CONF-900417--1

LA-UR 90-654

LA-UR--90-654

DE90 007502

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE

MODIFICATION OF SURFACE MECHANICAL PROPERTIES OF HIGH-CHROMIUM TOOL STEEL BY CARBON-IMPLANTED CODEPOSITED IRON-TITANIUM FILMS

AUTHOR(S)

Juha-Pekka Hirvonen, MST-7
Michael Nastasi, MST-7
Thomas Roland Jervis, MST-7
Tom George Zocco, MST-5

SUBMITTED TO

International Conference on Metallurgical Coatings
April 1-6, 1990
San Diego, California
Dr. W.D. Sproul, Conference Chairman

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MODIFICATION OF SURFACE MECHANICAL PROPERTIES OF HIGH-CHROMIUM TOOL STEEL BY CARBON-IMPLANTED CODEPOSITED Fe-Ti FILMS

J-P. Hirvonen, M. Nastasi, T. R. Jervis, and T. Zocco
Los Alamos National Laboratory, Materials Science and Technology Division
P.O. Box 1663, MS K765
Los Alamos, NM 87545

ABSTRACT

An iron-titanium film 300 nm thick was deposited on a tool steel (1.55% C, 0.3% Si, 0.3% Mn, 12% Cr, 0.8% Mo, and 0.8% V) by coevaporation of Fe and Ti. Subsequently this surface film was implanted with carbon at energies of 55, 120, and 200 keV to a total fluence of 1.24×10^{18} C^+/cm^2. This treatment produced a surface hardness of 15 GPa.

The effect of this coating on unlubricated wear and friction was tested in air at a relative humidity of 10% in a pin-on-disc tester using a 440C pin as a counterface. The sliding mechanism of the untreated substrate was found to be based on the transfer of pin material and subsequent growth of uneven oxide hillocks on the wear track. Oxide scales were observed also on a wear scar of the pin, presumably as a result of back-deposition. In contrast, the sliding mechanism on the coated sample was drastically different. A more uniform transfer film originating in the coating was found on the pin, resulting in sliding between identical materials. No wearthrough of the coating occurred during the test of 5000 cycles at a Hertzian pressure of 835 MPa, and the surface of the wear track showed extreme smoothness to the very end of the test. The friction coefficient was decreased from 0.7 for the uncoated to 0.2 for the coated surface. The wear track on the coated surface was also found to be slightly oxidized, as determined by a nuclear reaction [$^{16}O(d,p)^{17}O$]. The reduction of friction was mainly attributed to the increased hardness of the counterfaces and an adequate but controlled oxidation.

INTRODUCTION

Beam-modified surfaces based on a Fe-Ti-C system have been shown to possess superior mechanical properties [1-3]. Wear resistance is increased and friction reduced. A complete understanding of the dominating mechanisms has not been achieved despite extensive studies in the past few years. It is reasonable to assume that both mechanical and chemical properties of a modified surface contribute to an altered tribological behavior. In general, an increased surface hardness and an amorphous or a very finely dispersed precipitate structure in an amorphous structure were found to be correlated with the enhanced sliding performance [4,5]. Oxidation during sliding has also been shown to reduce adhesion between sliding surfaces [6], while preoxidation has been found to degrade the tribological properties of a titanium-implanted steel surface [7].

So far, gas carburization of a titanium-implanted steel [8], dual implantation of titanium and carbon [3], carbon implantation into an ion-beam-mixed surface [1], and ion- or laser-beam mixing of a multilayer Fe-Ti-C structure [3] have all shown good results. A limiting factor of all these techniques is the maximum thickness obtainable in the modified layer. In addition, the maximum titanium concentration is limited by sputtering in the case of ion implantation. However, hardness was found to be increased by the increased titanium concentration [9]; this, in addition to the increased thickness of the Fe-Ti-C layer, presumably has a beneficial effect on tribological performance. In this work we implanted carbon into an amorphous FeTi surface film deposited on a tool steel by codeposition of Fe and Ti. Because the range of carbon at energies commonly obtainable in implanters (≤200 keV) is of the order of 300 nm, thick codeposited layers can be treated with C implantations. In contrast, surface modification by Ti implantation, carburization, and ion-beam mixing is limited to layers approximately 100 nm thick.

PREPARATION OF SAMPLES AND MEASUREMENTS

Samples 3 mm thick were cut from a 10- × 40-mm flat perpendicular to a rolling direction. Austenizing annealing was carried out at 1040 °C for 10 min and the specimens were subsequently quenched in 10% aqueous NaCl solution. The samples were then tempered twice at 200 °C for 1 h. The microstructure after this treatment consisted of tempered martensite, carbides, and retained austenite. The hardness was 7 GPa.

