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The Chemistry of the Extreme Pressure Lubricant Additive Lead Naphthenate on Steel Surfaces

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The adsorption and chemical reactivity of the extreme pressure (EP) oil additive lead naphthenate (Pbnp) on steel surfaces is examined with X-ray photoelectron spectroscopy. In addition, the chemical compositions of AISI 440C and 52100 steel surfaces are studied as a function of sample cleaning treatment, including solvent cleaning, and treatments with acidic and basic solutions. At room temperature, Pbnp is shown to physisorb on the iron oxide overlayer present on both steel surfaces following solvent cleaning. A chemisorbed form of Pbnp is characterized by Pb 4f peaks chemically shifted by 0.3 to 0.4 eV to lower binding energy and significantly lower intensity of the C 1s feature associated with the Pbnp carboxylate group. This form of Pbnp is observed on acid- and base-pretreated surfaces that lose their iron oxide overlayers. The chemisorbed Pbnp surface species is also observed when the steel surfaces are scratched while being immersed in the Pbnp solution. When the Pbnp-treated steel surfaces are heated to simulate the EP conditions for which Pbnp is used, most of the Pbnp on the oxide-covered surfaces desorbs. In addition, metallic Pb is readily formed on the scratched surfaces and whenever significant amounts of metallic Fe are present. These results point to two possible modes of boundary protection: chemisorbed Pbnp under mild wear conditions and a layer of metallic Pb under severe wear conditions.

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PREFACE

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I. INTRODUCTION

Antiwear and extreme pressure (EP) additives for lubricating hydrocarbon oils have been developed with little understanding of the chemical mechanisms by which they provide protection. For example, EP additives, which reduce friction and limit wear under boundary lubricating conditions (metal-to-metal contact), must provide a low friction or antiwear interface between contacting metal parts in order to be effective. However, little is known about the chemical nature or the development of these interfaces.[1-4] This report endeavors to determine how the EP additive lead naphthenate (Pbnp) protects steel mechanical components, through studies of its adsorption and reaction behavior on steel surfaces with X-ray photoelectron spectroscopy (XPS).

The Pbnp molecule consists of a central Pb ion bonded through the oxygen atoms of a carboxylate group to long carbon chains terminating in cyclopentane rings. The carbon chains have variable length and provide the solubility of the additive in hydrocarbon oils. The mode of Pbnp boundary protection is unknown,[5] although its classification as an EP additive indicates that it works when subjected to harsh conditions of asperity contact and at elevated temperatures. Several possible modes for Pbnp boundary protection can be envisioned: the entire molecule could adsorb to provide a layer of protection, or the molecule could react with the surface in a variety of ways, leaving a partially reacted Pbnp molecule or simply layers of Pb and/or hydrocarbons.

The study of Pbnp chemistry on steel surfaces requires an intimate knowledge of the surface composition of the steel in question. Two different types of steel are studied in this work, AISI 440C stainless steel and 52100 bearing steel. Steel surface composition has been the subject of a significant amount of study[6] and is pursued in this report to gain a detailed understanding of the particular steel samples used in this work. High chromium stainless steels such as 440C are generally believed to exhibit a layered oxide structure on top of the bulk steel, with the surface region rich in chromium relative to the bulk.[6-10] A chromium oxide layer provides protection from further oxidation to give the steel its stainless quality. The surface of 52100 steel, which contains only 1%-2% Cr, should reflect its different bulk chemistry and should not possess a passivating layer of chromium oxide, making the 52100 surface composition more sensitive to its environment.

The chemistry of the Pbnp/steel interface is examined in this work by immersing actual steel coupons into dilute solutions of Pbnp in heptane. The Pbnp is exposed to different components of the steel surface region by chemically removing significant amounts of surface oxides prior to immersion and by scratching the surface during immersion to expose bulk steel. The samples are then introduced into the ultrahigh vacuum (UHV) system and studied with XPS in both the scratched and unscratched regions. The reactivities of both the Pbnp and steel surfaces are further studied as a function of temperature by controlled heating in the vacuum system, followed by XPS analysis. For the most part, the XPS results are discussed qualitatively, with emphasis on binding energy shifts and relative peak intensities.

There are three major goals in this work: (1) to understand the mechanism of Pbnp protection on steel; (2) to determine how Pbnp adsorption and reactivity are controlled by steel surface composition; and (3) to determine if particular chemical treatments enhance the performance of Pbnp by providing specific adsorption and/or reaction sites. If such a treatment is found, then methods for improving the performance of mechanical parts to be lubricated with Pbnp-containing oils may be found.

II. EXPERIMENTAL SECTION

Samples of 440C and 52100 steels were polished in the laboratory ambient with alumina powders down to 0.05 μm grit size, with water as polishing fluid. The samples were stored in a desiccator until needed for experimentation. After being cleaned with ethanol, samples were either mounted for introduction into the UHV system or subjected to chemical treatments. Acid etches were performed with 20% concentrated HCl in ethanol. Alkaline washes were performed with a buffered, commercial basic solution (Alum Etch 34) approximately 15% in deionized water, giving a pH of 12.8. Pure Pbnp is quite viscous and generally unsuitable for introduction into UHV systems. Therefore, solutions of 1% to 2% (weight/volume) of Pbnp (Bardahl) in heptane were prepared for sample treatment, simulating the use of this additive dissolved in hydrocarbon oils.

All sample treatments were performed in the laboratory ambient. Acid etches were carried out for 30 s in an ultrasonic bath followed by ethanol rinses. Alkaline treatments were conducted for periods of 1 h in an ultrasonic bath followed by a brief rinse with deionized water and immersion in ethanol. Samples were exposed to Pbnp by immersion in the Pbnp/heptane solution for 1 min followed by a heptane rinse and immersion in ethanol. During the Pbnp/heptane immersion, a portion of the steel surface (approximately 2 x 2 mm) was scratched with a diamond scribe with sufficient force to plastically deform the steel to a depth of approximately 1-2 μm. The scratching was performed to simulate wear extreme enough to break through the oxide layers and expose the metallic components in the bulk steel. Following all treatments, exposure to the atmosphere was minimized by keeping the samples immersed in ethanol. Prior to introduction into the UHV system, however, the samples were exposed to the atmosphere for periods of approximately 5 min during sample mounting.

The samples were analyzed using XPS with a Surface Science Instruments (SSI) SSX-100 small spot X-ray photoelectron spectrometer housed in a UHV system with a base pressure of less than 1 x 10^{-10} Torr. This instrument, which has been described in detail elsewhere,[11] uses a monochromatized Al Kα source. Instrument parameters used in this study included a 300 μm spot size and a 50 eV spectrometer pass energy. These conditions yield a gold $4f_{7/2}$ peak at 84.0 eV with a full width at half maximum of 0.95 eV. All binding energies given in this work are referenced to the spectrometer Fermi level. For most of the data reported in this work, the sample was oriented with its sample normal 60° from the center of the analyzer input (i. e., a 30° take-off angle). To investigate the oxide layer structure and thickness, the sample was rotated toward the analyzer to increase the effective electron scattering length. XPS sputter profiles were performed with a Leybold-Heraeus IQE 12/38 ion gun run at 2 kV accelerating potential in a rastering mode. The sputter rate was calibrated with a 100 nm thick SiO_2 layer on Si to be 0.43 nm/min. On the Pbnp-treated surfaces, spectra were obtained on both unscratched and scratched regions. The X-ray spot size was much larger than the width of an individual scratch, and spectra represent an average surface composition over several scratches.

Pbnp-treated samples were transferred under UHV to a sample preparation chamber for heating. Sample heating was performed by resistively heating a tungsten filament located behind the sample stage. The temperature was monitored by a chromel/alumel thermocouple in contact with the sample stage. The temperatures reported were those recorded by the thermocouple. However, previous calibration of thermocouple readings at higher temperature with an optical pyrometer showed actual sample surface temperatures to be significantly lower. We estimate our reported temperatures to be 25°-50°C higher than the actual sample temperature. Samples were heated for 30 min at the reported temperatures to ensure that the surface temperature reached a steady state. Pressure increases due to surface desorption were monitored during heating and normally peaked within the first 5 min of heating before gradually declining with time.

III. RESULTS AND ANALYSIS

A. 440C SURFACE COMPOSITION

Figure 1 shows the Fe and Cr $2p_{3/2}$ XPS peaks from a solvent-cleaned polished 440C steel surface as a function of detected electron take-off angle. In both sets of spectra, the sharper, less intense features at lower binding energy (706.7 eV for Fe and 574.1 eV for Cr)[12,13] represent ionization of core electrons from metallic species, while the broader features to higher binding energy are ionizations from surface metal oxides. The centroids of the oxide features, 710.4 eV for Fe and 576.6 eV for Cr, correspond closely to binding energies expected for Fe_2O_3 and Cr_2O_3, respectively.[12,14] Starting from the bottom spectra of Figure 1, the sample was rotated toward the analyzer in 20° increments, increasing the effective electron escape depth, thus allowing greater contributions from bulk species. The metallic peaks of both Fe and Cr become larger, relative to the oxide features, as the electron take-off angle increases from 30° at the bottom to 90° at the top of the figure . Not surprisingly, this confirms that oxide layers are formed on top of the metallic species.

More information regarding the surface composition of 440C was obtained with an XPS sputter profile. The atomic composition of the surface as a function of sputter time is given in Figure 2. The atomic percentages were determined from integrated peak intensities with the SSI software package, which uses atomic subshell photoionization cross sections and relative escape depths based on the photoelectron kinetic energies. The high initial C concentration, with a major peak having a binding energy near 285 eV, shows that the very surface of the sample is contaminated with a layer of hydrocarbons, which is quickly sputtered away. Very distinct regions are evident in the profile, particularly if the total Fe and O atomic concentrations are followed with time. After the first minute when hydrocarbons are removed, the total Fe signal increases with a small slope, while the O signal decreases linearly from 1 to 6 min of sputtering. At the 6 min mark, the slopes of both of these species change dramatically, with the Fe sharply rising and the O sharply declining until the 10 min mark. This behavior indicates that two very distinct oxide species are being sputtered away in these two time frames.

