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Thermal chemistry of a high temperature solid lubricant, cesium oxythiomolybdate

Part I *Thermo-oxidative stability of Cs_2MoOS_3*

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Cesium oxythiomolybdate (Cs_2MoOS_3) is a potential high temperature solid lubricant. It undergoes complex oxidation reactions at elevated temperatures, but continues to provide lubrication above the oxidation temperature. Therefore, in order to determine the nature of the lubricant at elevated temperature, it is necessary to understand the thermal chemistry of Cs_2MoOS_3 in an air environment. The thermo-oxidative stability of Cs_2MoOS_3 was evaluated between room temperature and 800°C in air. Melting and phase transition temperatures were determined. X-ray photoelectron spectroscopy, micro-Raman scattering and x-ray diffraction were used to identify the chemical species evolved at increasing temperatures. As-received Cs_2MoOS_3 was not pure. It also contained cesium molybdates, molybdenum oxides, and Cs_2SO_4. Between 300–400°C, the material began to decompose forming Cs_2SO_4 and MoS_2. Between 400–600°C, Cs_2MoOS_3 also formed cesium molybdates and molybdenum oxides. In addition, the Cs_2SO_4 began to oxidize to cesium oxides (which melted) and SO_x gas. Also, MoS_2 oxidized to MoO_3. At approximately 700°C, MoO_3 began to sublime. Upon cooling from 800°C, the material was primarily cesium oxides and Cs_2MoO_4, with small amounts of complex cesium molybdates and molybdenum oxides. © *2001 Kluwer Academic Publishers*

1. Introduction and background

Cesium oxythiomolybdate (Cs_2MoOS_3) has recently been considered as a high temperature solid lubricant. It was originally synthesized and characterized by Muller *et al.* in 1968 [1, 2, 3]. It has been shown to be an effective lubricant, providing a friction coefficient below 0.2 at 650°C [4]. Cesium oxythiomolybdate has been synthesized for tribological applications by three companies: Pennwalt, MRI, and Desilube. These materials are still experimental and are not commercially available in pure form. King and Forster [4] have noted that Cs_2MoOS_3 changes color from its original bright red-orange to a white powder during high temperature testing, indicating a change in chemical composition. They also discovered that the material changed from solid to liquid at approximately 600°C. Based on x-ray photoelectron spectroscopy (XPS) of wear tracks after friction testing, they postulated that there may be chemical interaction between this lubricant and silicon nitride substrates.

Thermogravametric analysis (TGA) has been used to study oxidation of Cs_2MoOS_3. When performed in air, King and Forster found that a 10% weight loss occurs over the temperature range 600–1000°C [4]. King and Asmerom also performed TGA [5] and saw a 2% weight loss in air to 280°C, and then a 4% weight gain at 410°C which was maintained up to 600°C. In nitrogen, behavior was similar, but there was no weight gain. Clearly, the weight gain was oxidation.

In the present study, Cs_2MoOS_3 was heated in air to temperatures between 25–800°C. The identity of the resulting compounds was probed with XPS, x-ray diffraction (XRD), and Raman scattering. Differential thermal analysis (DTA), differential scanning calorimetry (DSC), and TGA were carried out on Cs_2MoOS_3 and some of the decomposition products identified during this study. Fourier transform infrared spectroscopy (FTIR) was performed on Cs_2MoOS_3 powder. It is expected that more conclusive identification of the decomposition products may reveal the high temperature lubricant, leading to a simpler, more reliable, and less expensive material.

2. Experimental

Cesium oxythiomolybdate powder was obtained from Desilube Corporation and cold pressed into pellets for the thermal trials without further purification. In

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addition, several standard materials (Cs_2SO_4, MoS_2, MoO_3, and Cs_2MoO_4) which are possible decomposition products were obtained from Alfa-Aesar, and were 99.9% pure. Pellets were heated in air to 200, 400, 600, 700, and 800°C for 6 hours using a Ney 3-550 programmable oven and analyzed after cooling to room temperature. Materials heated over 650°C at least partially melted, and the pellet was contained in an alumina crucible. All samples were stored in ambient conditions until analysis was performed.