After the heat treatment, the samples were mechanically polished, finishing with 0.25-µm diamond paste. The final surface roughness was 0.03 µm (c.l.a.). A FeTi layer was deposited in a vacuum better than 10 µPa by evaporating iron and titanium simultaneously from different crucibles equipped with electron beam guns. Deposition rates were controlled with quartz thickness monitors. The film was also deposited on a SiO_2 substrate for precise determination of thickness and composition by Rutherford backscattering spectroscopy. These measurements showed a thickness of 300 nm and a composition of 45 at. % Fe and 55 at. % Ti.

As the final treatment, the samples were ion-implanted with ^{13}C isotopes, which allows utilization of nuclear-reaction analysis. Because of the thickness of the evaporated layer, three different energies were used. The energies, fluences, and calculated ranges are given in Table 1. During implantations the specimens were mounted onto a sample holder which had been cooled down to -150 °C. All implantations were carried in a vacuum of 10 μPa with an ion current of 320 μA.

The microstructure of the FeTi films after carbon implantation was examined with a transmission electron microscope (TEM).

Investigations of the surface hardness were performed using a commercially available nanoindenter that directly measures the load on a Vickers-type diamond indenter tip as a function of displacement from the surface. We chose to eliminate the effect of tip shape by normalizing the data to measurements of the as-deposited FeTi film taken under identical conditions. Measurements were made under a constant load rate of 250 mN/s to a depth of 800 nm. Twelve indents were made on each sample and the data were averaged in 10-nm increments. As discussed by Doerner and Nix [10], the actual depth of the indent must take into account the elastic recovery of the material as the indenter is removed. Elastic recovery was approximately 13% in these samples. Since the indents were made well through the modified surface, the effect of this recovery on the measurements was small.

Wear and friction tests were carried out using a pin-on-disc tester. A 440 C steel ball 6 mm in diameter was used as the pin. Before the tests the pins were polished with 0.25-μm diamond paste and ultrasonically cleaned. The load of 0.23 kg used in all measurements corresponds to a maximum Hertzian surface pressure of 835 MPa. The diameter of the wear track was 3.5 mm and the sliding speed was 10 mm/s. The friction force was monitored continuously with a calibrated force sensor. A maximum of 5000 cycles was used, corresponding to a total sliding distance of 55 m. All tests were carried out without lubrication in air at a relative humidity of 10%.

In two cases the sample in the wear and friction test was moved back and forth in order to obtain a 5-mm-wide, donut-shaped wear track for ion-beam analysis. These wear tracks were obtained under conditions similar to those described above, except for the average sliding speeds, which were 15 and 75 mm/s, respectively, and the total number of revolutions, which was 8500.

Following the tribological tests, both samples and pins were ultrasonically cleaned and examined in a scanning electron microscope (SEM). Material transfer was studied with energy dispersive spectroscopy (EDS).

Oxygen and carbon contamination was determined with the nuclear reactions $^{16}O(d,p)^{17}O$ and $^{12}C(d,p)^{13}C$, respectively. Implanted ^{13}C distributions were determined with the reaction $^{13}C(d,p)^{14}C$. Although this reaction does not have very good depth resolution, it was used here because ^{13}C distribution was obtained simultaneously with ^{16}O and ^{12}C. In all measurements a deuterium energy of 925 keV was used. Identical measurements were performed on the unworn surface as well as on two wide wear tracks.

Because this paper contrasts the tribological behavior of the modified surface with that of untreated steel, it also includes comprehensive studies of the untreated steel.

RESULTS

The microstructure of carbon-implanted FeTi films consists of very finely dispersed carbides. The TEM micrograph is shown in Fig. 1. In contrast to the microstructure of ion-beam-mixed, carbon-implanted FeTi layers an amorphous phase was not detected [5]. The detailed description of the microstructure will be given in an outcoming paper.

The surface hardness of the carbon-implanted FeTi film is 15 GPa. This is more than twice the value for the untreated substrate (about 7 GPa), and significantly higher than that of an ion-beam-mixed and carbon-implanted FeTi [5]. On the other hand, the hardness of the as-deposited FeTi film was about the same as that of the untreated substrate. This value is also higher than that of an ion-beam-mixed FeTi film [5]. The hardness as normalized to the unimplanted layer is plotted as a function of depth in Fig. 2. Although the implanted layer was 350 nm thick, the hardness begins to decrease at a depth of 100 nm.

Wear and friction measurements revealed remarkable differences between the uncoated and coated samples. Figure 3 shows friction coefficients for these two cases. The uncoated steel rapidly approached the steady-state value of 0.7, which remained unchanged throughout the test. In the case of the coated sample there was a run-in period of about 1000 revolutions, after which the friction coefficient was constant at 0.2.

