

# Lubrication of Mo, W, and their Alloys with H<sub>2</sub>S gas admixtures to room temperature air

W. Gregory Sawyer, Thierry A. Blanchet \*

*Department of Mechanical Engineering, Aeronautical Engineering, and Mechanics, Rensselaer Polytechnic Institute, Troy, NY 12180, USA*

## Abstract

The in situ lubrication of molybdenum and tungsten using admixtures of hydrogen sulfide to room temperature and pressure air was achieved. Raman spectroscopy confirmed the presence of molybdenum disulfide and tungsten disulfide solid lubricants on elemental molybdenum and tungsten specimens, respectively. Pin-on-disk experiments were conducted with elemental molybdenum, elemental tungsten, and alloys of molybdenum and tungsten in atmospheres containing hydrogen sulfide. Friction coefficients were continuously recorded and comparisons between the sliding friction coefficient in air and in the hydrogen sulfide atmospheres were evaluated. In general, hydrogen sulfide admixtures reduced the friction coefficient for all materials containing molybdenum or tungsten. Friction coefficients for self-mated elemental molybdenum and self-mated elemental tungsten were reduced to  $\mu = 0.15$  with hydrogen sulfide admixtures to air of 5% and 15%, respectively. In some cases friction coefficients as low as  $\mu = 0.08$  were recorded. © 1999 Published by Elsevier Science S.A. All rights reserved.

*Keywords:* Vapor phase lubrication; Molybdenum disulfide; Tungsten disulfide

## 1. Introduction

The friction coefficient of two contacting surfaces in relative motion is largely a function of the condition and chemistry of the surfaces in contact. If this contact contains an easily sheared surface film, sliding displacement can be accommodated with reduced frictional resistance. Lamellar solids such as graphite, molybdenum disulfide, and tungsten disulfide are commonly used to provide solid lubrication through such mechanisms.

A significant problem with solid lubricant surface films is that the film lifetime is finite due to wear. Vapor phase lubrication is a technique that uses chemical reactions to build a solid lubricating film even as the existing film is being worn away. Vapor phase lubrication is an in situ technique that can extend the film lifetime indefinitely in conditions where the film generation rate is sufficiently high.

Bowden and Rowe ran friction tests with molybdenum in vacuum environments of 0.01–0.1 atmospheres containing various gases with and without pre-deposited molybde-

num disulfide films [1]. In experiments run with molybdenum disulfide burnished onto molybdenum surfaces, the friction coefficient was  $\mu = 0.10$  at room temperature and increased monotonically with temperature ending with  $\mu = 1.0$  at 1100°C. In experiments run with molybdenum disulfide formed on molybdenum surfaces through exposure to hydrogen sulfide gas prior to sliding, friction coefficients were  $\mu = 0.20$  from room temperature up to 800°C. In the temperature range from 800°C to 1150°C, the friction coefficient increased monotonically ending with  $\mu = 0.50$  at 1150°C. Experiments with molybdenum in hydrogen sulfide atmospheres had friction coefficients of  $\mu = 0.90$  at room temperature, reached a minimum value of  $\mu = 0.20$  at 750°C, and then increased monotonically with temperature to  $\mu = 0.50$  at 1150°C. Mitchell suggested the possibility of using molybdenum components in a bearing running in a sulfiding atmosphere [2]. It was speculated that this atmosphere could convert the exposed molybdenum surfaces to molybdenum disulfide continuously during operation and this molybdenum disulfide would provide solid lubrication for the rolling elements.

Singer et al. found that the friction coefficient for molybdenum disks sliding against hemispherically tipped pins of SiC was between  $\mu = 0.10$  and 0.15 in high vacuum gas atmospheres containing SO<sub>2</sub> and O<sub>2</sub> gases.

