60-N load. The influence of oxides in reducing the wear rate is well known,[17] and the wear debris analysis (x-ray diffraction) also did confirm the presence of FeO, Fe_2O_3, and Fe_3O_4 besides the epsilon carbonitride. This corroborated the fact that the wear under these lower loads was governed by an "oxidative" mechanism and therefore considered to be "mild" as defined by Welsh.[18] The absence of large shiny metallic particles also did substantiate the point that the wear did not cross into the "metallic" (severe) regimen.

The wear behavior of the ANC specimen is depicted in Fig. 9(a). It can be observed that while under 80-N load, the test had run only up to about 6 km; the tests lasted for the full test sliding distance of 9.6 km under the lower loads. A comparison with Fig. 3(a) would reveal that the ANC specimens slid for longer distances for the same loads.

The pin wear loss data (while running against the ANC disc) depicted in Fig. 9(b) would reveal that the catastrophic wear of pin occurred only under the 80-N load. Further, under the 60-N
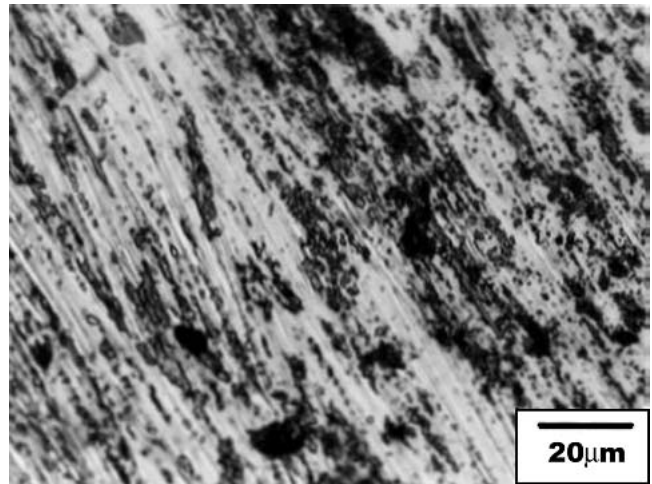

Fig. 8 Wear track of FNC-570 °C disc showing mild oxidation under 60-N load

test, a marginal increase in the pin wear rate can be seen beyond about 7.2 km of sliding, but the wear rate of pin remained steady up to 9.6 km of running under the 40-N load. The disc wear loss at 7.2 km (under 60-N load) was recorded to be 98 mg, and in terms of thickness of material removed, this weight loss corresponds to approximately 50 μm, which was marginally higher than the measured value of compound layer thickness in the 700 °C-treated sample. The slight increase in the wear rate beyond 7.2 km therefore can be attributed to the running of the pin on the subcompound layer regions. In the case of the tests under 40-N load, the part of the compound layer remained intact because the wear loss was around 82 mg at the end of the test after 9.6 km of sliding. It is interesting to note that the wear track under this condition shows dense/thick oxide patches (Fig. 10), which is obviously due to the slow and sustained heating of the tribo surfaces.