More information about the sliding mechanisms was provided by SEM and EDS studies. In the case of the untreated steel surface, significant transfer of pin material onto the wear track occurs [Fig. 4(A)]. The transferred material is then oxidized, as can be seen in Fig. 5, where both secondary and backscattered electron images of the wear track are shown. At the higher magnification the transferred material shows a submicron-size layered structure, such as reported by Rigney et al [11]. In contrast to the uneven wear track of the untreated sample, the wear track on the carbon-implanted FeTi film is extremely smooth, showing no traces of transfer [Fig. 4(B)]. Never during the test of 5000 cycles did the implanted film wear through. Although some pits and scratches are visible on the wear track, they have not caused brittle fracture or peeling of the surface layer. This indicates that the carbon-implanted FeTi film has considerable durability in addition to very high hardness.

SEM examination of the pins showed further differences in the sliding mechanisms of these two systems. Significant wear can be found on the pin slid on the untreated steel surface [Fig. 7(A)]. A great deal of the surface of the wear scar is covered by oxide. This can be seen in Fig. 7(B), where the corresponding image of backscattered electrons is shown. On the pin slid against the carbon-implanted FeTi film a more continuous metallic transfer film is observed [Fig. 7(C)] and the pin surface is undamaged. The composition of the transferred material was verified with EDS and confirmed to have originated in the carbon-implanted FeTi film.

The results of ion-beam analysis of the as-deposited and carbon-implanted films and the wide wear tracks are given in Table 2. The carbon contamination increased during implantation but remained unchanged in the wear tests. In contrast, the oxygen contamination decreased during carbon implantation but increased slightly in the wear tests. There is also a small but significant increase in the oxygen concentration as a function of a sliding speed. The implanted ^{13}C distribution showed a narrow peak at the surface, but otherwise was relatively uniformly distributed. Only minor changes were detected in implanted distributions on the wear tracks. The measured ^{13}C concentration was 1.12 x 10^{18} at./cm^2, which is in good agreement with the nominal implanted fluence.

DISCUSSION

The wear mechanism for untreated steel under conditions used in this study is evidently based on the transfer of pin material onto the wear track and subsequent oxidation. Wear debris is formed as a result of this oxidation. It is clear from Fig. 7 that remarkable wear of the pin has occurred. Profilometer measurements showed also that the steel surface had worn. For example, the maximum depth of the wear track in Fig. 4(A) was 800 nm. Wear of the steel surface probably occurred through mechanical alloying and back-deposition, as explained in Ref. 11.

Although a simple adhesion concept claims that the transfer occurs from a material of lower shear strength to one with higher strength, exceptions have been reported [12,13]. In our study the transfer occurred from the harder, carbon-implanted FeTi film to the softer pin material. Similar transfer was observed by Pope et al. [14] in the case of titanium- and carbon-implanted steel. In our case the transfer did not result from a rupture at the surface film/substrate interface, because the wear track was still entirely covered by the surface film even after 5000 cycles. Instead, we can assume that the transfer layer grew as a result of smearing and flattening of transferred particles during prolonged sliding. It is evident that this material transfer is one of the key factors in sliding of the 440C pin on the carbon-implanted FeTi film.

In general, a transfer layer has a very fine, nanocrystalline grain size [10]. It is also very hard. Because the hardness of the carbon-implanted FeTi film is also very high, sliding in this system after development of the transfer layer occurs between two hard surfaces. This can reduce friction by decreasing the real area of contact.

Normally a fine grain structure is associated with increased hardness. On the other hand, nanocrystalline grain structure requires an additional phase to stabilize it and maintain the high hardness. In a transfer layer this can be offered by the counterface material through mechanical alloying, or by the environment—through oxidation, for example. It is interesting to notice that in our case the transfer occurs from a material with a very fine microstructure. It is possible that the transfer layer from the carbon-implanted FeTi film is stabilized by itself. This may make this system less dependent on reactions induced by the environment or by mechanical alloying.