Other important features of the sputter profile are seen in the Cr and C concentration changes with sputtering. The total Cr signal slowly rises during the first 7-8 min of sputtering, then declines through the 11 min mark before stabilizing at about 17%-18% of the total composition. The Cr signal reaches a maximum relative to the Fe signal after 6 min, where the

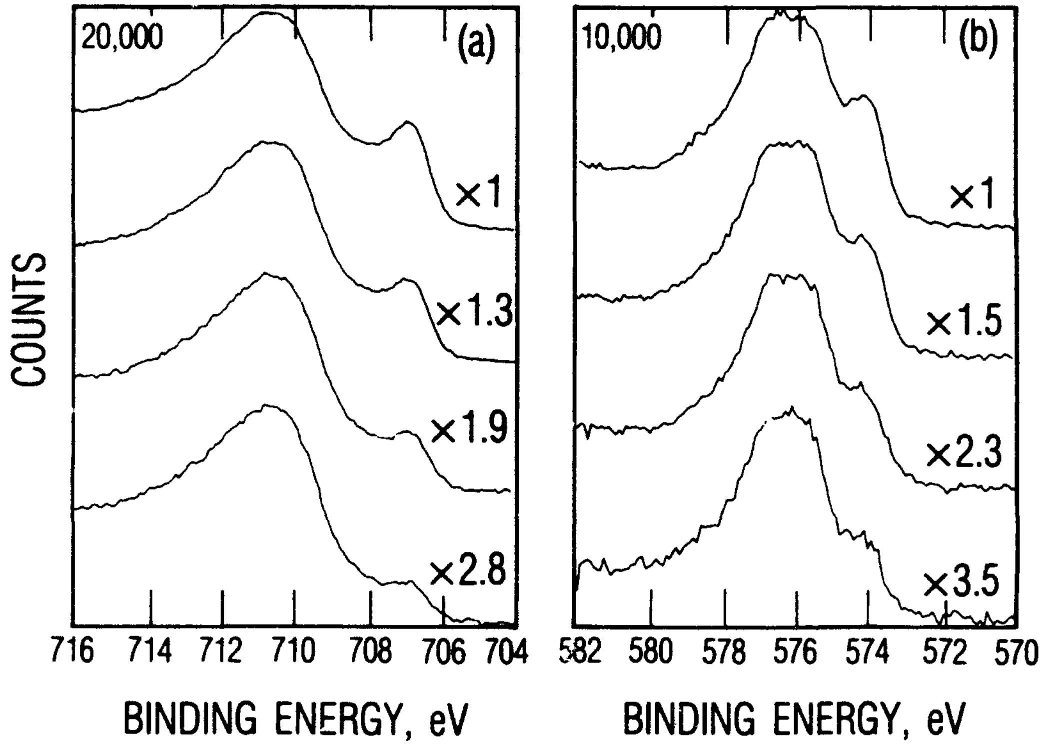

Figure 1. The (a) Fe $2p_{3/2}$ and (b) Cr $2p_{3/2}$ XPS peaks obtained from a 440C steel surface as a function of the detected electron take-off angle. From the bottom, the take-off angles for each set of data are 30°, 50°, 70°, and 90°. The spectral intensities are normalized to the intensity of the higher binding energy oxide features, and the factors by which the spectra were multiplied in the normalization are provided on the figure. The absolute intensities of the spectra are indicated by the total counts in the upper left corner, which indicate a scale of 0 to 20,000 for each spectrum in part (a).

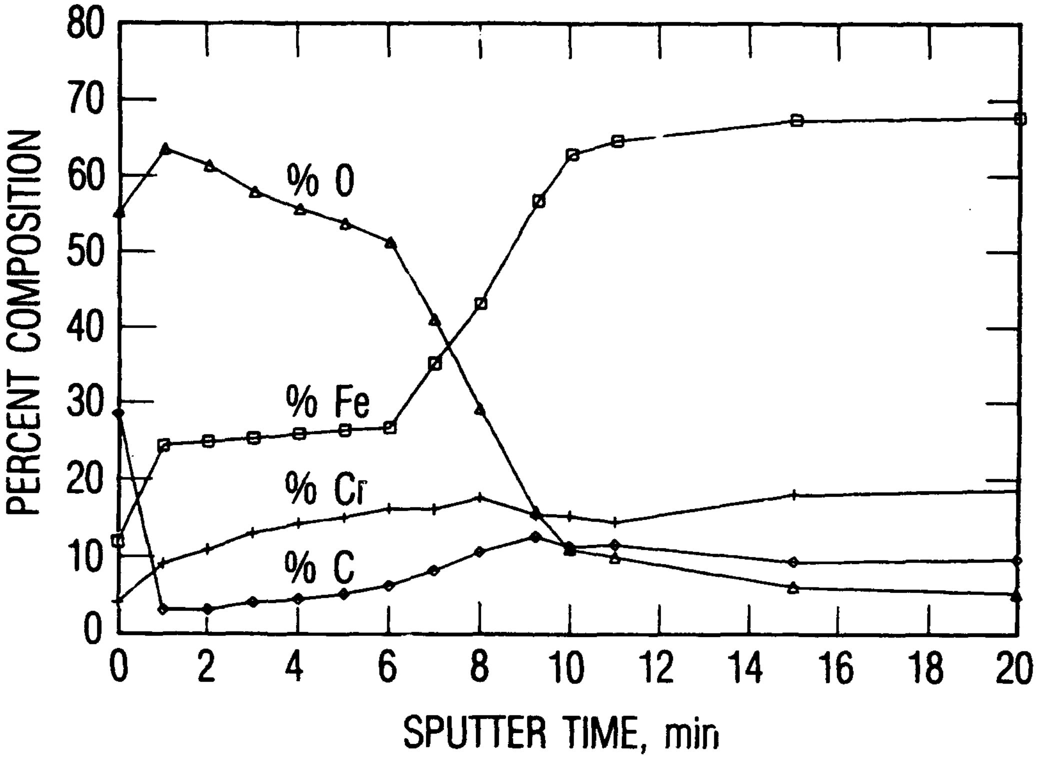

Figure 2. An XPS sputter profile of a 440C surface following solvent cleaning. The total atomic compositions are given, including all species present for each element, assuming a homogeneous distribution.

Fe:Cr atomic ratio is only about 1.7:1 (compared to 2.7:1 after 1 min and 3.9:1 after 20 min). This result shows the surface region (approximately 4.0 nm into the bulk) to be greatly enhanced in Cr relative to the bulk concentration. Segregation of Cr to the surface of high chromium steels is consistent with the literature and with the stainless quality of 440C.[6-10] After the first minute of sputtering, virtually the only C signal detected had a binding energy of 283.5 eV, which is characteristic of surface metal carbides. Note that the C concentration gradually rises through 6 min, increases more sharply from 6 to 9 min, and then gradually declines as the bulk steel is exposed.

Still more insight into the 440C surface structure is gained by closely examining the Fe and Cr $2p_{3/2}$ XPS peaks as a function of sputter time, which are shown in Figure 3. Figure 3 (a) shows the Fe signal at selected times. The important feature in these data is the decrease in iron oxide signal intensity relative to the metal signal early in the sputtering process, with the oxide peak virtually disappearing after 7 min. Conversely, the Cr peaks in Figure 3 (b) show little change in the relative oxide-to-metal signal intensities until the 6 min mark. From 6 to 10 min, the chromium oxide peak intensity decreases, leaving only the lower binding energy signal. These results explain the sputter profile of Figure 2 very well. After the hydrocarbon contaminant is removed, a layer of iron oxide is sputtered away or is chemically reduced. This process causes the significant decrease in the oxygen signal from 1 to 6 min and the increases in all other components due to increased sensitivity to species under the iron oxide overlayer. The possibility of chemical reduction of iron oxide with sputtering is supported by shift of the oxide peak to lower binding energy and by greater increases in the Fe metal signal intensity relative to those observed for the chromium oxide and metal peaks. In fact, pure Fe_2O_3 has been observed to reduce to Fe^{2+} and Fe^0 with Ar^+ sputtering.[15-17] The fact that the relative intensities of the chromium oxide and metal peaks are relatively unaffected by sputtering until the 6 min mark is consistent with a layered structure. After the iron oxide overlayer is removed, a chromium oxide underlayer is sputtered away from 6 to 10 min. This process causes the sharp decrease in the oxygen concentration and the sharp increase in the Fe and metallic Cr concentrations as more bulk steel becomes observable. The carbide concentration is greatest at 9 min, right at the chromium oxide/bulk steel interface. With this information, a picture of the 440C interface region emerges.[6] If the sputter rates of the two oxides are both similar to the SiO_2 sputter calibration rate, then the 440C surface has an iron oxide overlayer 2.6 nm ± 0.3 nm thick on top of a chromium oxide underlayer 1.7 nm ± 0.2 nm thick. Below these oxides is a region of high carbide concentration, with the bulk steel existing under this region.