DSC was performed on Cs_2MoOS_3 in a DuPont Instruments 910 DSC using a 10°C per minute ramp rate from room temperature to 580°C in oxygen. DSC was also performed on some of the standards to determine phase transition temperatures when literature values were not available. DSC measures the difference in energy input required to keep a sample and a reference at the same temperature as they are heated at a specific rate [6]. A reference, such as Al_2O_3, undergoes no transformations over the temperature range, so the energy per unit time needed to maintain the zero difference is proportional to the heat released or absorbed by the sample.

TGA was performed in a DuPont Instruments 901 instrument also using a 10°C per minute ramp rate from room temperature to 960°C in air. TGA measures the weight change of a specimen with temperature, and is particularly useful for studying chemical reactions which involve the evolution or consumption of a gas [6]. DTA was performed in a DuPont Instruments 910 DSC fitted with a DTA 1600 unit. The sample was heated from room temperature to 1000°C at a rate of 10°C per minute. The analysis was performed in ambient air. As in DSC, a standard which is known to have no transitions over the test temperature range is used [6]. The instrument measures the difference in temperature between a sample and the reference which are exposed to the same heating schedule (same energy input). Phase transformations are either endothermic or exothermic. When the instrument detects that the sample is cooler (or warmer) than the reference, the difference is plotted on a delta temperature vs. temperature plot indicating a phase transformation. The information gained from DTA and DSC is similar. However, DSC is limited to a temperature of 580°C without special fittings and sample holders. DTA has the capability of going well above 1000°C with a platinum sample holder.

In order to characterize the hygroscopic nature of Cs_2MoOS_3, Fourier transform infrared spectroscopy (FTIR) was performed on a sample kept at ambient conditions and one dried at 125°C for 90 minutes. A small amount of the sample powder was ground together with KBr and subsequently analyzed. The diffuse reflectance infrared Fourier transform spectroscopy technique was employed using a Bruker Equinox 55 FT spectrometer with a liquid N_2-cooled MCT detector. A diffuse reflectance accessory (Spectra-Tech, Inc.) with an on-axis ellipsoidal mirror was utilized. The spectra were measured at 4 cm^{-1} resolution and 500 scans were co-added. Spectra were obtained by rationing the resulting spectra against a ground KBr background.

X-ray photoelectron spectroscopy was performed in a Surface Science Instruments M-probe XPS instruments operated at a base pressure of less than 1×10^{-8} Torr. Using an Al anode, a 400×1000 μm line spot, and a 25 eV pass energy, the full width at half maximum of the Au $4f_{7/2}$ peak was 0.85 eV. Binding energy positions were calibrated against the Au $4f_{7/2}$ peak at 83.9 eV, and energy separations were calibrated using the Cu 3s and Cu $2p_{3/2}$ peaks at 122.39 and 932.47 eV, respectively. The detection limit was approximately 2.0%. Peak fitting was performed to calculate chemical composition. Samples were typically sputtered for 1 minute prior to analysis to remove surface carbon and oxygen. Sputtering changed the positions of peaks randomly no more than ±0.75 eV. Samples were insulating, so an electron flood gun was used for charge neutralization.

Chemical analysis for some samples was performed for Cs, Mo, and S. Cesium was analyzed with flame emission, which had an accuracy of ±2 atom percent. Molybdenum was analyzed with atomic absorption, with an accuracy of ±0.9 atom %. Sulfur was analyzed with a standard wet chemical method by which the sample was combusted in O_2 to convert the S to SO_4. It was then titrated with a barium perchlorate solution to determine the amount of S in the sample. This method provides an accuracy of ±0.6 atom %.

A Rigaku D/max-B diffractometer equipped with a thin film attachment and a monochromator was used to perform x-ray diffraction. Phase identification was performed using a computer-based system which has embedded in it the Powder Diffraction File (PDF) library [7].

Micro-Raman spectroscopy was performed with a Renishaw Raman microscope. Laser light at 514.5 nm from an Ar^+ laser was used for excitation. The sample was calibrated with the Si peak at 520.7 cm^{-1}. In some cases, Raman spectroscopy was performed on a SPEX 1877 0.6 m triple monochromator, also using a 514.5 nm Ar^+ laser source. The results from the two different instruments are directly comparable when the data is normalized.