Oxidation has been reported to play an important role in dry sliding of titanium-and carbon-implanted AISI 304 stainless steel [14]. In air, a total oxygen concentration of 10^{18} at. /cm^2 in a wear track has been determined, and even in vacuum with an oxygen partial pressure as low as 2.1×10^{-5} Pa a total oxygen concentration of $1–2 \times 10^{17}$ at./cm^2 was observed. Consequently, a reduced friction coefficient was found. In contrast, a much lower oxygen concentration level, 5×10^{16} at./cm^2, was determined after sliding in dry nitrogen, resulting in nearly no reduction in the friction coefficient. In our case the oxygen accumulation in wear tracks was also low, about 5×10^{16} at./cm^2, yet significantly reduced friction and wear was observed. This indicates essential differences in sliding mechanisms between titanium- and carbon-implanted steel and a carbon-implanted coevaporated FeTi film. It is important to notice that these two materials are different: the maximum titanium concentration in the ion-implanted AISI 304 case was 30 at. %,whereas in our case it was 55 at. %. In the implanted AISI 304 surface there were also other alloying elements, notably chromium. Consequently, the metallic content of the oxide on the implanted AISI 304 case was determined to be $Fe_{73}Cr_{21}Ni_4Ti_2$ [14]. The limited supply of iron and the absence of chromium in carbon-implanted FeTi film may change the oxidation kinetics, adhesion, and mechanical properties of oxides and thus alter the transfer and retransfer behavior. Nevertheless it seems evident that oxygen also plays an important role in the tribology of our carbon-implanted FeTi system.

A pin slid on the carbon-implanted FeTi film did not wear regardless of the transfer layer, although profilometer measurements showed that material was removed from the film. This was observed as loose wear debris. The very smooth wear track rules out back-deposition of the transferred material. Thus loose wear debris could have been formed either after material transfer to the pin or directly from the FeTi film. Because the transfer layer on the pin was continuous and smooth, the latter possibility is more likely. The further transfer from the film after a run-in period is reduced by the high hardness of the transfer layer on the pin.

CONCLUSIONS

Implantation of carbon into a codeposited FeTi film produces a modified layer of increased thickness and a flexibility to adjust the composition. It has been shown in this work that even under very severe test conditions this type of coating remarkably improves the tribological behavior of the hardened tool steel.

The enhanced tribological performance of carbon-implanted codeposited FeTi films is based on many unique properties of this material. During a run-in period at the onset of sliding, material is transferred from the harder carbon-implanted FeTi film onto the pin and a smooth, continuous deposit is formed. After this run-in period, sliding occurs between this transfer film and the carbon-implanted FeTi film. At this stage, in addition to the hardness of the counterfaces, an adequate but controlled oxidation plays the dominant role in reducing friction. Retransfer is also completely inhibited, leaving the surface of the wear track smooth and even. The intrinsic mechanical properties of the carbon-implanted codeposited FeTi film, such as hardness and toughness, are of great significance in supporting a thin oxide layer and maintaining the smoothness of the wear track.

ACKNOWLEDGEMENTS

Ion implantations and ion beam analysis were carried out in the Ion Beam Materials Laboratory at Los Alamos National Laboratory. This work was supported by the U.S. Department of Energy under contract No. W-7405-ENG-36 through the Los Alamos Center for Materials Science and by the U.S. Air Force Wright Aeronautical Laboratory under contract DEW-88-24 through B.D. McConnell.

FIGURE CAPTIONS

Fig. 1. Transmission electron micrograph of the microstructure of a carbon implanted, codeposited FeTi film.

Fig. 2. Hardness of a carbon implanted, codeposited FeTi film normalized to an as-deposited, codeposited FeTi film.

Fig. 3. Friction coefficient of an untreated steel and carbon implanted, codeposited FeTi film.

Fig. 4. Scanning electron micrograp of a wear track on an untreated steel (A) and carbon implanted, codeposited FeTi film (B) after 4000 wear cycles.

Fig. 5. Secondary (A) and backscattering electron (B) image of a transfer layer on an untreated steel after 4000 wear cycles.

Fig. 6. High magnification scanning electron micrograph of a wear track on an untreated steel showing an oxide hillocks and layered structure of the transfer layer.

Fig. 7. Scanning electron micrographs of pins after 4000 wear cycles. Secondary (A) and backscattering (B) image of the pin slid against an untreated steel. Secondary electron image of the pin slid against a carbon implanted FeTi film (C).

Table 1. Implantation energies, fluencies, and calculated ranges [15].

	Energy (keV)		
	55	120	200
fluence (10^{17} ions/cm^2)	3.6	4.2	4.8
range[a] (nm)	85±46	180±72	280±92

[a] range±stragling

Table 2. Carbon and oxygen concentrations of the samples (at./cm^2)

Sample	Oxygen	Carbon[a]
as-deposited	4.3×10^{16}	3.5×10^{16}
carbon implanted	3.0×10^{16}	1.5×10^{17}
wear track 1[b]	5.2×10^{16}	1.2×10^{17}
wear track 2[c]	6.0×10^{16}	1.5×10^{17}