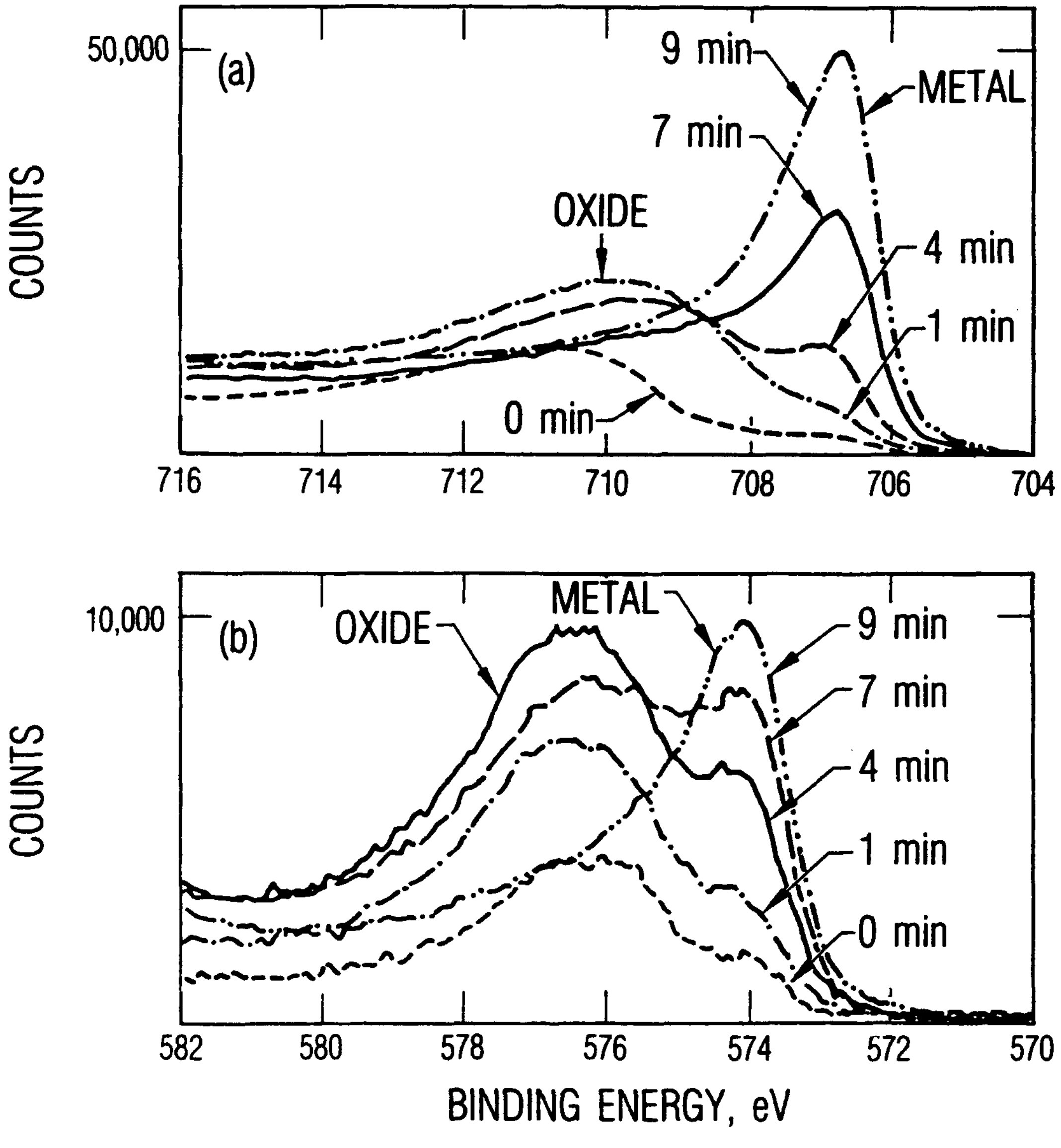

Figure 3. The (a) Fe $2p_{3/2}$ and (b) Cr $2p_{3/2}$ XPS peaks as a function of the sputter times listed on the figure. Note the different scales given for the Fe and Cr spectra, reflecting the differences in peak intensities related to surface concentrations. The oxide and metal peaks are labeled in the figure.

B. EFFECTS OF CHEMICAL TREATMENTS ON 440C

Figure 4 compares the Fe and Cr $2p_{3/2}$ peaks of solvent-cleaned 440C to different 440C coupons treated with the 30 s acid etch and the 1 h alkaline wash. In Figure 4 (a), the Fe peaks of the acid-etched sample (middle spectrum) show a significant decrease in the absolute iron oxide signal, while the Fe metal signal increases slightly relative to untreated 440C (top spectrum). Conversely, the Cr peaks in Figure 4 (b) show that the 30 s acid etch had little effect on the chromium oxide underlayer. Quantitative analysis of the relative amounts of Fe and Cr-- including both metal and oxides--present on the acid-etched surface (similar to the sputter profile procedure) give an Fe:Cr ratio of 1.25:1, a value lower than observed at any point in the sputter profile. Untreated 440C gave a range of Fe:Cr ratios, but usually close to 2.5:1. Surface Cr enrichment following acid treatments has been observed previously.[18,19] The Fe and Cr XPS results for the alkaline wash are given at the bottom of Figures 4 (a) and (b), and show a similar trend as the acid etch, in this case producing an Fe:Cr ratio of 1.32. Both treatments, therefore, appear to selectively remove iron oxide, while leaving the chromium oxide layer virtually unaffected.

The remaining iron oxide signal after both treatments is shifted to lower binding energy compared to the Fe_2O_3 on untreated 440C, suggesting the presence of intermediate oxides on the treated surfaces. The fact that some iron oxide is still detectable after both treatments could be attributed to several possibilities, including a heterogeneous surface structure due to incomplete removal of the iron oxide, a mixed iron-chromium oxide interfacial compound, or re-oxidation of some metallic Fe. When these surfaces are sputtered, both the iron and chromium oxide signals decrease very early in the sputtering process, indicating that both species are quite near the surface. Finally, previous work[20] has shown that etching 440C with acid of this concentration is difficult to control quantitatively; if exposed to the acid for too long, the steel sample is roughened and pitted, resulting in an increase in surface iron oxide, which forms as bulk steel is being exposed.

Other changes in the 440C surface chemical composition are also likely to occur with sample treatment. One might expect the surface to have more adsorbed hydrogen after the acid treatment, but this is impossible to determine with XPS. Conversely, the alkaline wash should tend to leave hydroxyl species on the steel surface, a phenomenon that can be explored by examining the oxygen 1s XPS signal. Typically, 440C surfaces cleaned in ethanol display two oxygen peaks with binding energies of 530.0 and 531.5 eV. The O 1s peaks of Fe_2O_3 (530.0) and Cr_2O_3 (530.2) overlap and produce the feature near 530.0 eV.[12] The 531.5 eV peak is quickly removed by sputtering and is attributed to adsorbed contaminants, probably ethanol.

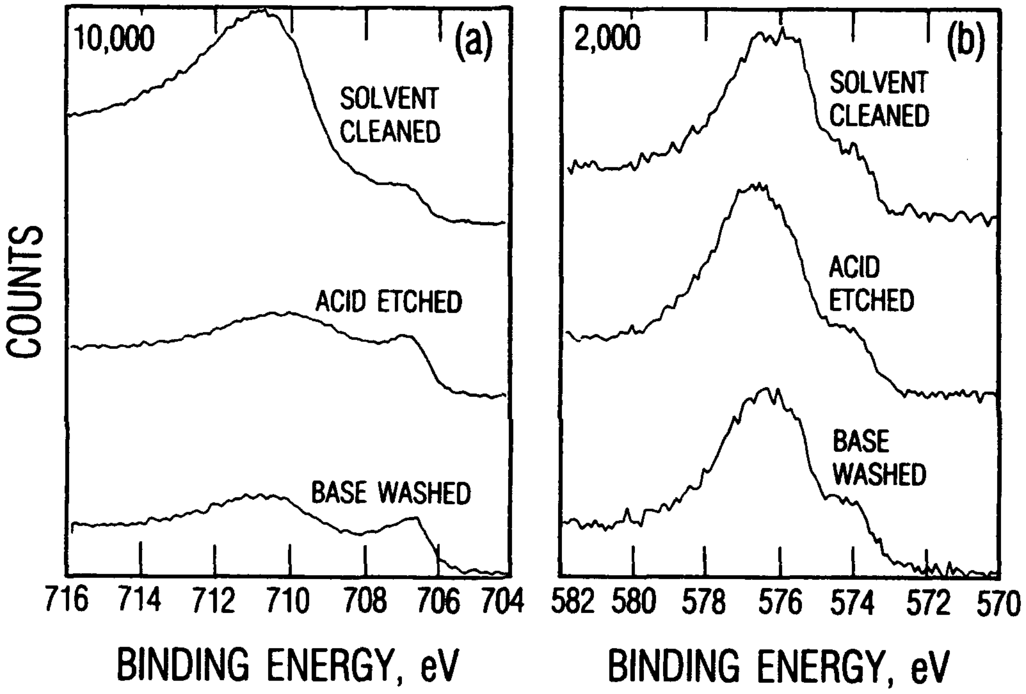

Figure 4. The (a) Fe $2p_{3/2}$ and (b) Cr $2p_{3/2}$ XPS peaks from different 440C surfaces as a function of sample treatment. The top spectra are from untreated 440C, the middle spectra were obtained from a sample following a 30 s acid etch, and the bottom spectra were obtained from a 440C surface following a 1 h alkaline wash.

Following treatment with the alkaline wash, a third peak was always observed near 533.0 eV, a binding energy consistent with the presence of adsorbed water.[21] Metal hydroxides are generally observed to have O 1s binding energies ranging from 531 to 532 eV[14,22] and could contribute to the peak near 531.5 eV on this sample.

C. Pbnp ADSORPTION ON 440C

Figure 5 compares (a) the Pb 4f peaks and (b) the C 1s peaks for several different 440C surfaces after immersion in the Pbnp/heptane solution. In the unscratched area of a solvent-cleaned sample [labeled spectrum (1)], the spin-orbit split Pb 4f peaks are rather broad singlets with the Pb $4f_{7/2}$ peak centered at a binding energy of 139.2 eV. The Pb binding energy is similar to that expected for Pb(II) compounds[5,23] and has been assigned in a previous study as molecular Pbnp.[5] The C 1s spectrum at the top of Figure 5 (b) is rather complex, showing a weak carbide feature at 283.5 eV, strong hydrocarbon-related features near 285 and 286 eV,[12] and a significant peak near 289 eV. The 289 eV C peak is near the expected binding energy for a carboxylate species,[24] lending support to the above assignment of the Pb peaks as unreacted Pbnp. Therefore, the 139.2 eV Pb $4f_{7/2}$ binding energy and the existence of a strong carboxylate peak will be used diagnostically to indicate unreacted physisorbed Pbnp. Several of these samples were studied, with similar results to those reported here. The Fe:Cr ratios for these surfaces are given in Table 1, which shows the unscratched areas to have values ranging from 2.48 to 2.64.

The Pb and C peaks obtained in the scratched region of the same solvent-cleaned 440C surface are spectra (2) in Figure 5 and show important differences when compared to the data obtained on the unscratched area. First, in the data from the scratched region, the Pb peaks are shifted to lower binding energy by 0.3 to 0.4 eV relative to the unscratched area. Second, very weak Pb features were usually observed near 136.6 eV on scratched surfaces. Third, the carboxylate C peak in Figure 5 (b) has a much lower intensity relative to both the other carbon species present and to the Pb signal in the scratched region.