To understand the progress of wear during testing and the influence of compound layer in the mechanism, a cross-section of the wear track of an ANC disc specimen was taken after stopping the test at the steady-state running condition. The specimen, before mounting in Bakelite, was given an electro-
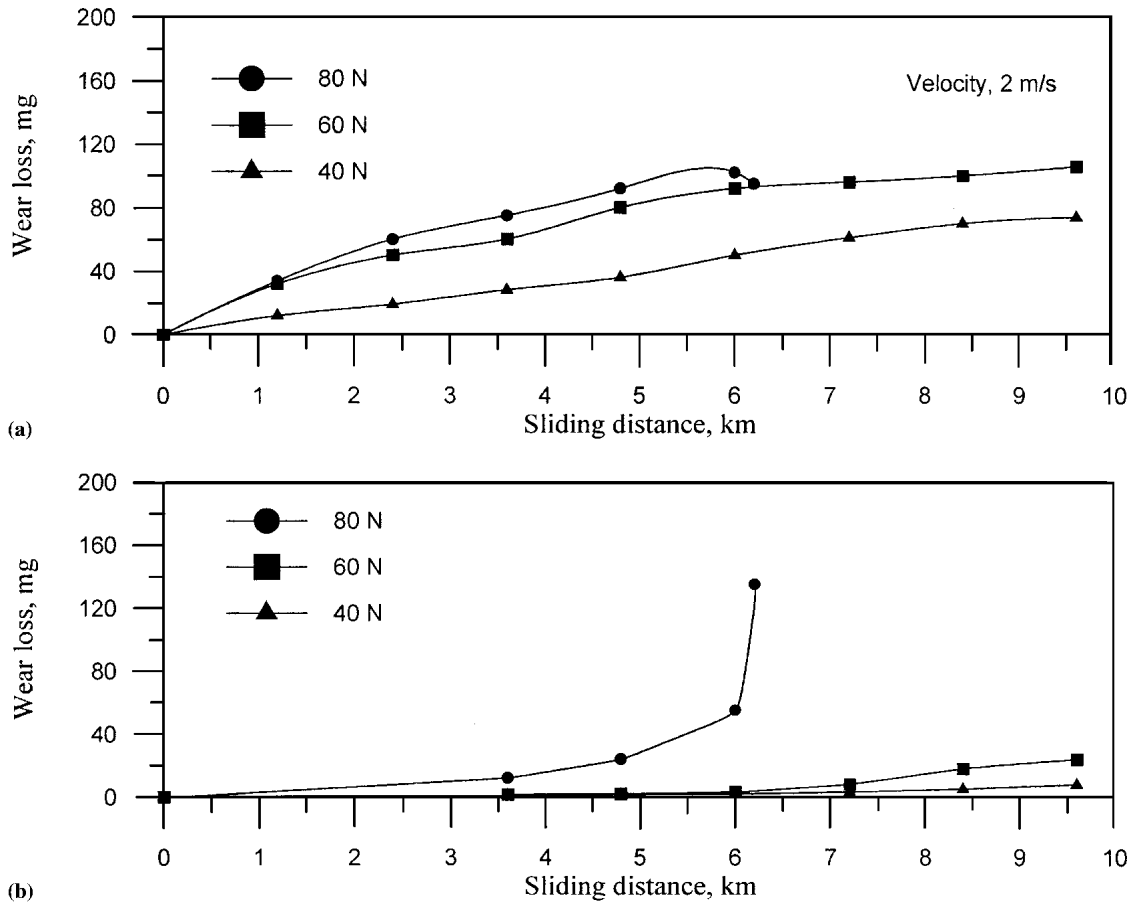
Fig. 9 Pin-on-disc wear data of nitrocarburized (ANC-700 °C) specimen. **(a)** Disc; **(b)** Counter pin
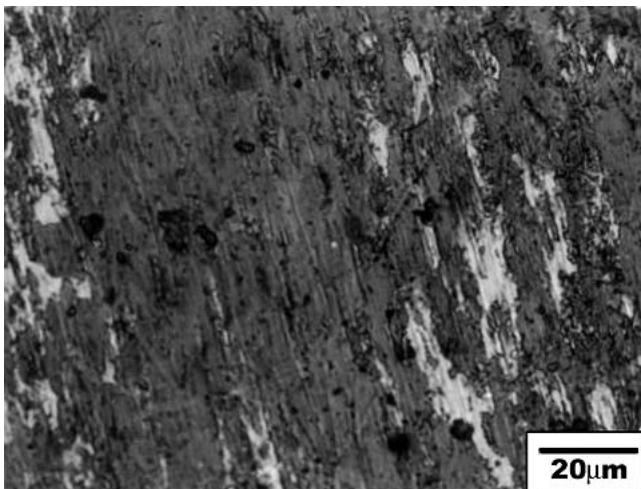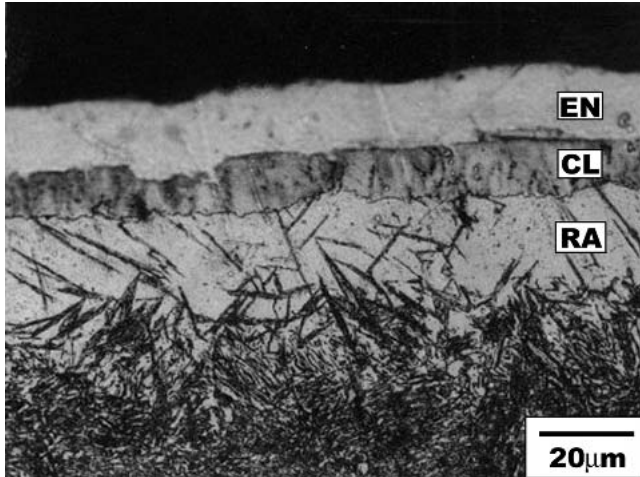