[a] excluding implanted ^{13}C

[b] sliding speed 15 mm/s

[c] sliding speed 75 mm/s

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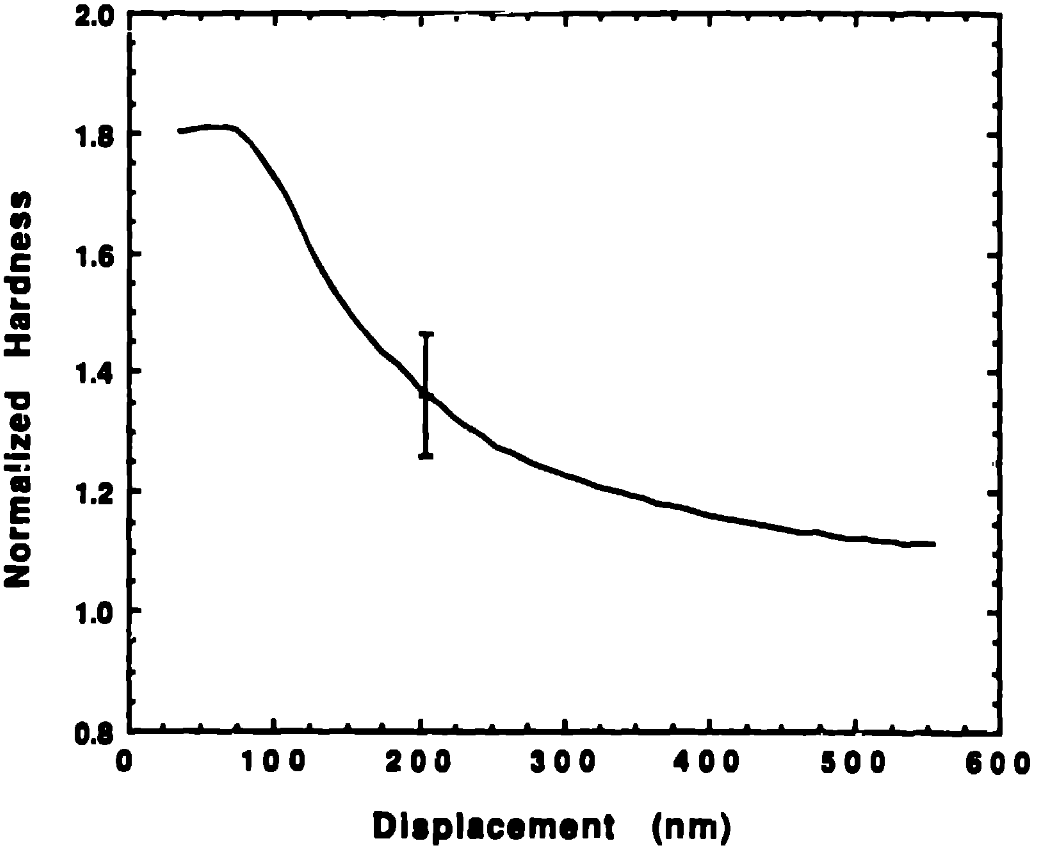
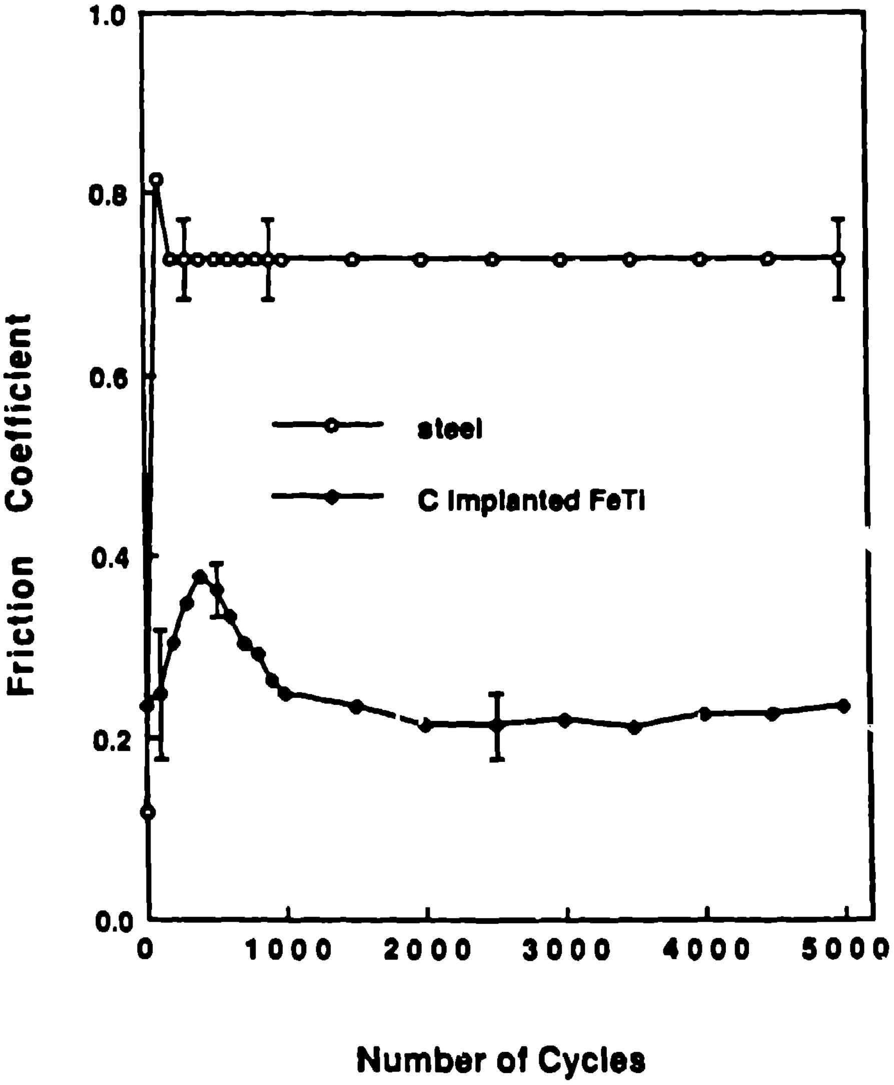
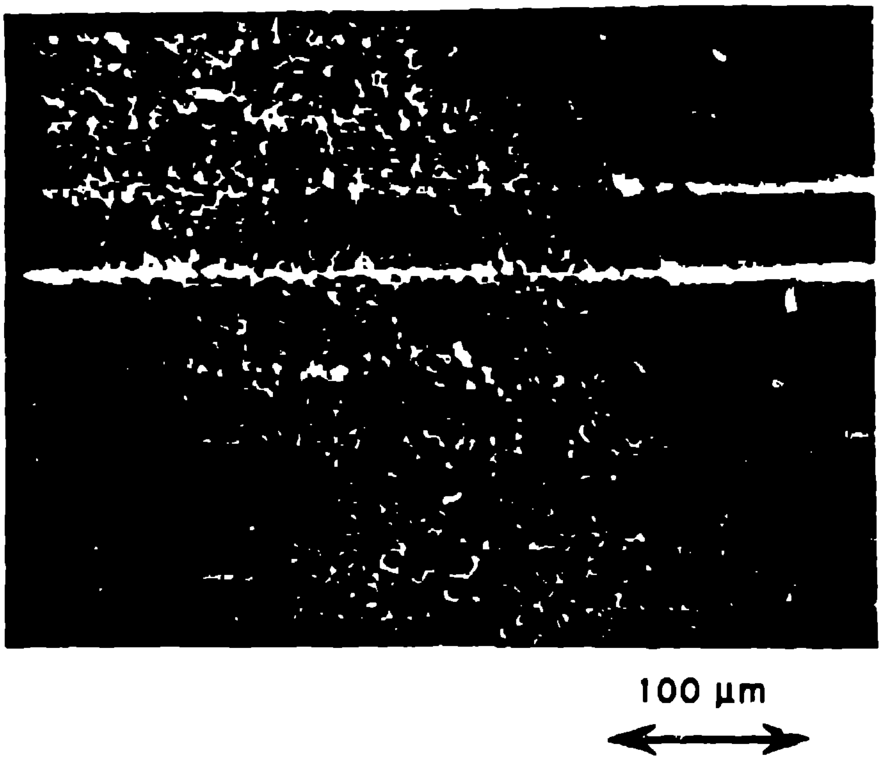