Figure 5 also shows the Pb and C peaks from the unscratched area of Pbnp-treated 440C samples that were pretreated with the acidic [spectra (3)] and basic [spectra (4)] solutions. In the spectra from the unscratched regions of these surfaces in Figure 5 (a), the Pb peaks on both the acid- and base-treated surfaces are shifted to lower binding energy by ~0.3 eV relative to the solvent-cleaned sample. This shift is similar to that observed on the scratched versus unscratched regions of the solvent-cleaned 440C surfaces. In addition, the carboxylate C peaks in Figure 5 (b)

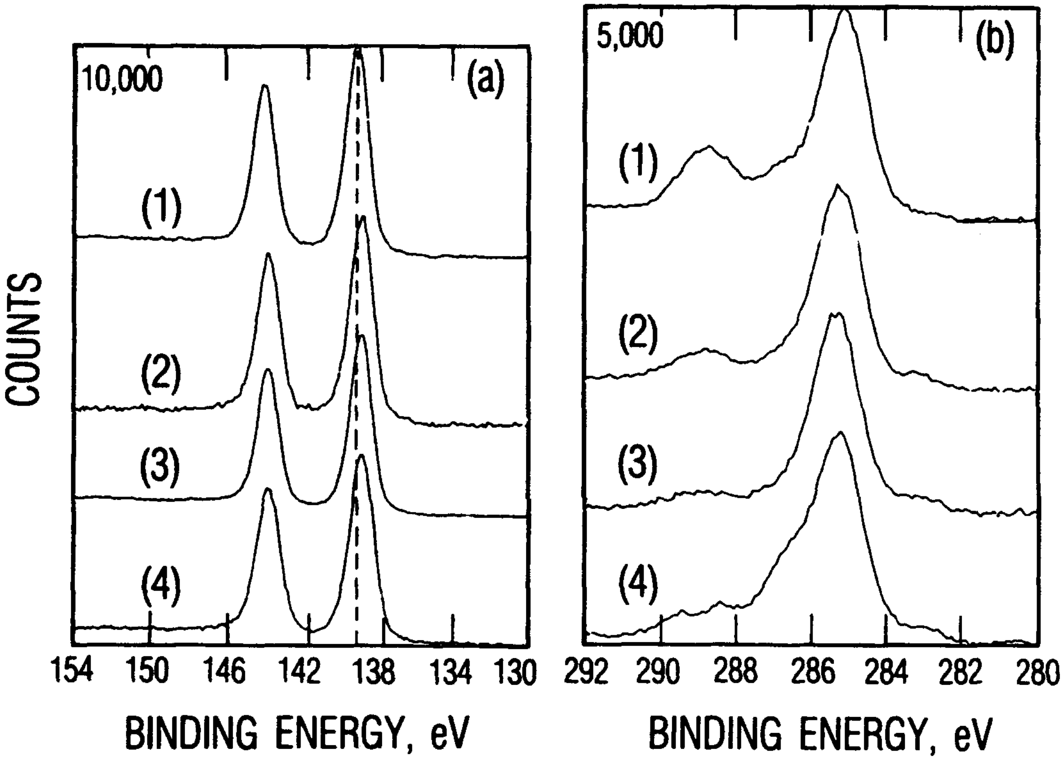

Figure 5. The (a) Pb 4f and (b) C 1s XPS peaks obtained from several differently pretreated 440 C samples after exposure to the Pbnp/heptane solution. The sample treatments were: (1) solvent-cleaned, unscratched; (2) solvent-cleaned, scratched; (3) acid-etched, unscratched; and (4) base-washed, unscratched. The top two sets of spectra were obtained from different areas of the same sample. The dashed line indicates the binding energy position of the Pb $4f_{7/2}$ peak on the unscratched, solvent-cleaned sample.

Table 1. The Fe/Cr atomic concentration ratios for all 440C surfaces treated with Pbnp. The ratios are given for scratched and unscratched areas as a function of sample pretreatment and temperature. Dashed lines indicate the sample was not subjected to the particular treatment.

Pre-treatment	Solvent Cleaned	25° C	250° C	350° C	450° C
Sample 1					
	unscratched	2.48	----	1.60	1.09
	scratched	4.52	----	2.12	1.18
Sample 2					
	unscratched	2.64	1.51(300°C)	1.50	0.89
	scratched	3.54	2.87(300°C)	2.59	1.28
Sample 3					
	unscratched	2.53	2.76	1.99	1.25
	scratched	3.88	3.18	2.08	1.44
Acid Etched					
Sample 1					
	unscratched	1.84	----	1.59	1.40
	scratched	3.85	----	1.56	1.00
Sample 2					
	unscratched	1.51	1.91	1.74	1.59
	scratched	3.21	3.24	2.76	2.14
Base Treated					
Sample 1					
	unscratched	1.06	1.11	0.63	0.34
	scratched	3.85	2.66	1.40	0.70
Sample 2					
	unscratched	1.09	1.11	1.02	0.46
	scratched	3.33	2.76	2.28	1.02
Sample 3					
	unscratched	1.38	1.63	1.50	1.17
	scratched	3.17	2.95	2.53	1.52

are weaker relative to both the hydrocarbon C signal and the Pb peaks on both of the pretreated surfaces. In particular, the acid-pretreated surface has very little carboxylate intensity. The C 1s spectrum also has a different shape on the alkaline-treated surface [Figure 5 (b) (4)], appearing to have a second high binding energy feature near 288 eV and a stronger peak near 286.5 eV. These peaks indicate the presence of C bonded to a more highly electronegative species (most likely oxygen) and could result from the interaction of the naphthenate chain with surface hydroxyls. The peaks are shifted to lower binding energy from the carboxylate carbon peak, which is a carbon bonded to two oxygen atoms.

The Pb and C peaks obtained from the scratched regions of the acid- and base-treated surfaces were very similar to the scratched surface for the solvent-cleaned 440C, although the binding energy of the Pb peaks and the carboxylate C intensity do vary with sample treatment. In general, the Pb $4f_{7/2}$ peak for all surfaces studied at room temperature was observed to range between 139.2 and 138.8 eV, excluding the small metallic peaks sometimes observed. The varying Pb binding energy and varying carboxylate peak intensity suggest that there are at least two forms of Pbnp present on all of the surfaces, unreacted Pbnp and a reacted chemisorbed form. The carboxylate peak seems weakest on both the scratched and unscratched areas of the acid-treated surface, indicating more complete breakdown of the Pbnp molecule on the acidified surface.

The Pb binding energy shifts and loss of carboxylate peak intensity indicate that most of the Pbnp has undergone some surface reaction in the scratched regions of all samples and on the unscratched regions of the pretreated samples. A very small amount of Pb is in a metallic-like state, as indicated by the small signal near 136.6 eV on scratched surfaces. However, most of the Pbnp is undergoing a more subtle change on the reactive surfaces. The nature of this reaction can be inferred from the binding energy of the Pb peak and the loss of carboxylate carbons. The Pb $4f_{7/2}$ binding energy of 138.8 eV is not consistent with any known forms of lead oxide (PbO: 137.4-138.2 eV; Pb_3O_4: 137.5-138.4 eV; PbO_2: 137.0-137.6 eV). However, this binding energy certainly indicates that Pb is in an oxidized state (Pb metal: 136.5 eV) and is generally in the range associated with Pb (II).[5,12] Coupled with the absence of carboxylate intensity, this Pb binding energy implies that the Pbnp has reacted with the scratched and pretreated surfaces by breaking the naphthenate C-O bonds, leaving behind an oxidized form of Pb and a hydrocarbon chain. The remaining carboxylate intensity could indicate that the reaction is simply the loss of one of the naphthenate chains from the molecule or that incomplete reaction of all surface Pbnp has occurred (perhaps due to insufficient numbers of active sites). Since the molecule may not be completely broken down, this form will be designated as reacted or chemisorbed Pbnp. The scratched 440C samples showing this behavior had Fe:Cr ratios of 3.5 to 4.5, indicating a significant increase in the amount of surface iron available to react with Pbnp. Table 1 shows that all pretreated surfaces were depleted in iron, with the acid-etched Fe:Cr ratios of 1.5-1.8 and the base-washed samples typically having ratios of 1.1 to 1.4. On both types of pretreated surfaces, the iron oxide features are much smaller than on the solvent-cleaned surface peaks, as expected from earlier results reported here.

D. TEMPERATURE EFFECTS ON Pbnp/440C

1. Pbnp Chemistry

On annealing in UHV to temperatures similar to (if not lower than) flash temperatures expected during metal-to-metal asperity contact during wear, the steel substrates, surface Pbnp, and other compounds present undergo surface dependent reactions. Figure 6 shows the (a) Pb, (b) C, (c) Fe, and (d) Cr XPS peaks on unscratched, solvent-cleaned 440C as a function of temperature. These data are from sample 3, as listed in Table 1, with an initial Fe:Cr ratio of 2.53. With respect to the Pbnp-related features, the Pb and C peaks show significant changes on heating. Heating to 250°C causes little change, except for small decreases in the Pb and hydrocarbon peak intensities. The carboxylate peak remains strong. On annealing to 350°C, the intensity of the Pb features decreased by more than a factor of 2, and the remaining Pbnp peaks shifted to lower binding energy by 0.3 eV relative to the room temperature data, indicating the presence of chemisorbed Pbnp. In addition, a very small Pb peak was often observed at 136.5 eV, near the binding energy of metallic Pb. Concurrently, the C 1s peaks undergo changes as the carboxylate peak intensity decreases along with the hydrocarbon peak. On heating to 450°C, virtually all of the Pb has been removed with small, but still observable, features remaining in both the metallic Pb and reacted Pbnp positions. Finally, the C 1s peak continued the changes described above, with the carboxylate species virtually eliminated and the hydrocarbon peak decreasing as well. The changes occurring in the steel Fe and Cr peaks of Figure 6 (c) and (d) will be discussed below.

