

# High temperature lubrication of various ceramics and metal alloys via directed hydrocarbon feed gases

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## Abstract

High temperature lubrication via the in situ deposition of lubricous carbon surface films from the pyrolytic decomposition of hydrocarbon feed gas has been confirmed on a variety of self-mated ceramic and metal alloy sliding contacts. Pin-on-disk tests were performed at 520°C in an atmosphere purged with nitrogen at 3 l/min, with a directed acetylene admixture supplied at 0.2 l/min, and compared to tests in nitrogen alone or air. Friction coefficients of less than  $\mu \approx 0.08$  were recorded for all metal alloys tested—AISI M50, 52100, 440C and 1018 steel, as well as K-Monel (500) and Hastalloy C276. Friction coefficients of less than  $\mu \approx 0.10$  were found for alumina, silicon nitride, tungsten carbide, and zirconia. Only soda lime glass showed no friction coefficient reduction upon acetylene admixture. In general, acetylene admixture also significantly reduced wear volume, with wear reductions of multiple orders of magnitude in many instances. © 1998 Elsevier Science S.A.

**Keywords:** Vapor phase lubrication; Solid lubrication; High temperature lubrication

## 1. Introduction

The need for workable approaches to the high temperature lubrication of ceramics and metal alloys continues to grow, and draw considerable attention. At temperatures below 350°C, conventional lubrication strategies have been demonstrated and employed repeatedly and reliably. However, at more extreme temperatures the number of options is significantly limited. One approach, vapor phase lubrication, has been successfully applied to wide range of materials, as surveyed by Rao [1]. Solid lubrication and powder lubrication, as well as vapor phase lubrication, indeed have limiting operational conditions such as temperature and environment. However, these lubrication schemes do extend the operational range of applications beyond the 350°C threshold otherwise posed by the thermal capabilities of fluid lubricant basestocks.

This study investigated a particular lubrication strategy in which a lubricous carbon film is generated and continuously replenished in situ via the pyrolytic decomposition of acetylene feed gas supplied to the environment of concentrated sliding contacts comprised of various self-mated materials. The method of deposition and replenishment of high temperature carbon solid lubricants from hydrocarbon feed gases

was investigated by Lauer and Bunting [2] in the 1980s. This lubrication method had since been proven effective for a handful of different materials by Lauer and Dwyer [3] using propane, benzene, and ethylene feed gases supplied to counterformal sliding contacts with initial contact pressures of roughly 300 MPa. More recently, Sawyer et al. [4] have shown that acetylene admixtures introduced into simulated exhaust gas environments are capable of lubricating silicon nitride sliding and rolling contacts with maximum Hertzian contact pressures initially as high as 2.2 GPa. In an effort to test the flexibility of this lubrication process in similarly concentrated contacts, an expanded variety of 11 materials were tested and compared under a single set of sliding conditions with and without acetylene admixture.

## 2. Background

Vapor phase lubrication of a number of different materials has been successfully demonstrated in several laboratories using assorted vaporized fluids. Such vapors may provide lubrication through condensation on the contact surfaces [5], through reactions with the contact surfaces to form solid lubricants (a process which can consume the sliding surfaces), or through polymerization or decomposition reactions at the contact surfaces to deposit solid lubricants. Smith et al.

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[6] successfully lubricated sliding contacts of self-mated alumina through tribopolymerization of vinyl octadecyl ether, diallyl phthalate and lauryl methacrylate monomers. These experiments were performed at temperatures of 145°C, and provided both friction coefficient reductions of 50% and reductions in pin wear volume of 99%.

Graham and Klaus [7] employed tricresyl phosphate and tributyl phosphate vapors delivered to steel sliding surfaces at temperatures of 370°C and generated lubricous polymeric films. Hanyaloglu and Graham [8] expanded this work to temperatures of 600°C for SiAlON/SiAlON and SiAlON/cast iron sliding contacts. In later work, Hanyaloglu et al. [9] investigated the lubrication of the nickel-based superalloy IN 750 using a vaporized aryl phosphate ester. Additionally, Hanyaloglu et al. [10] examined the lubrication of IN 800, IN 850, and MN 400 alloys by vapors of triaryl phosphate. These experiments were performed at modest contact pressures of less than 1 MPa, and furthermore profited from a predeposited film generated through exposure to vapor for 15 min prior to loading and sliding. Measured friction coefficients as low as  $\mu \approx 0.05$  were recorded.