2.0
1.8
1.6
1.4
1.2
1.0
0.8
Normalized Hardness
0
100
200
300
400
500
600
Displacement (nm)

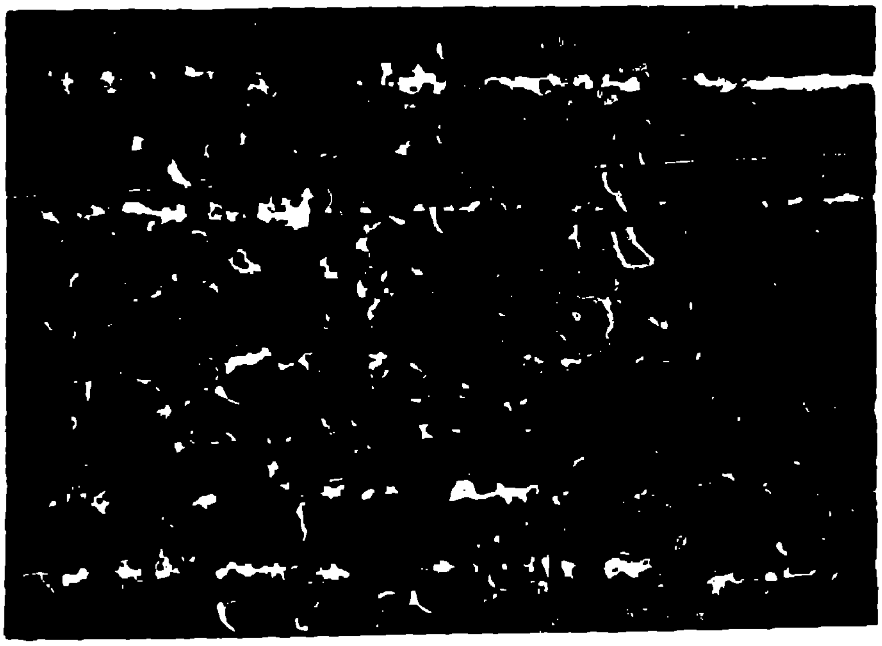

1.0
0.8
0.6
0.4
0.2
0.0
0
1000
2000
3000
4000
5000
Friction Coefficient
Number of Cycles
steel
C implanted FeTi

(A)



(B)

(A)