Pbnp had much different high temperature reactivity on the unscratched, acid-etched surface than on the solvent-cleaned 440C surface, as demonstrated by the Pb spectra in Figure 7 (a). The Pb peaks lose intensity upon annealing to 250° C but also shift a large component to a metallic-like species with a binding energy of 136.7 eV. The carboxylate peak intensity, which was already quite small before heating this surface, decreases greatly after the first heating. These changes continue as the heating temperature is increased to 350°C. After annealing to 450°C, even more Pb signal intensity is lost, from both the reacted Pbnp region and from the metallic-like lead

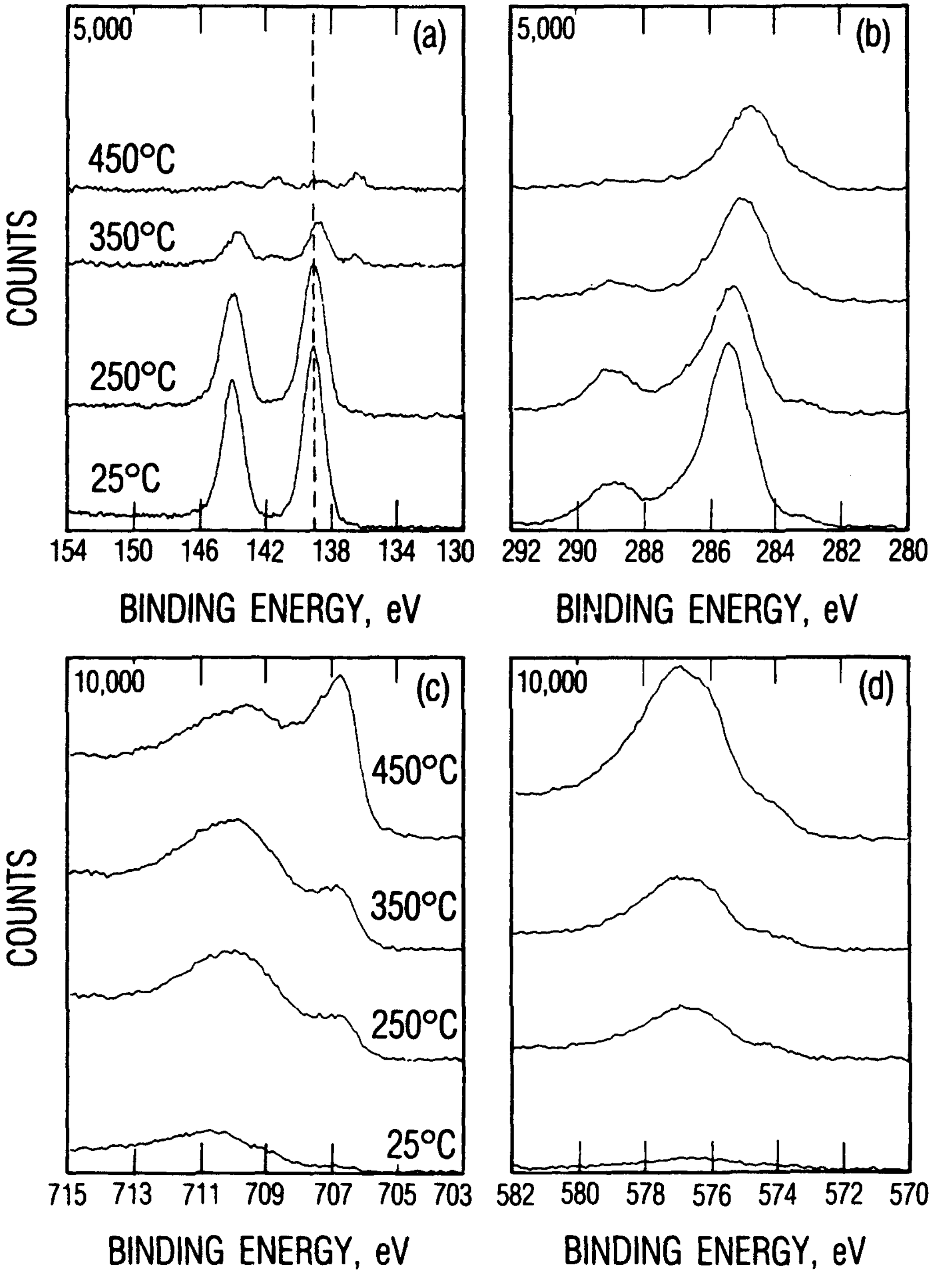

Figure 6. The (a) Pb 4f, (b) C 1s, (c) Fe $2p_{3/2}$, and (d) Cr $2p_{3/2}$ XPS peaks from the unscratched area of a solvent-cleaned 440C surface following Pbnp treatment as a function of sample heating temperature. The temperatures are listed in parts (a) and (c) of the figure.

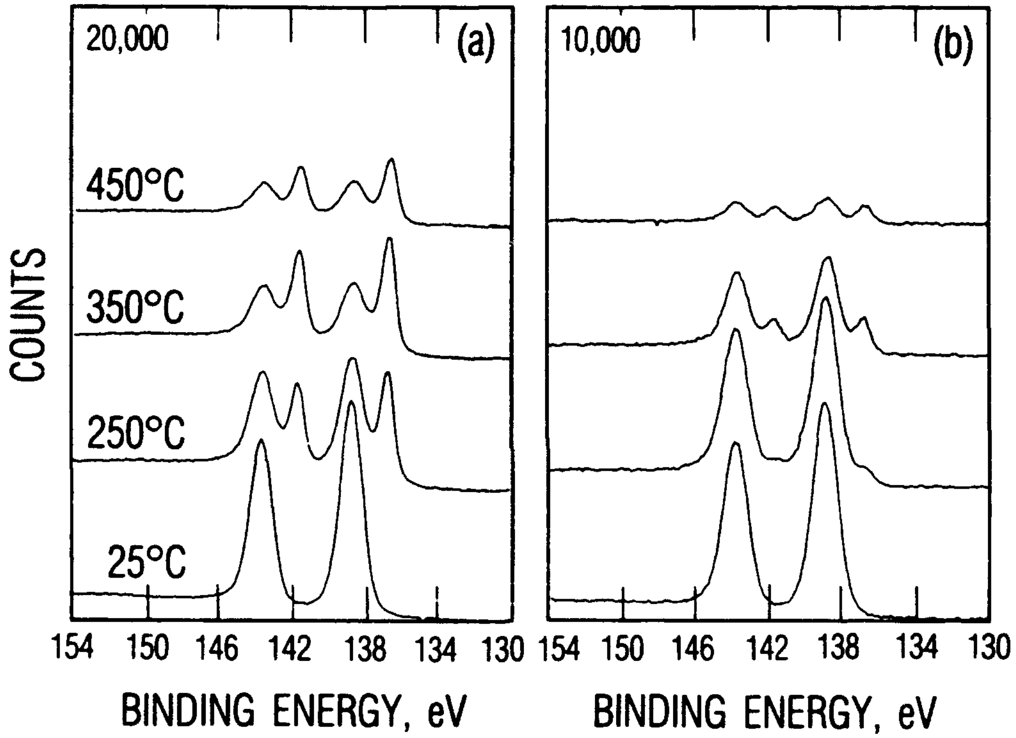

Figure 7. The Pb 4f XPS peaks from the unscratched areas of (a) an acid-etched 440C surface and (b) a base-washed 440C surface following Pbnp treatment and heating to the temperatures listed in part (a) of the figure.

region. But, unlike any other unscratched 440C surface, a large amount of metallic Pb remains after the high temperature treatment. In addition, some Pb signal near 138.8 eV remains, indicating this chemisorbed species to be strongly bound to the surface. The data presented here are for acid-etched sample 2, with an initial Fe:Cr ratio of 1.51. The other acid-etched sample studied had an initial Fe:Cr ratio of almost 2.0 and retained only metallic Pb after the 450°C heating. It should be noted that the remaining Pb signal is still fairly strong but looks small relative to the initial Pb peak which was unusually large for these surfaces. Finally, the C 1s peaks behave as expected for the Pb chemistry just outlined. The carboxylate C decreases along with the Pbnp species and disappears when metallic Pb is the only species (i.e., in sample 1 in Table 1).

Pbnp reactivity on the unscratched, alkaline-treated 440C surfaces is demonstrated in Figure 7 (b). Before heating, the unscratched area had a very small carboxylate carbon signal and a Pb $4f_{7/2}$ BE of 138.8 eV, quite similar to the unscratched, acid-etched surface. As shown in Figure 7 (b), heating to 250°C causes a small loss of Pb intensity along with the formation of some metallic Pb. A larger drop in Pb intensity is observed after annealing to 350°C, and much of the Pb signal is gone after the 450°C anneal, with small amounts of chemisorbed Pbnp and metallic Pb remaining. The Pbnp changes for this surface, having an initial Fe:Cr ratio of ~1.4, were very similar to the solvent-cleaned 440C surface, although more total Pb remained on the alkaline-washed surface. For samples with lower initial Fe:Cr ratios (~1.1), however, most of the Pb signal disappears with heating, and in some cases, all Pb signal is lost after the 350°C treatment. Most important, no significant amounts of metallic Pb formed on the unscratched areas of the low Fe, alkaline-treated 440C surface (alkaline-washed samples 1 and 2 in Table 1) at any time or temperature.

In general, all scratched 440C surfaces showed essentially the same high temperature Pbnp reactivity regardless of pretreatment, which is reasonable because the scratches penetrate deeper into the surface than the chemical treatments. The reactivity on the scratched area of a solvent-cleaned sample is shown in Figure 8. Initially, the Pb peaks on the scratched surface are shifted by 0.4 eV to lower binding energy, and the intensity of the carboxylate C has decreased by a factor of approximately 2 relative to unscratched 440C. In Figure 8 (a), the Pb peaks lose some intensity on annealing to 250°C, but more important, a significant amount of intensity shifts to a new peak with a binding energy of 136.6 eV, indicative of metallic Pb. Concurrently, the carboxylate C peak intensity decreases. The C peak corresponding to hydrocarbons near 285 eV has also lost intensity. These changes continue with increasing temperature, as shown in Figure 8 (a) and (b). On annealing to 450°C, only a very small amount of Pb is present with a binding