\* Corresponding author. Tel.: +1-518-276-8697; fax: +1-518-276-2623; e-mail: blanchet@rpi.edu

These friction coefficients were not a function of the gas pressure. In the experiments run in high vacuum atmospheres containing pure hydrogen sulfide, the measured friction coefficients were less than  $\mu = 0.01$  [3]. Additionally, the friction coefficients showed a dependence on the hydrogen sulfide gas pressure:  $\mu = 0.06$ ,  $\mu = 0.01$  and  $\mu = 0.008$  for hydrogen sulfide gas pressures of 4, 13 and 40 Pa, respectively. In another study by Singer et al., using XPS, the molybdenum disulfide films formed on the molybdenum surfaces from reactions with hydrogen sulfide and were measured to be approximately 0.3 nm in thickness [4]. In this same study, thermodynamic calculations of equilibrium phases of solid–liquid–gas reactions with molybdenum and hydrogen sulfide at 298°K and 10 Pa predicted Mo(s), MoS<sub>2</sub>(s), H<sub>2</sub>(g), and H<sub>2</sub>S(g).

Of particular interest to the authors of this paper was whether or not hydrogen sulfide admixtures to room temperature and pressure air would be capable of generating molybdenum disulfide on molybdenum at a sufficient rate to provide any lubricating benefit. It was further speculated that the hydrogen sulfide admixtures to room temperature and pressure air might also be capable of generating tungsten disulfide surface films on tungsten. The presence of molybdenum and tungsten in several alloys prompted a continued study of using hydrogen sulfide as a vapor phase lubrication system for alloys which have varying amounts of molybdenum and tungsten.

## 2. Experimental

Material pairs were tested in a pin-on-disk tribometer at room temperature and pressure in atmospheres of laboratory air and laboratory air with various concentrations of hydrogen sulfide. Nine material pairs were tested. Two of these material pairs (self-mated 304 stainless steel and self-mated elemental silicon) did not contain molybdenum or tungsten. Self-mated elemental molybdenum and ele-

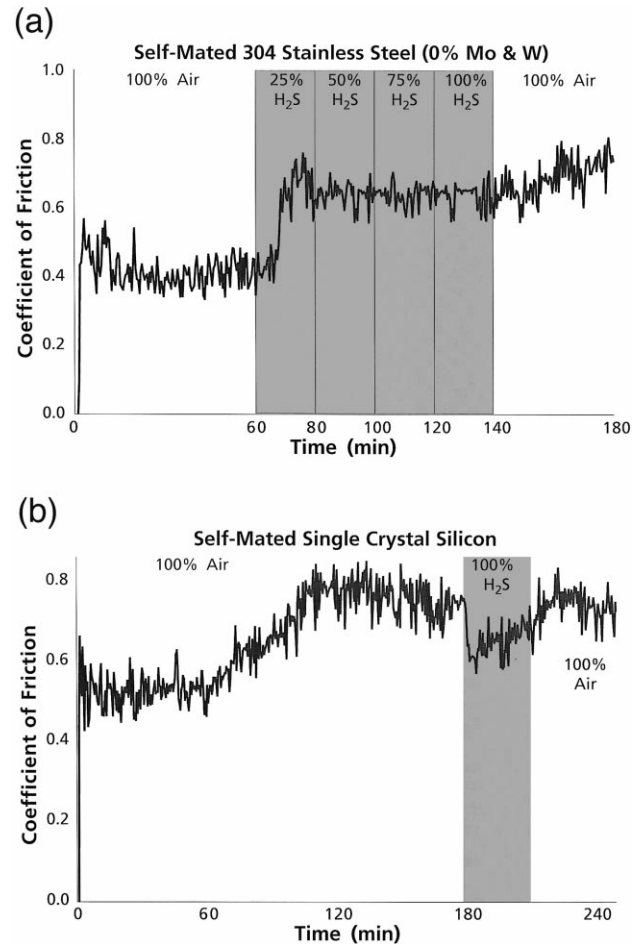


Fig. 1. Coefficient of friction traces for various self-mated materials containing no molybdenum or tungsten. 1.6 N normal load, 67 mm/s sliding velocity, and room temperature and atmospheric pressure gas atmospheres. (a) 304 stainless steel, (b) elemental single crystal silicon.