Lauer [11] recently reviewed the mechanism of lubricous carbon deposits generated by the pyrolysis of hydrocarbon gases at the contact surfaces. This lubrication scheme has been demonstrated using reactions of various carbonaceous gases, including oxides of carbon [12]. Lauer and Bunting [2] demonstrated the ability of ethylene to generate a lubricating film of carbon on a variety of metallic and ceramic surfaces containing nickel as a potential catalyst at temperatures ranging from 450 to 650°C. Lauer and Dwyer [3] subsequently measured friction coefficients of  $\mu < 0.1$  for sapphire pins on SiAlON, silicon carbide, zirconia, and zirconia–alumina disks by providing ethylene, propane or benzene feed gases to the tribosurfaces at temperatures ranging from 100 to 700°C. In that study, it was demonstrated that attainment of such lubrication performance by pyrolysis of hydrocarbon feed gases in fact does not depend upon the inclusion of nickel within the tribosystem.

### 3. Experimental

Eleven different self-mated material pairs were tested in a pin-on-disk tribometer. These specimens can be separated by material types. Six of these materials are metal alloys, of these four are AISI steels and two are nickel-based superalloys. The five remaining materials are ceramics, with four being engineering ceramics and one glass. The four different AISI steels tested were M50, 52100, 440C, and 1018, while the two nickel-based superalloys were Hastalloy C276 and K-Monel (500). The ceramic materials included three commercially available structural ceramics, as well as tungsten carbide, and soda lime glass. The structural ceramic materials chosen were alumina, silicon nitride, and zirconia. Due to their chemical stability, low density, and high temperature

strength, several ceramics have been considered candidate materials for high temperature bearing applications.

Disk specimens were 25.4 mm × 25.4 mm square, and spheres of 3.18 mm diameter served as hemispherically-tipped pin specimens. All specimens were washed and cleaned with anhydrous methyl alcohol in an ultrasonic vibratory cleaner prior to testing. Both the disks and the pins had initial surface roughnesses which were less than 0.1  $\mu\text{m}$  rms.

The pin-on-disk tribometer is comprised of two nested chambers. The inner chamber contains the contacting pin and disk specimens, a precursor admixture line, and an electric resistance heater. The disk is mounted on top of a drive spindle, while the hemispherically-tipped pin is contained within a holder at the end of a cantilevered arm. As precursor gases which pyrolytically deposit lubricous carbon may also combust, utilization of this lubrication technique requires that an atmosphere is provided to the contact region which displaces  $\text{O}_2$ . Thus the inner chamber also includes a purge line through which nitrogen may be provided. The outer chamber contains the inner chamber, and it may also be purged with nitrogen gas to blanket the inner chamber from laboratory air. This tribometer is capable of continuous operation above 520°C in a variety of environments. The pin holder arm pivots about a hinge located outside of the outer chamber, and normal force loading is accomplished by placing dead weight on the pin holder arm. A motor controller maintains a constant disk spindle speed. The temperature of the test environment is monitored using a thermocouple located at the center of the disk surface. This thermocouple also provides feedback to a temperature controller for the heater circuit.

Strain gauges are mounted on the base of the pin holder arm, near the arm's pivot, for the measurement of friction forces. The strain gauges are located in ambient air, outside of the outer chamber, arranged on the pin arm to form a temperature-compensated bridge to avoid thermal drift. Connected to this tribometer and strain gauge bridge is a computer controlled data acquisition system which monitors the strain gauge bridge voltage signal at an acquisition rate of 10 kHz. An average value of this voltage signal is recorded to a datafile for each consecutive 10 s period, along with a corresponding friction coefficient. In each friction trace (Figs. 1 and 2) instantaneous data points at sliding distances of 5, 15, 25, 35, 45, 55, 65 and 75 m are highlighted with a symbol. These symbols are not intended to exhaustively represent friction measurements taken, nor average values over any period, but are simply provided to distinguish between the various test environments.

All 11 materials were tested in self-mated contacts under identical load, speed and temperature conditions. The specimens were heated 520°C over a 15-min period. This constant temperature was maintained for another 15 min prior to the initiation of sliding, as well as for the 30 min sliding test. The contact sliding speed and normal load were 44 mm/s and 2.2 N respectively, producing a total sliding distance of approximately 80 m.