3. Results

3.1. Observed physical changes

At room temperature, the Cs_2MoOS_3 powder was bright red-orange and had a sharp sulfurous odor. When heated to 200°C, the color deepened and the odor became less intense. At 400°C, the material was completely black, and the odor was gone. At about 625°C, it began to turn gray, and by 650°C, Cs_2MoOS_3 began to melt into a yellow liquid. Both black solid and yellow liquid persisted to about 750°C, at which point the black solid disappeared and all that remained was the yellow liquid. Upon cooling below 500°C, the yellow liquid turned into a white solid with no odor. The melting points and colors of several possible decomposition/oxidation products of Cs_2MoOS_3 which may be useful in compound identification are shown in Table I, along with the same data for Cs_2MoOS_3, and the 800°C product.

TABLE I Possible Cs_2MoOS_3 oxidation products

Compound	Color	Thermal transitions (°C) (in air)	Reference
Cs_2MoOS_3	red-orange	m. p. 600+	DSC
800°C product	white	m. p. 503	DSC
Cs_2SO_4	white	m. p. 1010	(8)
MoS_2	black	oxidizes to MoO_3 at approx. 400	(9, 10)
MoO_3	pale green or yellow	sublimes at 700 m. p. 795	(8, 11)
Cs_2MoO_4	white	Phase trans. at 244 & 572 m. p. 1026.5	(DSC, 12, 13)
Cs_2O_2	pale yellow	m. p. 590	(8, 14, 15)
Cs_2O	orange	m. p. 495	(8, 14, 15)
Cs_3O	–	m. p. 180	(15)
CsO_2	–	m. p. 450	(15)
Cs_2O_3	chocolate brown	m. p. 400	(8, 15)

3.2. Thermal analysis

DSC analysis of Cs_2MoOS_3 is shown in Fig. 1. Four oxidation reactions were observed for Cs_2MoOS_3 below 600°C at approximately 220, 300, 475 and 538°C. These reactions could include the formation of Cs_2MoO_4, Cs_2SO_4, molybdenum oxides, cesium oxides, and complex cesium molybdates. There was no melting point detected up to 580°C. The DTA results are shown in Fig. 2. The arched shape of the spectrum is a function of the equipment and the reference material, and has no significance. The DTA results mirrored the DSC results up to 580°C. However, at approximately 600°C, a small melting peak was observed. This peak would not have appeared in the DSC spectrum since the instrument's upper temperature limit was 580°C. This peak is likely to be the melting of cesium oxides, which occur between 400–600°C [8, 14, 15]. It is important to note that the heating rate of 10°C/minute is not an equilibrium condition, and peaks will shift to temperatures that are higher than would occur at a slower heating rate.

TGA in air is shown in Fig. 3. It exhibited a weight loss (3.5%) between 100–300°C, then a weight gain occurred up to 102%, which persisted to about 850°C. At that temperature, the weight dropped off significantly with increasing temperature. The weight loss was likely the loss of water vapor and/or sulfur as SO_2 or SO_3 gas. A simple calculation shows that oxidation of Cs_2MoOS_3 to Cs_2SO_4 and either MoO_3 or MoS_2 would involve a weight gain. However, oxidation to Cs_2MoO_4 or cesium oxides and SO_x gas would result in a weight loss. Therefore, loss of SO_x gas below 300°C is likely only if these compounds were produced. The weight gain above 300°C was most likely due to the oxidation reaction of Cs_2MoOS_3 to Cs_2SO_4 and MoO_3 or MoS_2, since the other possible oxidation reactions would result in a weight loss. These reactions are consistent with the oxidation temperatures observed by DSC and DTA.