mental tungsten specimens were also tested. The remaining five material pairs were self-mated Hastelloy C276 (15% Mo and 4 wt.% W), self-mated Inconel 625 (9% Mo),

Table 1  
Composition (wt.%) of test alloys as provided by manufacturers

	Mo	W	Ni	Fe	Cr	Cu	Si	Al	Ti	Mn	Co	C	Nb(+Ta)
304 SS	–	–	9.2	68.7	19	–	1	–	–	2	–	0.08	–
Hastelloy C276	15.5	3.8	59	5.4	15.6	–	0.025	–	–	0.41	0.2	0.004	–
Inconel 625	9	–	58	5	22	–	0.5	0.4	0.4	0.5	1	0.1	3.75
AL6XN SSS	6.3	–	24	48	20.5	0.1	0.4	–	–	0.4	–	0.02	–
HD-17D	–	90	7	3	–	–	–	–	–	–	–	–	–
Tungsten carbide	–	88.2	–	–	–	–	–	–	–	–	–	6	5.8

Table 2  
Hardness measurements of test materials (Rockwell A)

	304 SS	Hastelloy C276	Molybdenum	Inconel 625	AL6XN SSS	Tungsten	HD-17D	Tungsten carbide
R <sub>a</sub>	30	38	40	41	36	57	46	76

self-mated AL6XN super stainless steel (6% Mo), elemental tungsten pin on HD-17D (90% W) disk, and 304 stainless steel pin on tungsten carbide disk. The compositions of the non-elemental materials are provided in Table 1, while the hardness of all test materials (except single crystal silicon) are provided in Table 2.

The pin-on-disk apparatus was made entirely of aluminum alloys with stainless steel hardware and gas lines. The tribometer has an inner chamber that contains the specimens, an air gas line, and a hydrogen sulfide gas line, nested within an outer chamber. The entire tribometer apparatus is located inside of a laboratory fume hood.

The pin specimens are cylindrical rods 3.2 mm in diameter loaded on their flat ends. The disk specimens are  $25.4 \times 25.4 \text{ mm}^2$ . Both the pin and disk specimens are lapped and polished, finishing with  $0.1 \mu\text{m}$  diamond grit on a felt-polishing wheel. Initial surface topography of specimens was not further quantified. Prior to testing, specimens are thoroughly washed, dried, and cleaned in an ultrasonic vibratory cleaner containing anhydrous methyl alcohol.

The prescribed normal load (dead weight) was 1.6 N. The sliding velocity was 67 mm/s. Both the normal load and the sliding velocity were maintained constant for all experiments. At the base of the pin holder arm is a strain gauge bridge connected to a power supply, amplifier, and signal conditioner. A computer data acquisition system monitors the amplified and conditioned signal and converts this voltage to a friction coefficient. This data is then plotted and recorded to disk.

The experimental protocol was to run the material pairs in laboratory air purged through the inner chamber at 5 l/min for 1 h (240 m of sliding) or until a steady friction coefficient could be observed. After this initial period of sliding, hydrogen sulfide gas was introduced into the inner chamber and sliding continued over a period of at least 30 min (120 m of sliding). This period of sliding in a hydrogen sulfide-containing atmosphere was then followed by a return to the air environment. The tests were halted once the friction coefficient returned to the steady states values of friction coefficient observed during the initial period of sliding in air. Upon the termination of a test the specimens