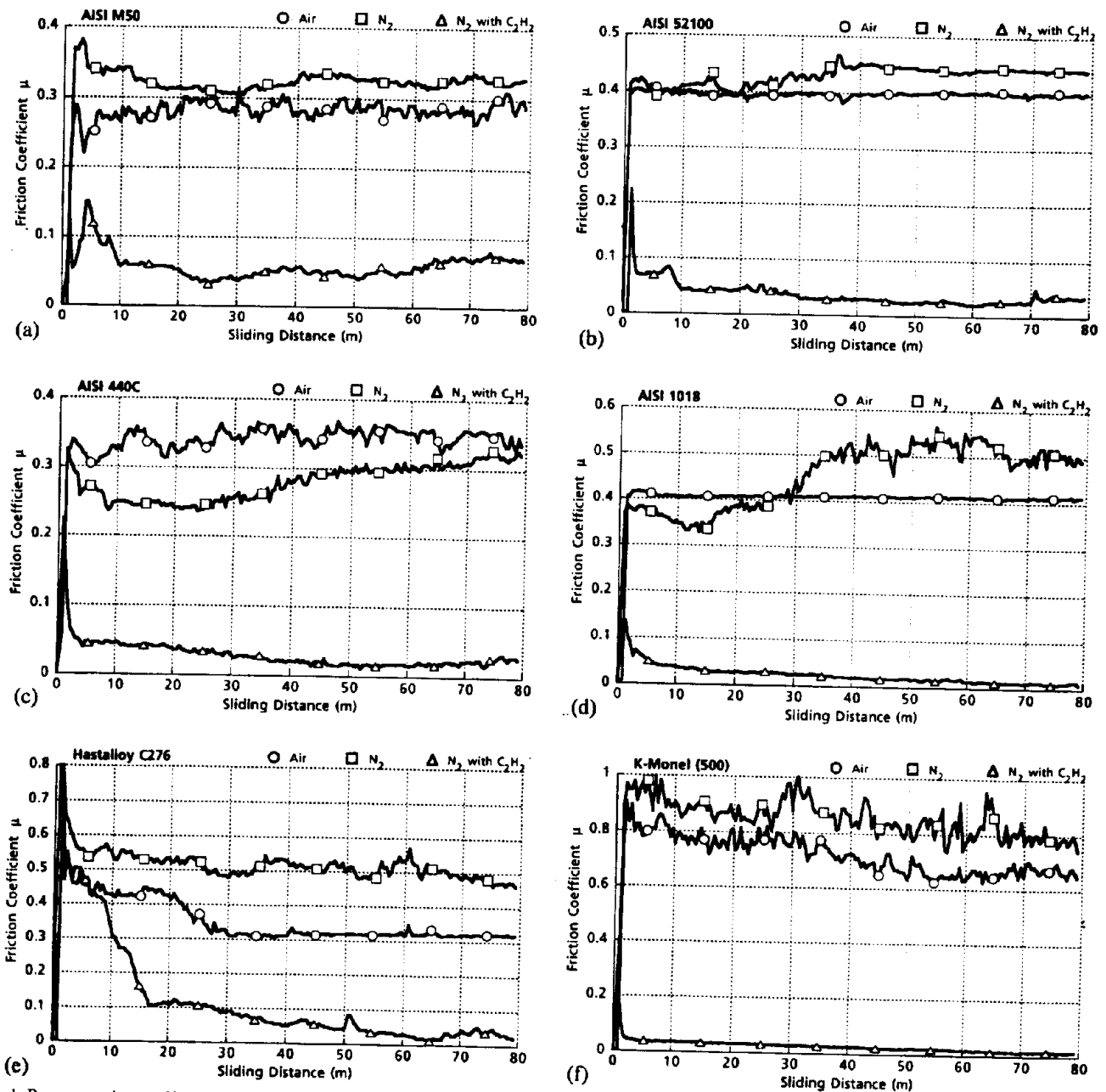


Fig. 1. Representative coefficient of friction traces for various self-mated metal alloys during pin-on-disk tests performed at 520°C, 44 mm/s sliding velocity, and 2.2 N normal load in air, or in nitrogen atmosphere with or without acetylene admixture. (a) AISI M50, (b) AISI 52100, (c) AISI 440C, (d) AISI 1018, (e) Hastalloy C276, (f) K-Monel (500).

For each material, tests were performed in a nitrogen environment. The purge line distributed extra-dry grade nitrogen throughout the inner chamber at a volume flow rate of 3 l/min. The outer chamber was purged, also with extra-dry nitrogen, at 8 l/min to blanket the inner chamber from intrusion of ambient laboratory air. For each material numerous tests were performed in the nitrogen environment with and without an admixture of a 0.2 l/min flowrate of acetylene gas directed towards the pin-on-disk contact, supplied through a stainless steel supply line. No predeposition of carbon solid lubricant was employed. Initiation of acetylene admixture was coincident with the initiation of sliding. Tests performed in nitro-

gen alone were repeated three times and the tests in nitrogen with acetylene admixture were repeated a minimum of five times. Benchmark tests were also performed in air, with no nitrogen purge or acetylene admixtures provided to the test chambers.