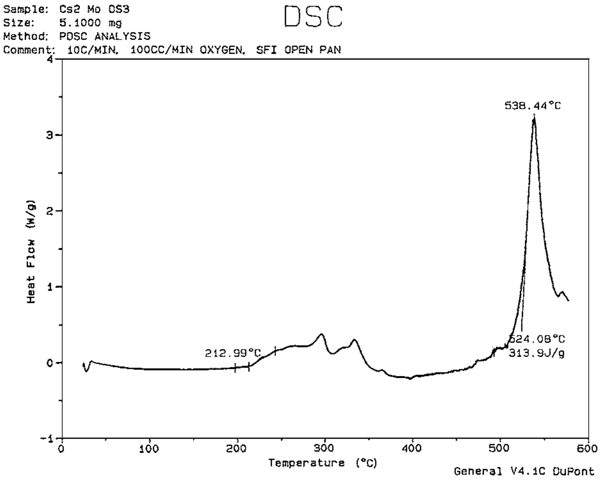

Figure 1 DSC spectrum of Cs_2MoOS_3 in oxygen (heating rate 10°C/minute).

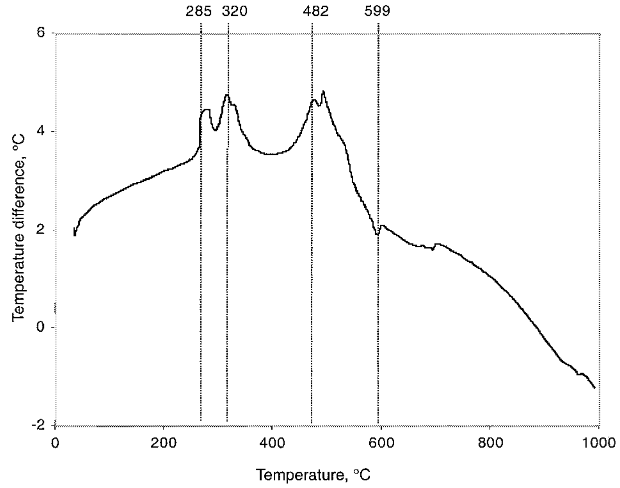

Figure 2 DTA spectrum of Cs_2MoOS_3 in air (heating rate 10°C/minute).

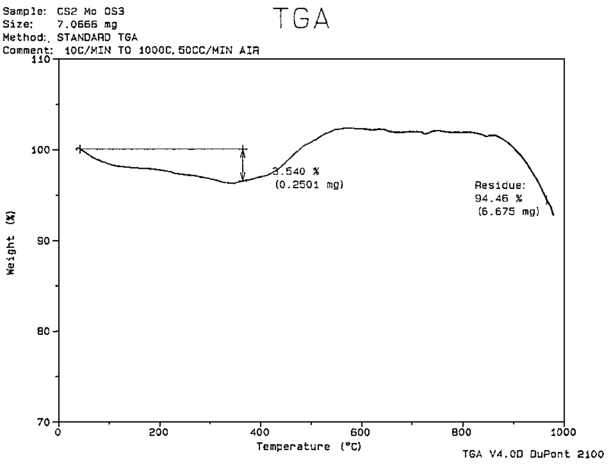

Figure 3 TGA spectrum of Cs_2MoOS_3 in air (heating rate 10°C/minute).

After heating to 800°C, a white oxidation product was formed. DSC was performed on this material. A sharp melting point was observed at about 503°C, and a small phase transition peak at 290°C. It did not oxidize below 600°C. The melt is likely due to cesium oxides, and the phase transition could be due to Cs_2MoO_4, which was observed by DSC to have a similar transition at 244°C.

3.3. Fourier transform infrared spectroscopy

The results of FTIR are shown in Fig. 4. The primary O–H stretch associated with adsorbed water occurs