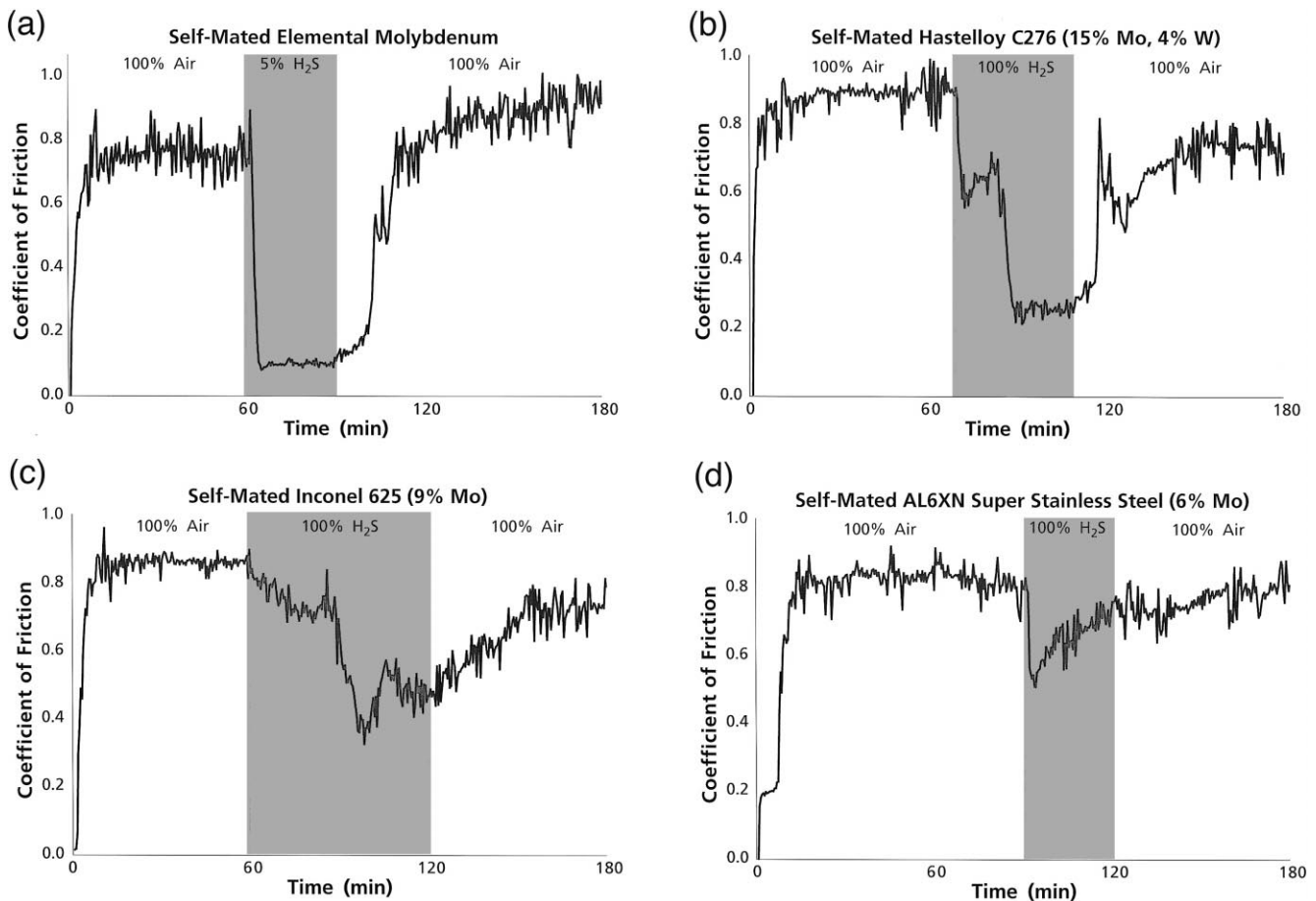


Fig. 2. Coefficient of friction traces for various molybdenum-containing materials. 1.6 N normal load, 67 mm/s sliding velocity, and room temperature and atmospheric pressure gas atmospheres. (a) Self-mated elemental molybdenum, (b) self-mated Hastelloy C276, (c) self-mated Inconel 625, (d) self-mated AL6XN super stainless steel.

were observed by optical microscopy and Raman spectroscopy. In these preliminary studies no effort was made to make post-test measurements of mass loss, as wear occurring during periods of sliding in the presence of hydrogen sulfide could not be distinguished from wear occurring during periods of sliding in the absence of the admixture by such a single measurement.