Post-test sliding surfaces were observed by optical microscopy. The diameter of the circular wear scar formed on the hemispherically-tipped pin was recorded and used to calculate the volume of material lost from the pin during sliding. Raman spectroscopy, using a linear photodiode array detector and 30 mW power incident argon ion laser light focused within a micrometer-scale spot placed on regions of

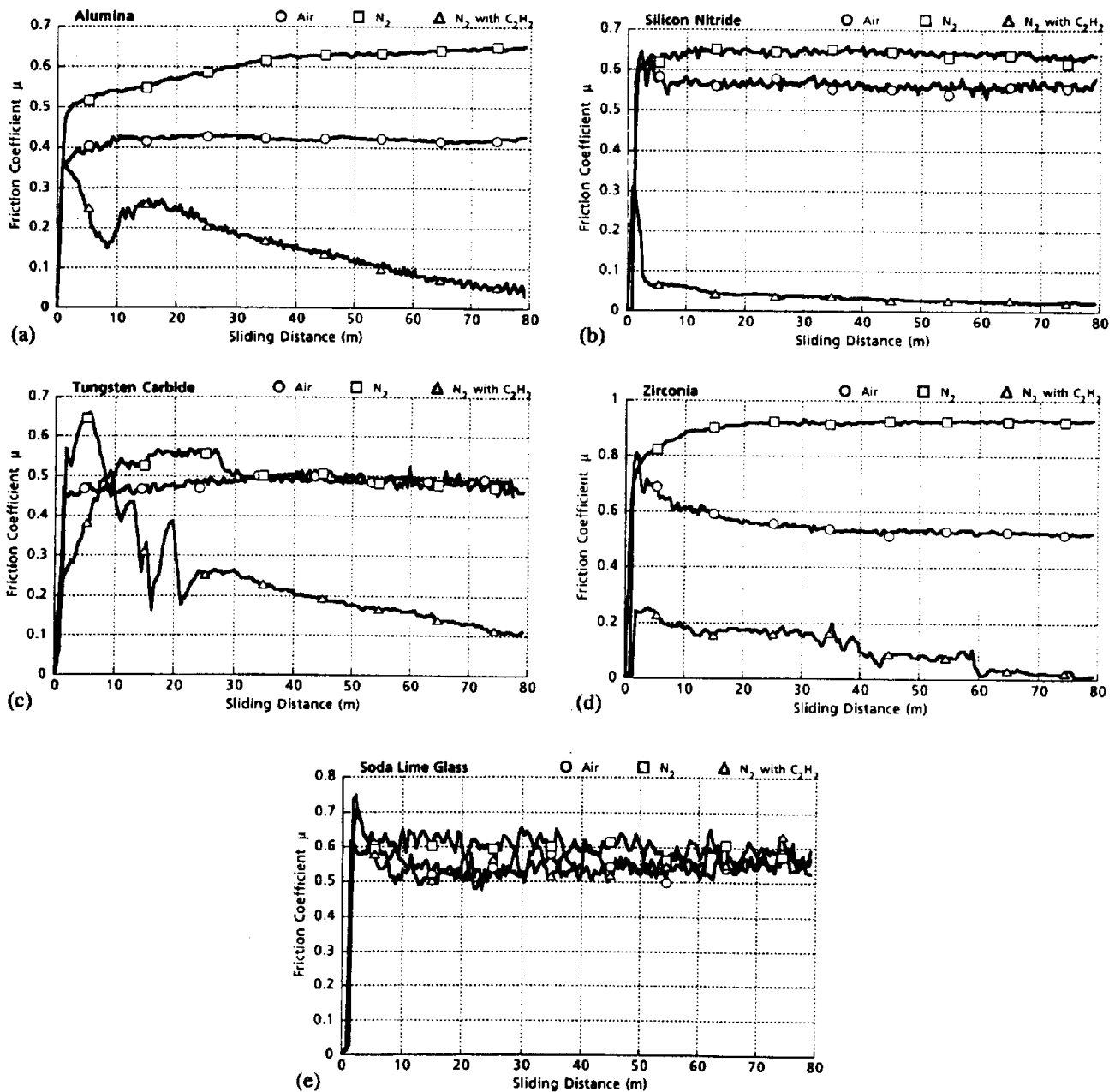


Fig. 2. Coefficient of friction traces for various self-mated ceramics during pin-on-disk sliding tests, performed at 520°C, 44 mm/s sliding velocity, and 2.2 N normal load in air, or in a nitrogen atmosphere with or without acetylene admixture. (a) alumina, (b) silicon nitride, (c) tungsten carbide, (d) zirconia, (e) soda lime glass.

interest, was used to characterize carbon deposits on post-test sliding surfaces. A collection time of 24 min was used for each spectrum.