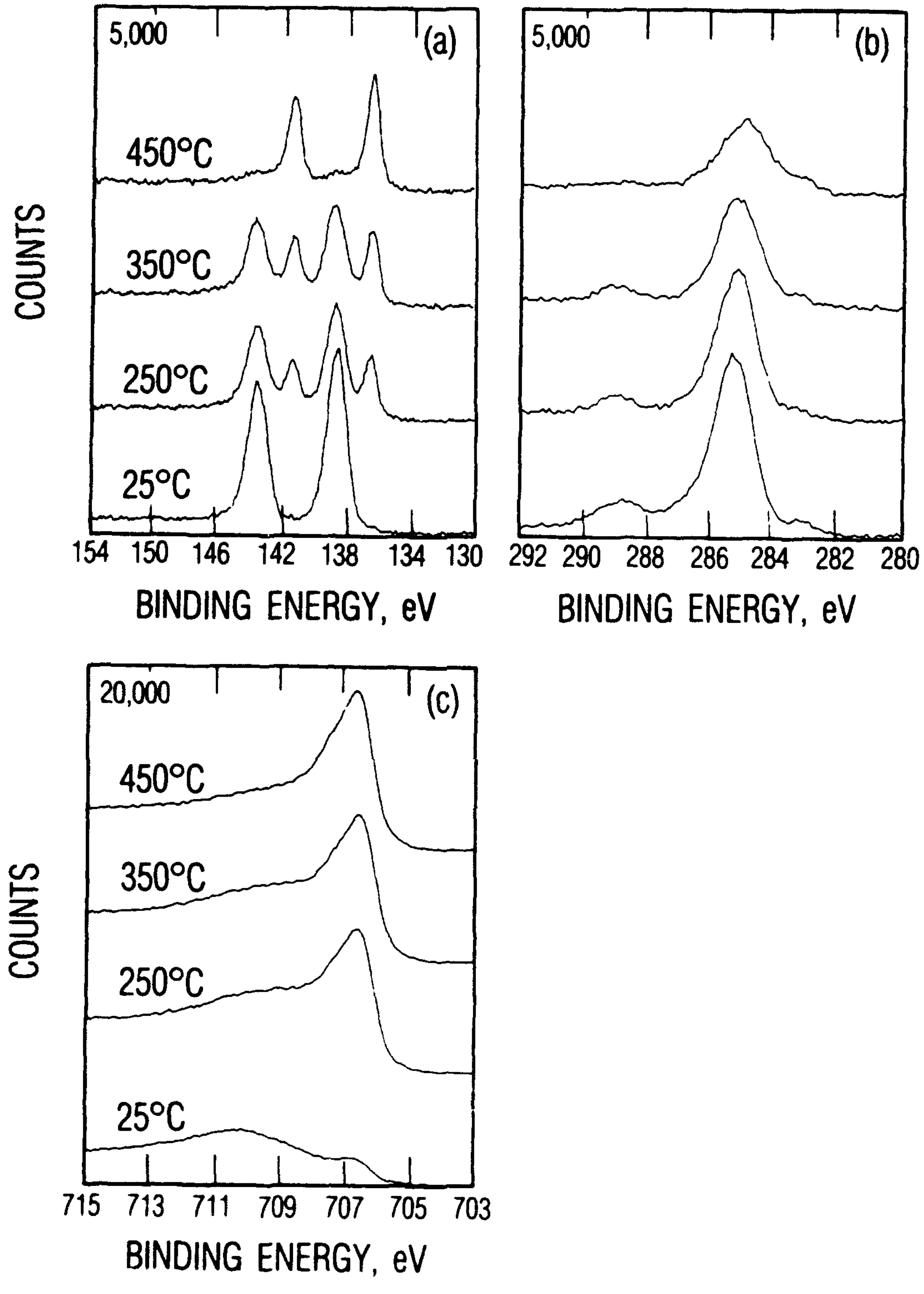

Figure 8. The (a) Pb 4f, (b) C 1s, and (c) Fe $2p_{3/2}$ XPS peaks from the scratched region of a solvent-cleaned 440C surfaces following Pbnp treatment as a function of sample heating temperature. The temperatures are given in parts (a) and (c).

energy of 138.8 eV, while the metallic Pb peak is quite strong, retaining more of the original Pb intensity than any of the unscratched 440C surfaces. In addition, any traces of the carboxylate C peak have vanished, and the hydrocarbon peak is much weaker than observed on the unscratched region of the same sample.

2. Steel Substrate Chemistry

While the Pbnp is undergoing temperature dependent reactions, the surface compositions of the 440C substrates are also changing significantly. The trends of the changes are generally independent of sample pretreatment, but samples do differ in the extent of the changes observed. These changes are evident in the Fe and Cr XPS peaks of Figures 6 (c) and (d) and 8 (c), and in the Fe:Cr ratios in Table 1. On heating to 250°C, small changes are observed in the Fe and Cr peaks on the unscratched, solvent-cleaned surface in Figure 6. These changes include intensity increases in the Fe and Cr peaks due to the thermal desorption of some surface species and a small decrease in the amount of iron oxide present relative to the metallic Fe signal. More significant changes are observed on the scratched surface in Figure 8 (c) after the 250° C heating, where more iron oxide signal intensity is lost relative to the metal. At higher temperatures, two distinct phenomena are evident on all surfaces: the Fe:Cr ratios decrease (Table 1), and the ratio of metallic Fe to the iron oxide increases. The Cr 2p peaks grow in intensity throughout these temperature changes, but very little significant change in the chemical nature of the surface Cr is observed; i.e., the dominant species is always Cr oxide. On some surfaces, the intensity of the chromium oxide peaks increases as the iron oxide loses intensity, perhaps indicating the more thermodynamically stable Cr_2O_3 is being formed from Fe_2O_3 and Cr metal.[25]

The extent of the changes in the 440C surface composition varies with the unscratched surface studied. This variation may be related to inconsistent sample mounting, resulting in varying levels of thermal contact of samples with their sample holders, in addition to actual differences in surface reactivity. However, some trends are evident in the steel surface composition and the reactivity of Pbnp on these surfaces. The two base-treated samples with very small initial Fe:Cr ratios had the smallest Fe:Cr ratios following the 450°C heating and also retained virtually no Pb in any form. Conversely, the acid-treated surfaces had much more surface Fe following the heat treatments and also retained significant amounts of Pb, primarily in the metallic state. Surfaces with intermediate Fe:Cr ratios following the 450°C heating also showed intermediate Pbnp reactivity, retaining some Pbnp and some metallic Pb, while generally experiencing incomplete loss of surface iron oxide species. In general, the presence of any remaining Pbnp-like species at 138.8 eV seemed to correlate with the presence of remaining iron oxides. Finally, the scratched regions of virtually all surfaces had more Fe present following heating than did the unscratched areas, generally displayed more complete loss of iron oxide at lower temperatures, and retained more Pb in a metallic form. These results point to a strong correlation between the formation of metallic Pb from chemisorbed Pbnp and the presence of metallic Fe.

E. 52100 STEEL SURFACE COMPOSITION

The surface chemical composition of 52100 steel reflects the differences in the bulk chemistry of this material relative to 440C stainless steel. The most notable difference is the lack of significant amounts of chromium.[26] Under the layer of hydrocarbon contamination, the 52100 surface is composed mostly of iron oxide, the thickness of which is highly dependent on sample handling. Comparison of the relative intensity of the iron oxide XPS signal to that of the iron metal signal (calibrated by the measurements on 440C) allows an estimate of the 52100 oxide thickness to be made. Our solvent-cleaned 52100 samples displayed a slightly larger metallic iron peak relative to the oxide peak than our 440C samples, giving an upper limit of ~4.0 nm thick iron oxide layer, approximately the total thickness of both the iron and chromium oxide layers on 440C. It should be emphasized that this oxide thickness is specific to our sample handling and should not be considered universal for 52100 steel. Small amounts of chromium (both oxide and metal) and carbon (as carbide) were also observed near the surface; however, it is clear that the chemistry of the iron oxide overlayer should dominate the surface chemistry of 52100 steel.

Similar chemical treatments as those described earlier for 440C were performed on 52100. Acid etches with HCl/ethanol for varying time periods were explored with a simple result: an acid etch for any period of time caused the iron oxide layer to grow thicker, indicating that corrosion of the surface was occurring. This result emphasizes the unique reactivity of stainless steels due to the chromium oxide underlayer. Further acid-etching experiments were not pursued on 52100, after this finding. The alkaline washes, however, appear to remove the iron oxide overlayer on 52100, as evidenced by a significant decrease in the relative intensity of the iron oxide XPS signal. It is not known how effective the oxide removal was, as the samples were exposed to laboratory air for approximately 5 min during preparation for introduction into the UHV system and could have re-oxidized.

F. Pbnp ADSORPTION ON 52100 STEEL

At room temperature, the chemistry of Pbnp on solvent-cleaned 52100 steel was very similar to that described above for 440C. Specifically, the XPS results at the bottom of Figure 9 (a) and (b) show a high binding energy form of Pb (139.1 eV) and a very strong carboxylate carbon peak near 289 eV [Figure 9 (b)] on unscratched 52100 steel following solvent cleaning, indicative of physisorbed Pbnp. The carboxylate peak on this surface was the strongest observed on any surface, which may indicate that this surface was the most inert with regard to Pbnp chemisorption at room temperature. On scratched 52100, the Pb peaks are shifted to lower binding energy by roughly 0.3-0.4 eV, and the carboxylate carbon peak is much weaker. This similarity of room temperature Pbnp interactions on the two steels is logical, as the Pbnp is interacting with iron oxide in the unscratched regions and primarily with metallic iron in scratched regions of both samples.

Following a 1 h wash in the alkaline solution, the unscratched 52100 steel area again showed a Pb peak shifted to lower binding energy by 0.3 eV relative to the solvent-cleaned 52100 surface. In addition, the carboxylate C intensity was much lower than observed on the solvent-cleaned 52100 surface, and the peak was shifted to ~ 288.2 eV, which supports the earlier observations of such species on the alkaline-washed 440C surface. Nearly identical results were obtained on the scratched area of alkaline-washed 52100. These results suggest that the base treatment followed by immediate immersion into the Pbnp/heptane allows the Pbnp to interact with a significant amount of metallic iron or at least provides sites with which the Pbnp molecule can chemisorb and react.

G. TEMPERATURE EFFECTS ON Pbnp/52100

Figure 9 also presents Pb 4f and C 1s XPS results for the temperature treatments for Pbnp adsorbed on solvent-cleaned 52100 steel. The general reactivity of the Pbnp observed is similar to Pbnp/440C, with the Pb 4f peaks both shifting to lower binding energy, to positions assigned earlier as chemisorbed Pbnp and metallic Pb, accompanied by the loss of surface carboxylate species and hydrocarbon desorption [Figure 9 (b)]. There are, however, several important differences for 52100 compared to 440C. As shown in Figure 9 (a), significant amounts of metallic Pb are formed on solvent-cleaned, unscratched 52100 surfaces as the temperature is increased. Much of the Pb present on the solvent-cleaned 52100 desorbs on heating to 250 and 350°C; however, metallic Pb is formed at 350°C, and the reaction is complete at 450°C.