Fig. 10 Optical micrograph of ANC-700 °C disc wear track showing severe oxidation (tested under 40-N load)

less nickel (Ni) coat for the purpose edge retention while polishing. The optical micrograph of this section shown in Fig. 11(a) reveals the bright EN layer over the compound layer, which can still be seen intact with no traces of material transfer from pin. The retained austenite zone that is characteristic of austenitic nitrocarburizing is also seen below the compound layer. Figure 11(b) shows the optical micrograph of the cross-section of the track after the failure by adhesive transfer. The compound layer can be seen to have fully worn away, but a dark layer with tiny and rounded white etching particles can be seen beneath the edge protective electroless Ni coat. Apparently, these are the characteristic primary Cr carbide particles of the SAE52100 material of the pin, which gets transferred by adhesive-wear mechanism. This observation reaffirms the beneficial influence of the compound layer in resisting adhesive wear, arising from the hexagonal closed packed structure of the epsilon carbonitride in the compound layers.

4. Conclusions

In conclusion, nitrocarburizing treatment of medium C steel at elevated temperature promotes higher compound layer thickness growth and also develops a retained austenite zone beneath the compound layer. The compound layer hardness is marginally higher in the ANC-treated specimen, which is due to predominantly epsilon carbonitride in the compound layer. The wear rate and wear mechanism of the nitrocarburized specimens were found to be dependent on the normal load. The wear rate is controlled by the porosity and hardness of the
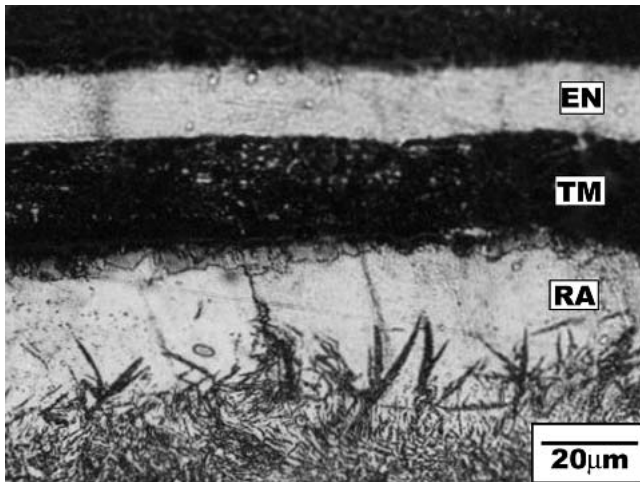
Fig. 11 Optical micrograph of cross-section of wear track of ANC-700 °C specimen **(a)** during steady-state running and **(b)** after failure. EN = electroless Ni coat; CL = compound layer; TM = transferred material; RA = retained austenite

compound layer. Finally, the transfer of material from pin to disc during the wear tests was decided/governed by the wearing (rate) of the compound layer and the presence of compound layer resists such adhesive transfer of material.

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