#### 4. Results

For each material tested, example friction traces measured in air, and nitrogen with and without the acetylene admixture, are overlaid for comparison, Figs. 1a–f and 2a–e. In general the friction coefficients at 520°C for the metal alloys in the

absence of acetylene were between  $\mu \approx 0.3$  and 0.6, with K-Monel (500) having a friction coefficient above  $\mu \approx 0.8$ . All six of these materials had large drops in friction coefficient upon acetylene admixture, with steady-state friction coefficients between  $\mu \approx 0.02$  and  $\mu \approx 0.06$  recorded. In addition, much audible noise was present during sliding tests in the absence of acetylene. This noise was absent once acetylene admixture provided reduced friction.

In air or nitrogen alone, the engineering ceramics and soda lime glass had friction coefficients between  $\mu \approx 0.4$  and 0.9. Tests performed in nitrogen with acetylene admixtures on

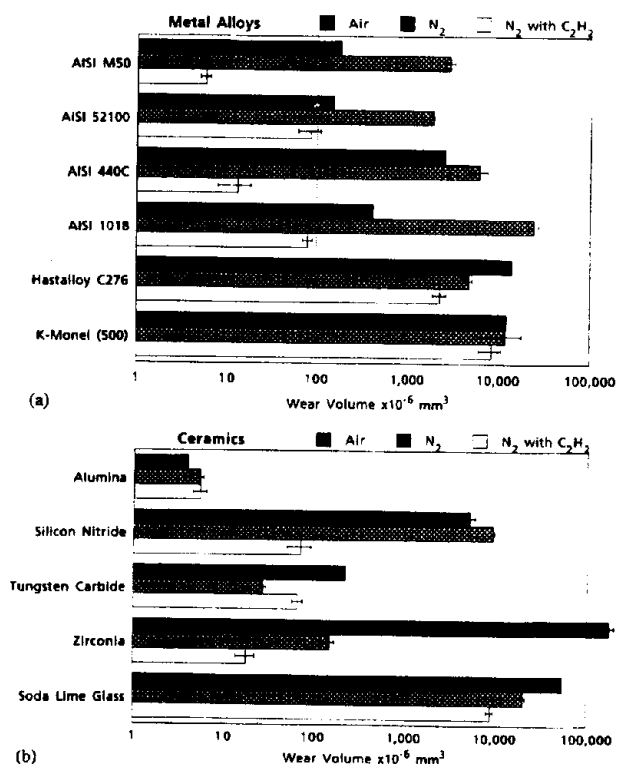


Fig. 3. Pin wear volumes lost during 80 m sliding distance in pin-on-disk tests, performed at 520°C, 44 mm/s sliding velocity, and 2.2 N normal load in air, or in nitrogen atmosphere with or without acetylene admixture. (a) metal alloys, (b) ceramics.

alumina, silicon nitride, and zirconia all resulted in steady-state friction coefficients below  $\mu \approx 0.06$ , while at test completion a reduced friction coefficient  $\mu \approx 0.1$  was measured for tungsten carbide. Alumina and tungsten carbide both had friction coefficients that dropped gradually, still approaching lower steady-state levels even after 80 m sliding distance. In contrast, the soda lime glass showed no significant reduction in friction coefficient upon exposure to an admixture of acetylene.

For each material tested, the average pin wear volume that occurred during 80 m of self-mated sliding contact is displayed in Fig. 3. The provision of an acetylene admixture to an inerted (nitrogen) atmosphere resulted in considerable reductions in wear for all metal alloys tested, as compared to that measured in either air or nitrogen alone. The steels all showed wear reductions of between one and three orders of magnitude upon acetylene admixture compared to that measured in the presence of nitrogen alone, as well as considerable reductions in wear even when compared to that measured in air atmospheres. Similarly large reductions in wear were provided to the silicon nitride and zirconia ceramics by introduction of acetylene, with more modest reductions observed for soda lime glass. Though acetylene admixture provided large reductions in the friction of alumina and tungsten carbide self-mated contacts, similar reductions in wear were not always observed under the conditions used in this study.

## 5. Discussion

Lauer and Bunting's [2] demonstration of high temperature friction reduction via carbon deposits continuously replenished from pyrolysis of hydrocarbon gas streams was performed with sliding contacts between bodies coated with or containing nickel. A common misperception resulting from the demonstration was that utility of the lubrication technique may be limited to bearings whose contacting surfaces contain nickel, thought necessary to catalyze the pyrolytic decomposition. Even if bearing surfaces were nickel-coated, it was furthermore suggested that the effectiveness of the lubrication technique may be limited by the lifetime of the thin coating. Later, Lauer et al. [13] demonstrated that both the high temperature sliding friction and wear of self-mated silicon nitride contacts could be reduced by 'prenucleating' the hydrocarbon (ethylene in that case) feed gas using a heated nickel-containing surface that was both non-bearing and remote, located upstream of the contact.