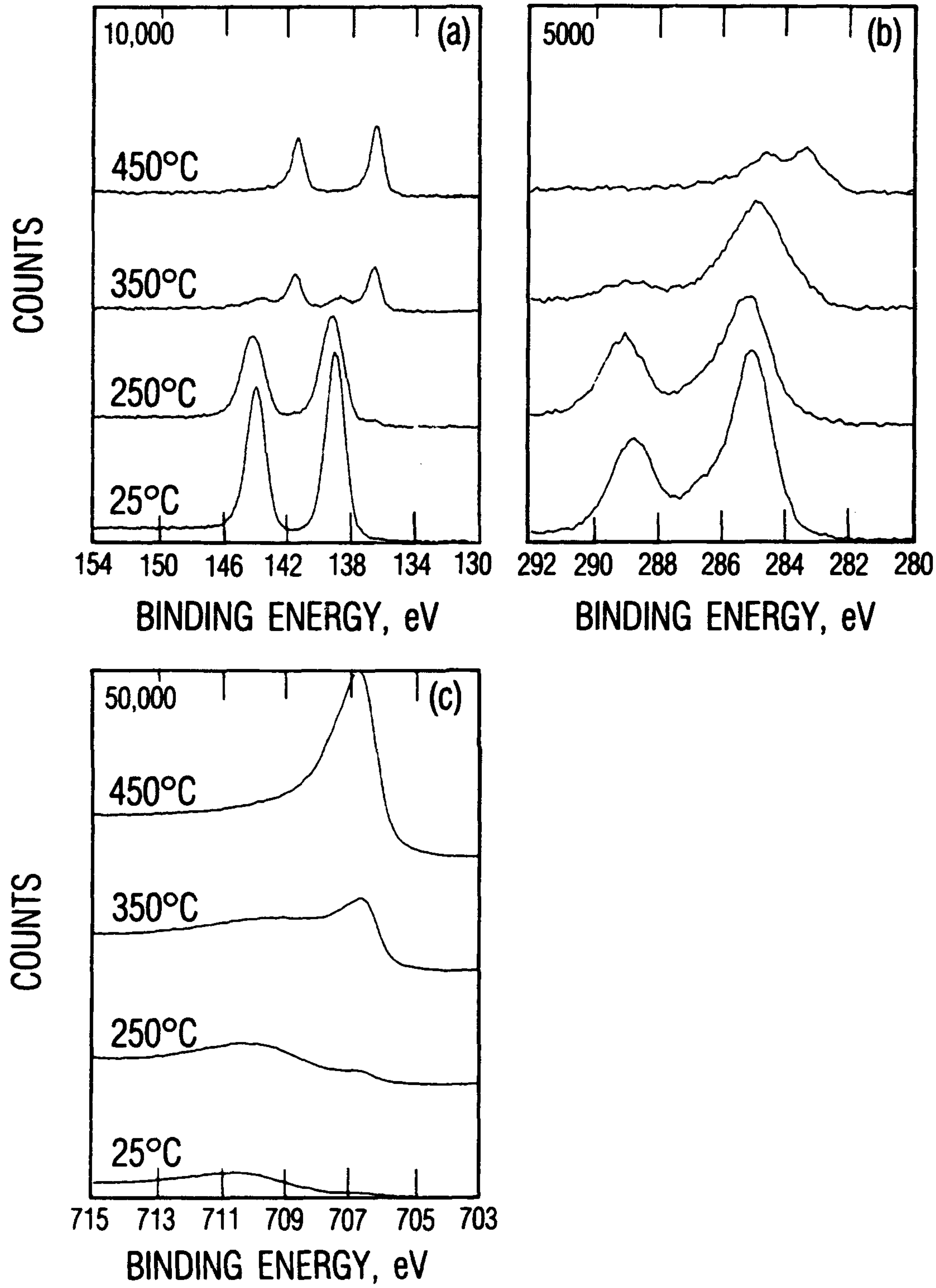

Figure 9. The (a) Pb 4f, (b) C 1s, and (c) Fe $2p_{3/2}$ XPS peaks obtained from the unscratched region of a solvent-cleaned, Pbnp-treated 52100 steel surface after heating to the temperatures listed in parts (a) and (c) of the figure.

Simultaneously, the carboxylate and hydrocarbon peak intensities drop dramatically relative to a carbide peak near 283.5 eV [Figure 9(b)]. A strong carboxylate peak remains after heating to 250°C but decreases greatly after the 350°C treatment.

Figure 10 (a) compares the Pb peaks of the scratched 52100 surface (middle spectrum) to the unscratched area (bottom spectrum) after heating to 250°C. The scratched area of the solvent-cleaned 52100 surface was quite reactive, with a significant amount of metallic Pb forming at 250°C and the C peaks behaving as expected, again retaining a strong carbide feature. The reaction to metallic Pb was observed to be virtually complete after the 350°C heating. Most of Pb initially present on the scratched surface as chemisorbed Pbnp before heating was retained after heating as metallic Pb (i.e., very little desorption of Pb compounds occurred).

The base-treated 52100 surface proved to be the most reactive unscratched surface studied, as shown in Figure 10 (a). Metallic Pb formed on both the unscratched and scratched areas of this sample at 250°C, with only a very small amount of unreacted material remaining (only the unscratched region is shown). At 350°C, the reaction to metallic Pb seems to be almost complete, along with the desorption of hydrocarbons. It is apparent, therefore, that the Pbnp reacts with 52100 surfaces under all the conditions tested and that this reaction occurs more completely and at a lower temperature than on a similarly treated sample of 440C.

An examination of the reactivity of the 52100 steel substrate as a function of sample treatment does much to clarify the Pbnp reactivity results just discussed. The changes in the Fe $2p_{3/2}$ peak of Pbnp solvent-cleaned 52100 following heat treatments are shown in Figure 9 (c). These data show more complete reaction to metallic iron at lower temperatures than observed on 440C. The Fe $2p_{3/2}$ peak of the various 52100 surfaces studied after the 250°C heating are shown in Figure 10 (b). The emergence of metallic iron and the concurrent loss of iron oxide is evident on all surfaces. The data show, however, that the tendency for 52100 to form metallic iron on heating depends strongly on the surface treatment and may depend on the thickness of the oxide layer before heating. In Figure 10 (b), the solvent-cleaned, unscratched surface shows little conversion to metallic Fe at 250°C, and complete conversion is not achieved until heating to 450°C [Figure 9 (c)]. In the scratched region of this sample, the Fe metal peak intensity increases significantly on heating to 250°C, and the reaction is virtually complete following the 350°C treatment. These results should be compared to the Pbnp reactivity just discussed. On the unscratched, untreated 52100 surface, metallic Pb was formed only during the 350°C anneal, with much of the Pbnp simply desorbing at 250°C. In contrast, the scratched area formed some metallic Pb at 250°C, with almost complete conversion at 350°C. The reduction of Pbnp to metallic Pb,

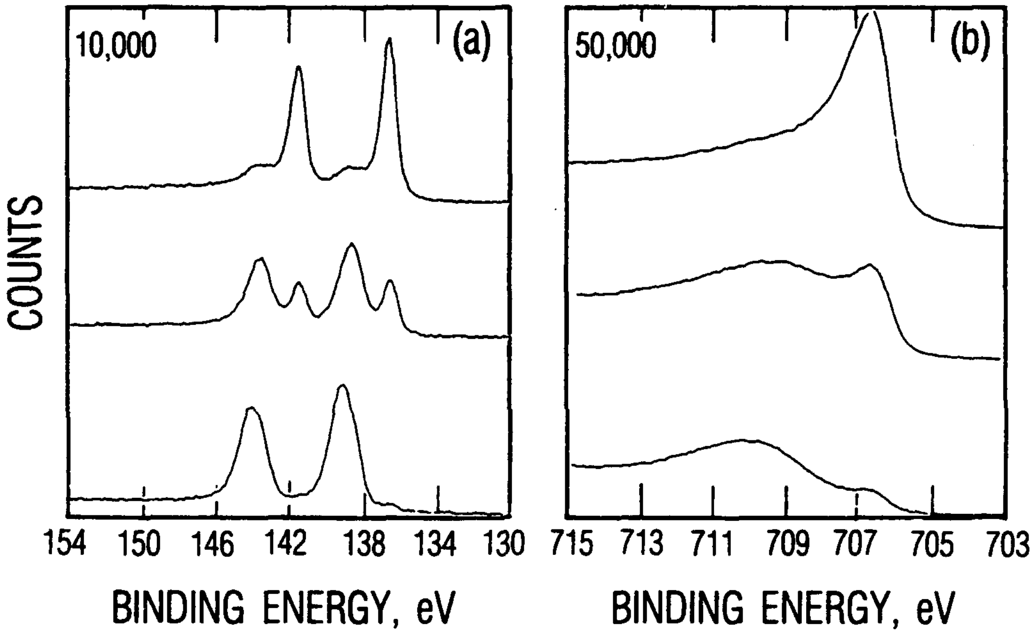

Figure 10. The (a) Pb 4f and (b) Fe $2p_{3/2}$ peaks from Pbnp-treated 52100 steels after heating to 250°C. From the bottom of the figure, the spectra were taken on unscratched solvent-cleaned 52100, scratched solvent-cleaned 52100 (middle), and unscratched, alkaline-washed 52100 (top) surfaces.

therefore, is again strongly correlated with the emergence of metallic iron. The iron on the alkaline-treated 52100 surface showed even greater reactivity than that on the untreated surface, as shown in Figure 10 (b). In both the unscratched and scratched areas of this surface, virtually all of the iron oxide present was reduced to metallic iron during the 250°C anneal. Concurrently, most of the Pbnp on these areas was reduced to metallic Pb at 250°C, again showing the strong correlation discussed above. Small amounts of iron oxide and chemisorbed Pbnp are present after the 250°C anneal, but heating to 350°C caused both of these species to be reduced to metallic forms.

IV. DISCUSSION

The layered structure of 440C stainless steel presents several different possible chemical environments with which boundary or extreme pressure oil additives can interact. Additives that interact strongly with iron oxide would provide the most protection for 440C, as this overlayer exists at the very surface of the steel. The chemical interactions of additives with the chromium oxide underlayer become important when the iron oxide layer is eliminated, which would occur if the iron oxide layer were worn away or were chemically removed. Finally, if the mechanical parts experience wear through both oxide layers, then chemical interactions of additives with the bulk steel metallic iron and chromium and chromium carbides will determine the mode of boundary protection. For the 440C samples studied in this work, the total oxide thickness of only 4.0-4.5 nm indicates that relatively little wear would have to occur before bulk steel is exposed.

The simpler chemical composition of 52100 steel presents fewer possible chemical environments for additive interaction. This steel can be viewed most simply as consisting of an iron oxide overlayer on bulk steel, which is primarily metallic iron. The thickness of the oxide layer on 52100 varies significantly, depending on sample handling, making the amount of wear required to reach the bulk variable. The polished samples studied in this work had oxide layers approximately 4.0 nm thick, so that the amount of wear required to eliminate the oxide was about the same as the 440C samples.