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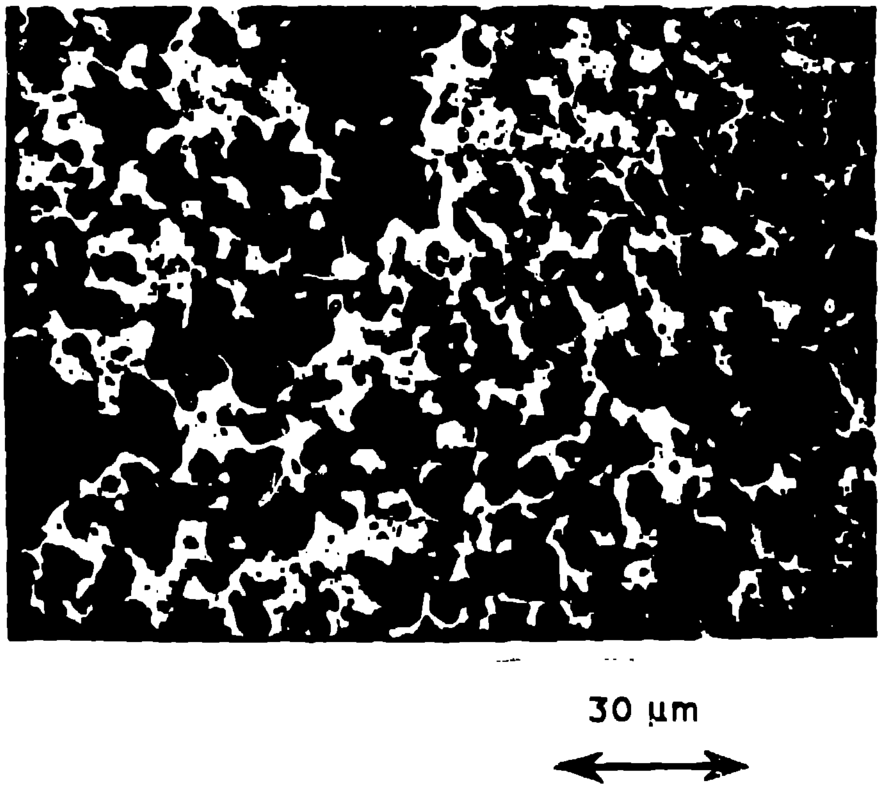
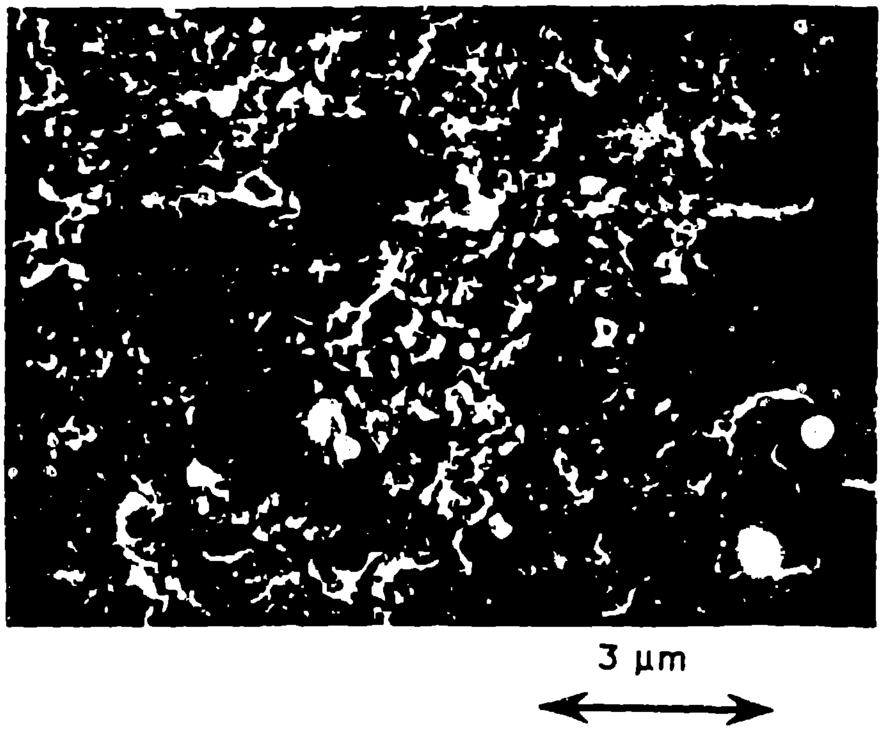
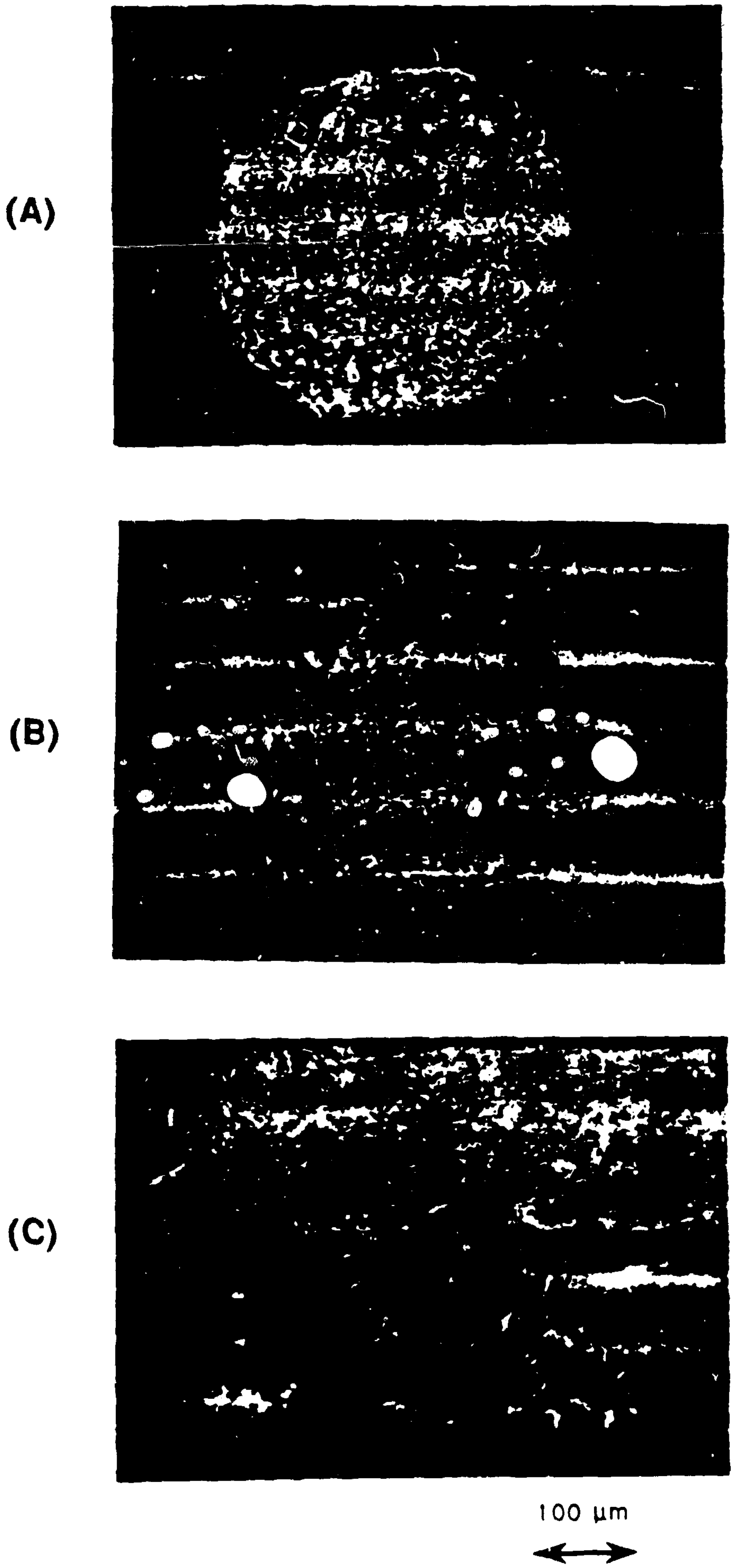



3 µm


(A)
(B)
(C)
100 µm