Even in the absence of nickel-containing surfaces, ethylene feed gases alone have been shown capable of providing considerable reductions in both friction and wear of various ceramics [3,13,14]. Acetylene is of even greater effectiveness as a precursor feed gas [14], and 20-fold and 650-fold reductions in sliding friction and wear, respectively, of self-mated silicon nitride have been attained at 520°C, even in the absence of 'prenucleation' by such nickel-containing surfaces [4]. In addition to two nickel superalloys, the study presented here demonstrated the ability of acetylene gas admixed to an inert nitrogen atmosphere to provide order-of-magnitude reductions in the high temperature sliding friction of contacts comprised of a variety of self-mated steel alloys not containing nickel, compared to friction measured in nitrogen alone. Similar friction reductions were also achieved in self-mated sliding contacts of the four representative engineering ceramics (alumina, silicon nitride, tungsten carbide, and zirconia). Acetylene feed gas furthermore provided reductions in the sliding wear of nearly all of these various contacts, in many cases by multiple orders of magnitude.

The provision of lubricous carbon deposits to contacting surfaces of each of the tested materials by pyrolysis of acetylene precursors is confirmed via Raman spectroscopy of pin wear scars (Figs. 4 and 5). Characteristic  $sp^3$  disorder and  $sp^2$  graphitic scattering bands are observed, respectively, at approximately 1350 and 1580  $cm^{-1}$  relative wavenumber. In the case of soda lime glass, these bands are superimposed atop a sloped, fluorescence background. These carbon deposits exist as isolated islands on the wearing surfaces, with characteristic diameters of several micrometers. Typical thicknesses of these deposits, as determined by stylus profilometry [12] as well as by Auger electron spectroscopy depth profiling [14], are several tenths of a micrometer.

Though acetylene admixture provided large reductions in the friction of alumina and tungsten carbide self-mated contacts, corresponding reductions in wear were not always observed for these two materials under the standard condi-