### 3. Results

For each material pair tested, the experimental protocol had three consecutive periods. These periods were (in order): initially sliding in air; followed by sliding in an environment containing hydrogen sulfide; and ending with a return to sliding in air. The friction traces of tests run with self-mated 304 stainless steel and self-mated single crystal silicon are shown in Fig. 1a and b, respectively. Both 304 stainless steel and single crystal silicon contain no molybdenum or tungsten, and thus serve as controls. In the case of 304 stainless steel, the friction coefficient actually increases upon the introduction of hydrogen sulfide gas to the inner chamber.

In all cases of molybdenum and molybdenum-containing materials (Fig. 2a–d), the friction coefficient was reduced, to varying extents, upon the introduction of hydrogen sulfide gas. With as little as 5% hydrogen sulfide admixture, the sliding friction coefficient of elemental molybdenum was reduced over 5-fold, when compared to the initial period of sliding in air. The lowest recorded value of friction coefficient was below  $\mu = 0.10$ . All of the molybdenum-containing alloys, Hastelloy C276, Inconel 625 and AL6XN super stainless steel showed reductions in friction coefficient when run in hydrogen sulfide atmospheres. Of these alloys, Hastelloy C276, which contains approximately 15% molybdenum as well as 4% tungsten, showed the greatest reduction in friction coefficient from  $\mu = 0.90$  in air to  $\mu = 0.25$  in 100% hydrogen sulfide atmospheres.

Tungsten and tungsten-containing materials (Fig. 3a–c) all showed reductions, to varying extents, in friction coefficient when run in atmospheres of hydrogen sulfide. In the case of self-mated elemental tungsten the friction coefficient was affected by the concentration of hydrogen sulfide in the atmosphere. Friction coefficients of  $\mu = 0.85$ ,  $\mu = 0.75$ ,  $\mu = 0.25$  and  $\mu = 0.15$  were measured for 0%, 5%, 10%, and 15% hydrogen sulfide concentrations, respectively. Abundant solid lubricant formation in the presence of 15% hydrogen sulfide allowed low friction to be maintained for an extended sliding duration upon the stopping of admixture flow. The elemental tungsten pin on the HD-17D (90% tungsten alloy) had a reduction in friction coefficient to  $\mu = 0.15$  in atmospheres containing only 5% hydrogen sulfide. When run in atmospheres of 10% hydrogen sulfide, the combination of 304 stainless steel and