Chemical and physical treatments have been shown to modify steel surface chemical composition in fairly predictable ways. In the case of 440C stainless, the chromium oxide underlayer provides a reaction barrier for both basic and acidic surface treatments. Treatment with a buffered alkaline solution removed the iron oxide overlayer in a highly selective fashion, leaving behind a surface that was dominantly chromium oxide. The acid treatments used in this work were much more difficult to control. Previous work has shown that etches longer than the 30 s treatment used in this work roughen the surface and actually produce greater amounts of surface iron oxide than the shorter etch times.[20] It is quite likely, therefore, that the 30 s etch used here did cause surface damage, exposing some bulk steel. Chemical treatments on 52100 steel, which lacks the chromium oxide underlayer, have different effects. Acid treatments with HCl/ethanol corrode the surface, producing an oxide layer thick enough to obscure any photoemission from the bulk steel. Conversely, the alkaline etch appears to remove the iron oxide overlayer; however, significant amounts of oxide are detected, probably due to re-oxidation of the exposed bulk steel. Finally, ion sputter etching could conceivably be used to selectively remove the iron oxide overlayer by carefully controlling the ion dose.

The relative utility of the three methods for controlling the surface composition of 440C surfaces can be addressed with reference to the XPS-determined Fe:Cr ratios following sample treatments. In the sputter profile, the etching rate was quite slow (0.43 nm/min), allowing for very controlled removal of surface species. The lowest Fe:Cr ratio obtained in the profile was 1.7:1 after the sixth minute. In addition, the chromium oxide signal shows the effects of sputtering before all of the iron oxide signal is eliminated, which could be caused by surface roughness effects or by the presence of a mixed iron-chromium oxide interfacial compound. The range of Fe:Cr ratios obtained following the acid treatments was 1.25-1.84:1,[27] indicating the relative lack of control over this treatment. Alternatively, the alkaline wash treatment produced a range of ratios of ~1.1 to 1.4:1. The relatively small values and narrow range indicate that the alkaline treatment is effective at controllably removing the iron oxide overlayer. In addition, the low-end values for the chemical treatments may indicate that the alternative ion sputtering process chemically reduces some of the iron oxides to iron metal while also removing material. This could lead to a possible "knock on" effect, where not all of the iron is removed before the chromium oxide sputtering starts, leading to larger Fe:Cr ratios than can be obtained through chemical processes.

The chemical interaction of Pbnp with steel surfaces is highly dependent on surface treatments prior to and during immersion in the Pbnp solution, showing that the steel surface chemical composition plays a vital role in the protective action of Pbnp. On untreated steel surfaces, Pbnp appeared to physisorb at room temperature on the iron oxide layer on either 440C or 52100 steel. This conclusion is based on the presence of the relatively high binding energy form of Pb and the strong carboxylate C peak, indicating molecular Pbnp on these surfaces. It should be noted that the presence of hydrocarbon contamination could prevent Pbnp from interacting with the iron oxide. Chemical treatments with acidic or basic solutions on 440C and basic solutions on 52100 produce surfaces capable of chemisorbing Pbnp by breaking carbon oxygen bonds in the carboxylate group or by breaking Pb-O bonds with dissolution of the Hnp (naphthenic acid). It is possible that the chemical pretreatments activate the surfaces by leaving acidic or basic surface species capable of breaking down the carboxylate on an oxide or metal surface. The steel surface species present on 440C following these treatments should be dominantly chromium oxide. As mentioned above, however, the acid etch is fully capable of exposing metallic Fe. On 52100, the alkaline etch likely removes substantial amounts if not all of the iron oxide, and the immediate immersion into the Pbnp solution might allow the molecule to interact with metallic Fe or at least an incompletely oxidized form of surface iron. Certainly, scratching the steel surface while it is immersed in Pbnp/heptane provides metallic Fe with which the additive can interact. The chemisorbed forms of Pbnp present on all of these surfaces appear quite similar, characterized by the Pb $4f_{7/2}$ binding energy of 138.8 eV and elimination of some of the carboxylate groups on the surface.

On heating, Pbnp either desorbs or reacts by breaking down, with the extent of the breakdown dependent on the chemical nature of the steel surface. One obvious result of this work is that the production of metallic Pb from chemisorbed Pbnp coincides with the appearance of metallic Fe on the substrate. This is evidenced by the reactivity of Pbnp on all of the scratched surfaces studied, where metallic Pb was always formed to significant extent by annealing to 250°C and almost completely at 350°C on 52100 and 450°C on 440C. On unscratched 440C, a small amount of metallic Pb was formed while, on unscratched 52100, large amounts of metallic Pb were formed. This reactivity is explained by the reduction of surface iron oxide to metallic iron, a process which is particularly effective on 52100 but could also occur on 440C. The alkaline wash virtually eliminates the iron oxide overlayer on 440C, leaving only the chromium oxide underlayer to interact with Pbnp. It is evident that although the Pbnp will chemisorb on the chromium oxide, it will not reduce to metallic Pb on this surface. In contrast, the alkaline etch either eliminates the iron oxide or significantly lessens its thickness on 52100, allowing the Pbnp to interact more easily with metallic Fe. In fact, the alkaline-washed 52100 surface was the most reactive studied, with virtually all the surface iron oxide and Pbnp reduced to the metallic species on heating to 250°C. In general, the greater Pbnp reactivity on 52100 relative to 440C may be simply explained by the enhanced ability of the 52100 surface to form metallic Fe on heating in the UHV system. The acid-etched 440C surface produces the perplexing result in this study. If only the iron oxide overlayer were selectively removed, then Pbnp would interact with chromium oxide and similar reactivity to the alkaline-washed surface should result. However, significant amounts of metallic Pb formed on this surface which might lead one to suspect the presence of metallic Fe. The most likely source of this metallic Fe is from the bulk steel exposed by the acid roughening of the surface, causing the chromium oxide layer to be breached in some locations.

The principal goal of this work was to address the possible mechanisms of boundary protection of Pbnp on steel surfaces. A small amount of the physisorbed form of Pbnp that is dominant at room temperature on iron oxide apparently overcomes an activation barrier to chemisorption on heating and then becomes rather strongly bonded. This conclusion is based on the fact that chemisorbed Pbnp (characterized by the 138.8 eV Pb $4f_{7/2}$ binding energy) is retained by the 440C surfaces after heating only when some iron oxide is present. This chemisorbed species could provide some boundary protection of the steel surfaces.

In an EP boundary condition, however, contacting metal asperities likely break through the outer iron oxide layer, which is only about 2.5 nm thick on 440C, or through both oxide layers, and create fairly high local surface temperatures. The interaction of chemisorbed Pbnp with the chromium oxide underlayer of 440C seems quite weak, as samples on which the iron oxide layer was most effectively removed retained no Pb after heating. Conversely, the interaction of Pbnp with metallic surfaces produces a chemisorbed Pbnp species that breaks down to metallic Pb at elevated temperatures. This behavior is observed on all scratched surfaces, acid-etched 440C, and alkaline-washed 52100 steel. On all of these surfaces, Pbnp was likely exposed to metallic Fe, and the iron oxides on these surfaces are readily reduced to metallic Fe on heating. The high temperature reactivity of Pbnp on the metallic species in steel probably most closely resembles the EP boundary conditions for which Pbnp is currently used, implying that metallic Pb formation is crucial in the EP protection mechanism for Pbnp. The fact that metallic Pb has been used as a solid lubricant in certain applications lends credence to this model of additive effectiveness.[28,29] In addition, this concept of solid lubricant film formation from additive molecules is similar to that proposed by Sakurai, explaining the boundary protection of Mo-S-organic compounds, which appear to decompose to MoS_2.[30,31] However, the role of steel surface chemistry in additive breakdown is unknown for the Mo-containing compounds.[32] The hydrocarbon portion of the Pbnp molecule could also provide some boundary protection, but it was observed to desorb more readily from the metallic surfaces than from the oxides. Therefore, Pbnp appears to have two modes of boundary protection: the chemisorbed molecules adsorbed on iron oxides, which should exist under relatively mild wear conditions, and a metallic Pb layer when wear occurs through the oxide layers under EP conditions.

The final point to address is the possibility of enhancing Pbnp performance by performing specific pretreatments prior to lubrication with Pbnp-containing oils. This is a complex issue and is clearly dependent on the steel type being used and the wear conditions expected. Since Pbnp does appear to have some beneficial interactions with iron oxide, it might be advisable to leave the native oxide layer on the surface, particularly if mild wear conditions are expected. Chemical treatments aimed at removing the iron oxide overlayer of 440C would appear to be unwise, as the Pbnp seems to do little to protect the chromium-rich oxide underlayer at elevated temperatures. The acid etching of 440C did appear to enhance the amount of Pbnp chemisorbing to the surface and enable metallic Pb to form. However, the surface roughening of the etch may have played a major role in these effects by exposing bulk steel, and such treatments are generally unadvisable for precision-machined mechanical parts. On the 52100 surface, however, the removal or thinning of the iron oxide overlayer with the alkaline wash definitely improved the ability of this surface to retain metallic Pb. In fact, all steel surfaces will form metallic Pb more readily with thinner oxide layers that can be more quickly worn away than thicker layers. The question that must be addressed for specific uses of pretreatments is the relative utility and protective capability of the steel oxide layers versus the protection afforded by the formation of a metallic Pb layer.

V. SUMMARY

The chemistry of the EP additive lead naphthenate has been shown to be highly dependent on the chemical composition of the steel substrate on which it is adsorbed. At room temperature, Pbnp appears to physisorb on the iron oxide overlayer present on most steel surfaces, but will chemisorb to chromium oxide underlayers of stainless steels or bulk metallic species in any steel exposed by chemical or physical means. On heating to simulate EP boundary conditions, Pbnp again displayed surface-dependent reactivity. While most of the Pbnp desorbed from oxide surfaces on heating, a small amount of Pbnp chemisorbed to iron oxide after heating to 350°C and remained strongly bonded to the surfaces. In addition, Pbnp was observed to break down to form a layer of metallic Pb in the presence of metallic Fe. The high temperature reactivity of Pbnp was particularly high on scratched 440C and 52100 steel surfaces that readily reduce to metallic iron on heating in UHV. The results point to two possible mechanisms for Pbnp boundary protection: (1) the formation of chemisorbed Pbnp species on surface oxides under relatively mild wear conditions and (2) the formation of a layer of metallic Pb when severe wear conditions expose metallic Fe.

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Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; development and analysis of thin films and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; development and evaluation of hardened components; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion; spacecraft structural mechanics, spacecraft survivability and vulnerability assessment; contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; lubrication and surface phenomena.

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