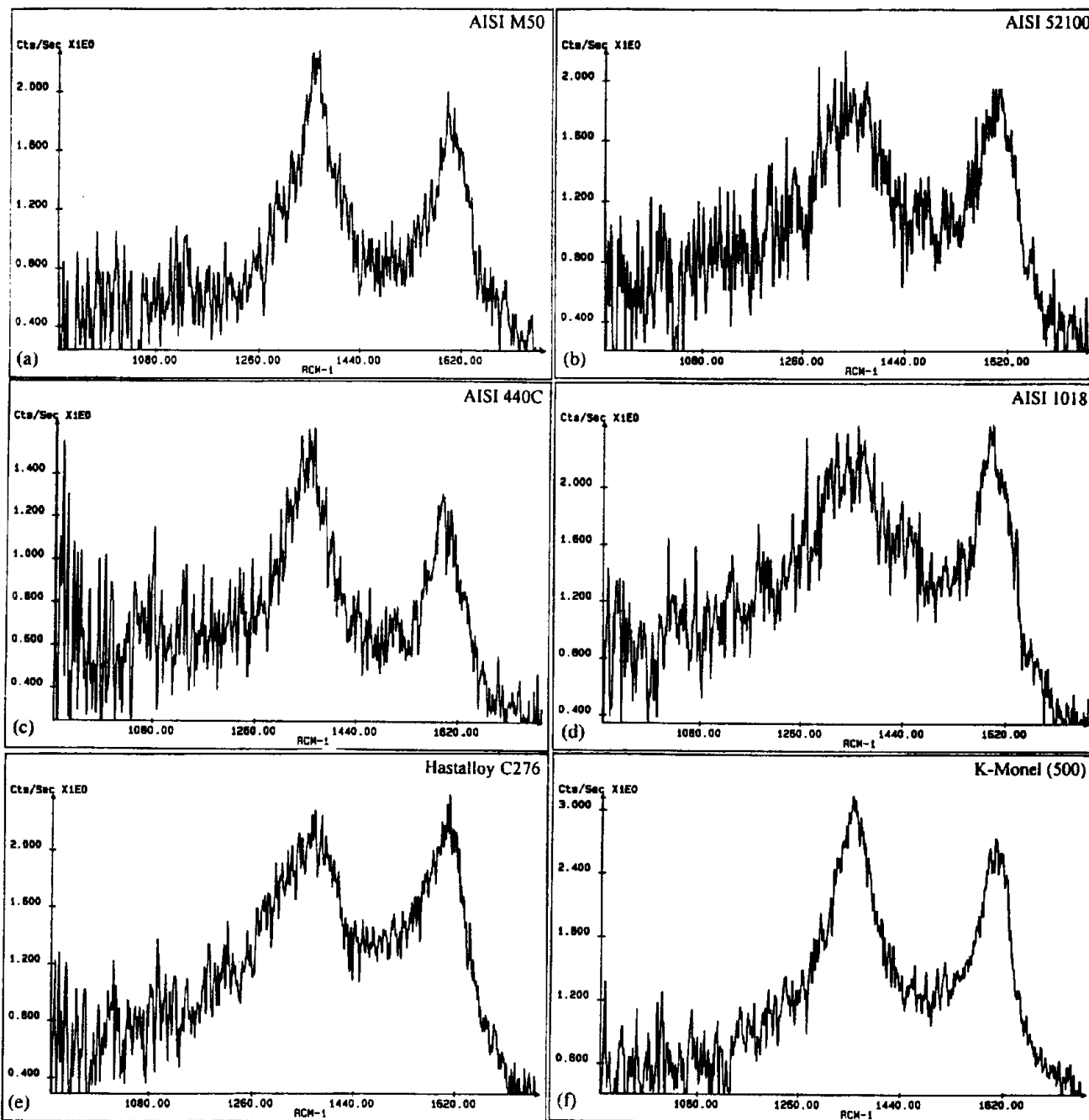


Fig. 4. Representative Raman spectra of carbon deposits within the wear scars on various metal alloy pins following self-mated pin-on-disk tests performed at 520°C, 44 mm/s sliding velocity, and 2.2 N normal load in nitrogen atmosphere with acetylene admixture. (a) AISI M50, (b) AISI 52100, (c) AISI 440C, (d) AISI 1018, (e) Hastalloy C276, (f) K-Monel (500).

tions used in this study. It should be noted that of the 11 materials investigated, these are also the two materials that displayed the greatest wear resistance in inert atmosphere (nitrogen alone). Additionally, alumina and tungsten carbide displayed the most gradual reductions in friction upon acetylene admixture, with higher friction conditions persisting throughout the initial portion of the sliding test. The single measurement of wear volume made after the 80 m sliding distance can be considered as one contribution from the initial high wear rate transient portion of the sliding test, as well as

a second contribution accumulated under subsequent steady-state conditions. For wear-resistant materials such as the alumina and tungsten carbide in sliding tests of shorter duration, one may suspect that the wear contribution from the initial transient period far outweighs the subsequent relatively small contribution accumulated during the limited steady-state period. In such cases it is unlikely that acetylene admixture initiated coincidentally with the onset of sliding will greatly affect total wear, as carbon deposition is not sufficiently rapid to combat that predominant contribution occurring during the