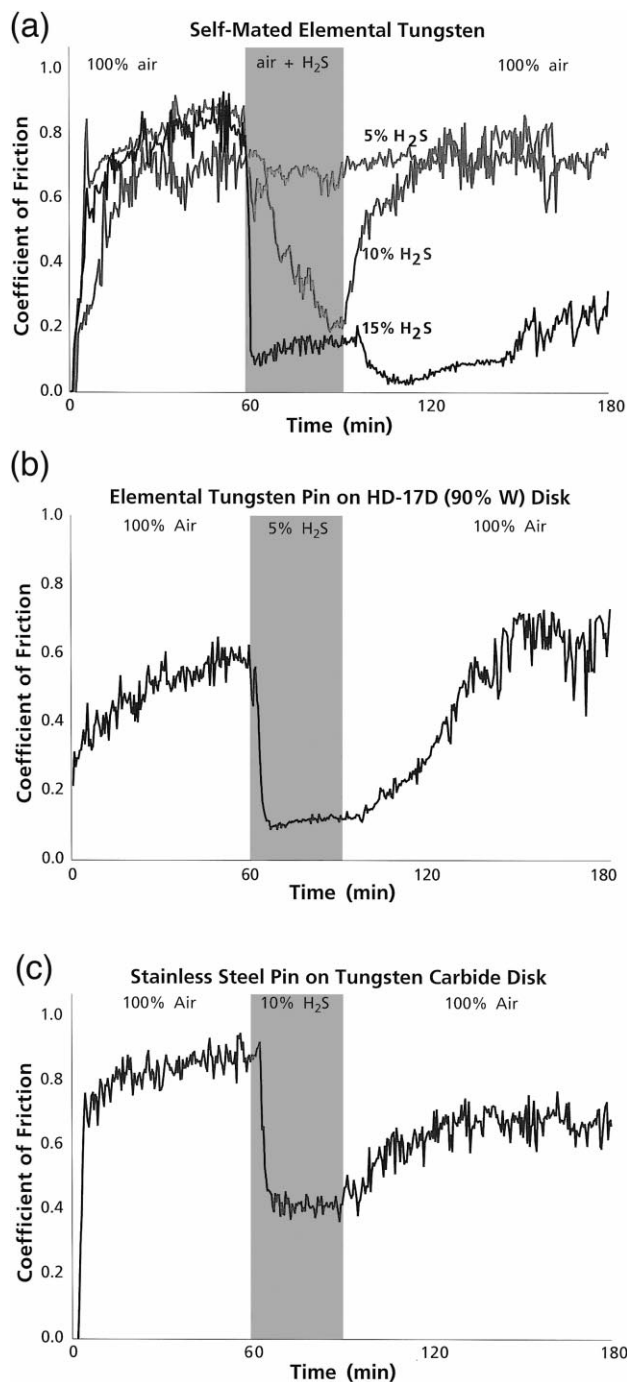


Fig. 3. Coefficient of friction traces for various tungsten-containing materials. 1.6 N normal load, 67 mm/s sliding velocity, and room temperature and atmospheric pressure gas atmospheres. (a) Self-mated elemental tungsten, (b) elemental tungsten pin on HD-17D, (c) 304 stainless steel pin on tungsten carbide.

tungsten carbide had a 2-fold reduction in friction coefficient over those recorded when sliding in air.

Raman spectroscopy was performed on dark islands found within the disk wear tracks on the self-mated elemental molybdenum and tungsten specimens (Fig. 4a and b). On the molybdenum specimens, these regions had

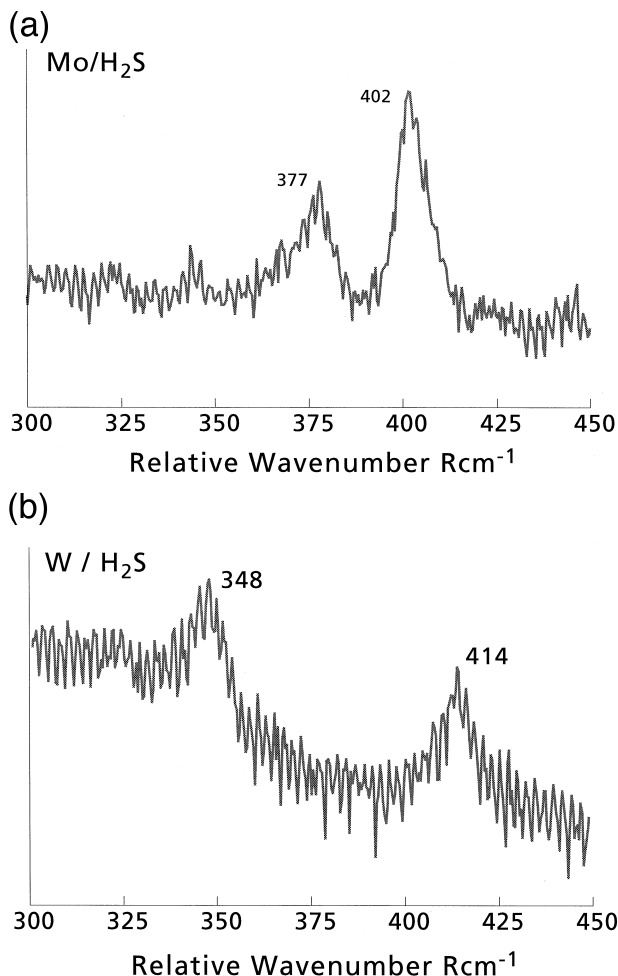


Fig. 4. Raman spectroscopy of tribochemical film found within the disk wear track following self-mated pin-on-disk tests with 1.6 N normal load, 67 mm/s sliding velocity, at room temperature and atmospheric pressure, in an air environment containing hydrogen sulfide gas. (a) Molybdenum disulfide formed on molybdenum, (b) tungsten disulfide formed on tungsten.

peaks at 377 R cm<sup>-1</sup> and 402 R cm<sup>-1</sup>, representative of molybdenum disulfide. On the tungsten specimens, these islands had peaks at 348 R cm<sup>-1</sup> and 414 R cm<sup>-1</sup>, representative of tungsten disulfide.