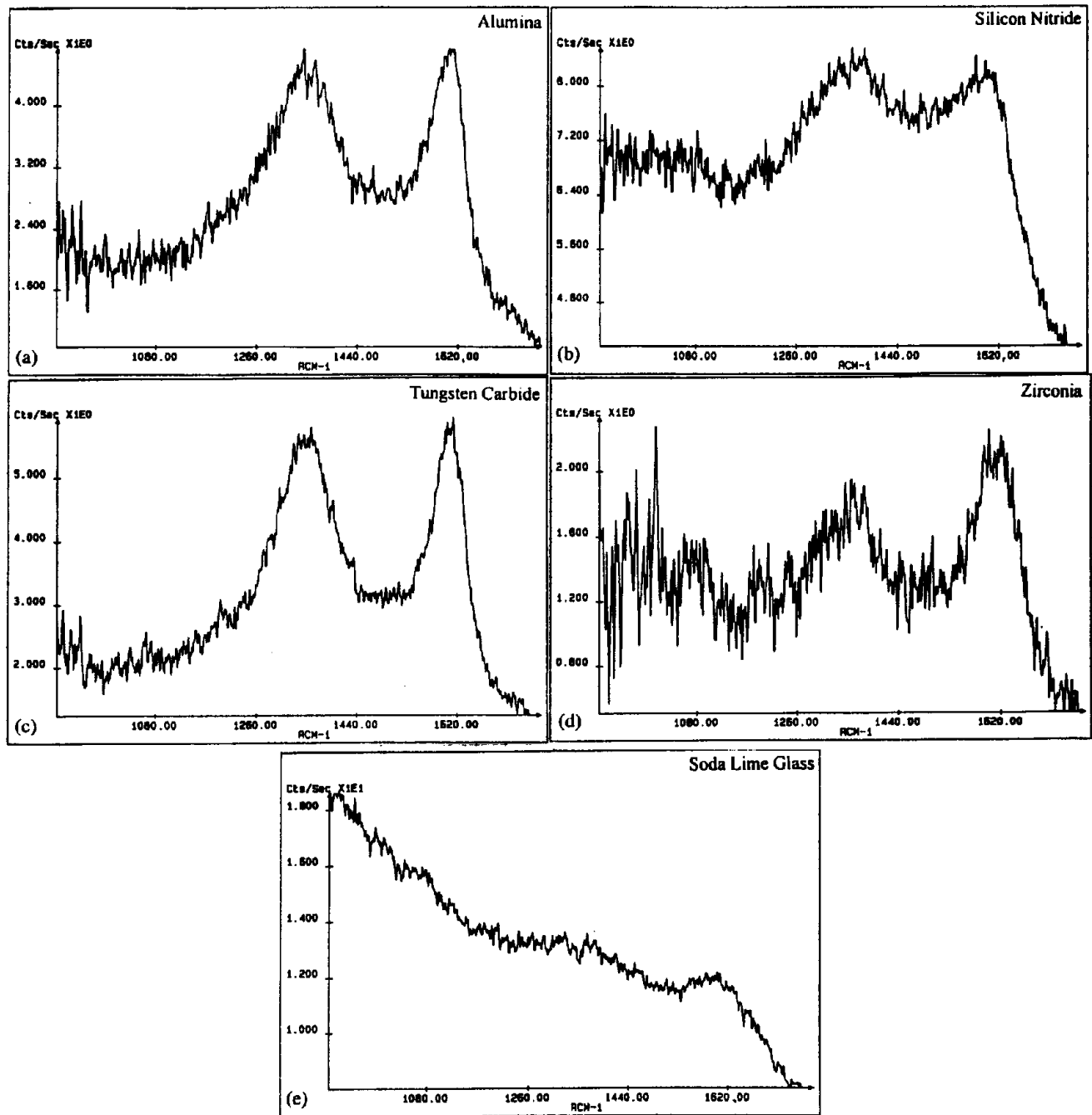


Fig. 5. Representative Raman spectra of carbon deposits within the wear scars on various ceramic pins following self-mated pin-on-disk tests performed at 520°C, 44 mm/s sliding velocity, and 2.2 N normal load in nitrogen atmosphere with acetylene admixture. (a) alumina, (b) silicon nitride, (c) tungsten carbide, (d) zirconia, (e) soda lime glass.

initial high wear rate transient period. If instead tests were of increased duration and the wear contribution under steady-state unlubricated conditions thus augmented, it is suggested that acetylene admixture would also manifest itself for both of these materials through considerable reductions of total wear. Furthermore, the run-in wear contribution occurring during the initial period of sliding may also be combatted through pre-exposure of tribosurfaces to the precursor feed gas prior to sliding.

High temperature, extended duration lubrication using carbon deposits continuously replenished upon bearing surfaces through pyrolysis of hydrocarbon gas of course necessitates provision of an  $O_2$ -free atmosphere to prevent combustion of the precursor. In the absence of any lubrication strategy, the atmosphere in which a bearing contact otherwise operates is often air. In such instances inert gas may not be the preferred benchmark atmosphere for testing, but the performance of the lubrication technique might be better gauged against

behavior in air. For example, the wear of each of the steels tested here was indeed lower in air than in nitrogen alone, perhaps the result of oxide surface films obstructing adhesive interactions between the underlying metal which would otherwise occur. Nonetheless, even when gauged against air, the potential benefits of reduced wear and friction provided by an acetylene hydrocarbon precursor within an inert atmosphere are clearly demonstrated at high temperature for a variety of materials.

## 6. Conclusions

(1) The ability of directed (acetylene) hydrocarbon admixtures to provide large reductions in both the friction and wear of a broad variety of ceramics and metal alloys in high temperature, concentrated, self-mated sliding contacts through pyrolysis and deposition of solid lubricous carbon has been clearly demonstrated.

(2) At 520°C, the AISI steels tested (M50, 52100, 440C, and 1018) all demonstrated sliding friction coefficients less than  $\mu \approx 0.06$  with wear volume reductions typically in excess of an order of magnitude for tests utilizing acetylene admixture. Tests applying the acetylene admixture to nickel superalloys Hastalloy C276 and K-Monel (500) enabled friction coefficients of less than  $\mu \approx 0.04$ , with more modest wear volume reductions than those measured for the steels.

(3) Alumina, silicon nitride, and zirconia ceramics showed friction coefficients below  $\mu \approx 0.05$  during tests with directed acetylene admixture, while the reduced coefficient of friction  $\mu \approx 0.1$  for tungsten carbide was still dropping towards a steady-state value at test completion. Acetylene admixtures provided clear reductions in the sliding wear of silicon nitride and zirconia, whether compared to that measured in air or nitrogen alone.

(4) Though providing low friction, the ability of lubricous carbon deposits to reduce the wear of self-mated alumina and tungsten carbide contacts, when compared to that measured both in air and nitrogen alone, could not be established in these short duration sliding tests. This anomaly, as well as the inability of acetylene admixtures to reduce the friction of self-mated soda lime glass sliding contacts, are not fully understood at this time.

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