#### 4. Discussion

The vapor phase lubrication of molybdenum and tungsten using admixtures of hydrogen sulfide to room temperature and pressure air environments resulted in over five fold reductions of sliding friction coefficients. Reduced friction was provided by the formation of islands of solid lubricating molybdenum disulfide and tungsten disulfide surface films through reaction of the contacting bodies with the hydrogen sulfide gas admixture. In the cases where there was abundant hydrogen sulfide with elemental molybdenum and tungsten, the generation of lubricous

islands required only a few tenths of a meter of sliding to establish adequate coverage and reduce the sliding friction coefficient (Figs. 2a and 3a).

The effectiveness of vapor phase lubrication is enhanced by actions which cause the rate of solid lubricant film formation from the vapor phase to increase relative to the rate of film removal by mechanical wear [5]. In the experiments run with elemental tungsten in atmospheres of different concentrations of hydrogen sulfide, the trend of decreasing friction coefficient with increasing concentration is in keeping with this competitive rate model. In the experiments run on molybdenum alloys (Fig. 2b–d) the reduction in the friction coefficient, which becomes more pronounced with increasing molybdenum content, is also in keeping with this model as molybdenum is a reactant in the solid lubricant film formation reaction.

A similar trend may also be observed with tungsten-containing materials, where contacts of bodies with high tungsten content (elemental tungsten and/or HD-17D 90% tungsten alloy) were more effectively lubricated by hydrogen sulfide admixtures than contacts involving tungsten carbide, for example.

Though hydrogen sulfide is a by-product of many commercial processes, including hydrodesulfurization of petroleum, its toxicity must be kept in mind. As OSHA's acceptable ceiling concentration is 20 ppm lubrication via hydrogen sulfide admixtures is not recommended for casual industrial use [6].

#### 5. Conclusions

Hydrogen sulfide admixtures to room temperature and pressure air environments were found capable of generating lubricous surface films on self-mated molybdenum as well as tungsten specimens in sliding contact. Raman spectroscopy reveals that the surface films generated on the molybdenum and tungsten surfaces are molybdenum disulfide and tungsten disulfide, respectively.

Experiments with molybdenum- and tungsten-containing materials showed a reduction in sliding friction coefficient in hydrogen sulfide atmospheres. Hastelloy C276, which is approximately 15% Mo and 4 wt.% W, showed the greatest reduction in sliding friction coefficient of the molybdenum- and tungsten-containing alloys ( $\mu \sim 0.25$ ).

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## References

- [1] F.P. Bowden, G.W. Rowe, Lubrication with molybdenum disulphide formed from the gas phase, *The Engineer*, Nov. 1957, 667.
- [2] D.C. Mitchell, Bearing Assembly, United States Patent Office, Patent Number 2,697,645, 1954.
- [3] I.L. Singer, T. Le Mogne, C. Donnet, J.M. Martin, Friction behavior and wear analysis of SiC sliding against Mo in partial pressures of SO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>S gases, *Tribol. Trans.* 39 (1996) 950–956.
- [4] I.L. Singer, T. Le Mogne, C. Donnet, J.M. Martin, In situ analysis of the tribochemical films formed by SiC sliding against Mo in partial pressures of SO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>S gases, *J. Vac. Sci. Technol. A* 14 (1996) 38–45.
- [5] T.A. Blanchet, J.L. Lauer, Y.F. Liew, S.J. Rhee, W.G. Sawyer, Solid lubrication by decomposition of carbon monoxide and other gases, *Surf. Coat. Technol.* 68/69 (1994) 446–452.
- [6] Hydrogen Sulfide, *Kirk–Othmer Encyclopedia of Chemical Technology*, 3rd edn., Wiley, New York, Vol. 22, 1978.