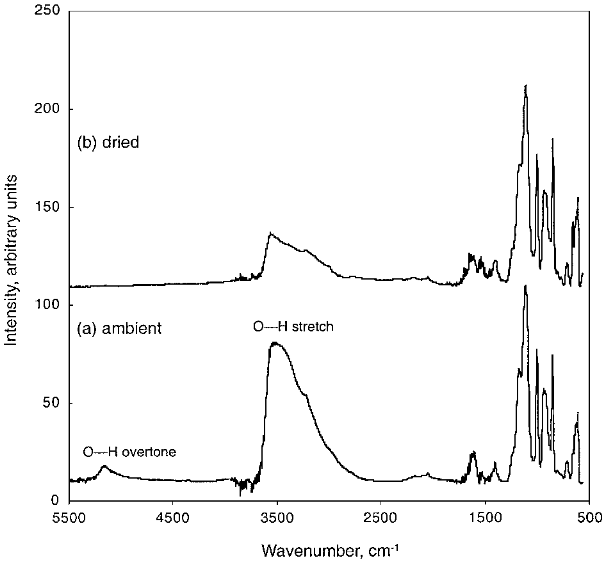

Figure 4 FTIR spectra of Cs_2MoOS_3 (a) stored in ambient conditions and (b) dried at 125°C for 90 minutes.

between 3700 and 3000 cm^{-1}. This stretch was present in the spectra for both the powder stored in ambient conditions (ambient powder) and the powder which was dried before analysis (dried powder). However, the peak height was over two times greater for the ambient powder than the dried powder, indicating approximately twice as much water was present. There was also an O–H overtone present at 5150 cm^{-1} in the spectrum for the ambient powder, which was absent in the spectrum for the dried powder. The spectra were otherwise nearly identical. Clearly, water was adsorbed by Cs_2MoOS_3, and the powder can be considered slightly hygroscopic. These results also confirm that at least part of the weight loss observed by TGA was due to water evaporation.

3.4. X-ray photoelectron spectroscopy

Chemical compositions as determined by XPS for Cs_2MoOS_3 heated to various temperatures is shown in Table II. The XPS data is reported without inclusion of carbon, as it is a contaminant from the environment and was easily removed after a few seconds of sputtering. Carbon was only present when no sputtering was performed. All the O was included, as it was extremely difficult to differentiate O contamination from oxygen contained in Cs_2MoOS_3. Surface sputtering was expected to remove most of the surface O contamination as well as the C contamination. Ascertaining the atomic concentration of sulfur was complex. The difficulty was due to the proximity of the molybdenum $3d_{3/2}$ and $3d_{5/2}$ peaks (230 and 227 eV) and the cesium 4s peak (231 eV) to the sulfur 2s peak at 229 eV. The sulfur 2p peaks at 164/165 eV are between the cesium $4p_{3/2}$ and $4p_{1/2}$ peaks at 162 and 172 eV, respectively. The sulfur peak chosen for analysis was the 2p peak at 164/165 eV. The peak was deconvoluted assuming that the cesium peaks remained a constant 10 eV apart. Peak shifting, broadening, and asymmetry toward lower binding energy were common due to sample charging and charge neutralization using an electron flood gun.

TABLE II Atom percent compositions of Cs_2MoOS_3 heated to 800°C, as determined by XPS

	Atomic percent composition			
Temperature (°C)	Cs	Mo	O	S
calculated, stoichiometric	28.6	14.3	14.3	42.9
25	29.1 (51)	17.1 (20)	26.8	27.0 (18)
200	36.0	12.0	43.1	8.9
400	41.4 (53)	6.1 (20)	51.0	1.5 (18)
600	45.0 (54)	5.3 (20)	49.7	0 (17)
700	32.5 (57)	7.1 (24)	60.4	0 (4)
800	14.8 (29)	17.9 (37)	67.4	0 (0)

Parantheses ( ) indicate chemical composition determined by other methods: CS—flame emission, Mo—atomic absorption, S—titration.

Notice that even at room temperature the Cs_2MoOS_3 did not have the expected stoichiometric composition; it was low in sulfur and high in oxygen. As the powder was heated to increasing temperature, the percentage of oxygen increased, indicating that the material oxidized. The percentage of sulfur decreased with temperature and appeared to be nearly zero by 400°C. The concentration of Mo decreased between 400–600°C, and then abruptly increased at 800°C. Also, the amount of Cs at first appeared to increase, and then abruptly dropped off. Examination of the relative elemental ratios revealed that both the Cs : O and the Mo : O ratios continuously dropped, but that the Cs : Mo ratio first increased, then decreased.

Titration of sulfate confirmed the absence of S after heating to 700 and 800°C, but found a significant amount of S in samples heated to 600°C or below −17 atom % in the 600°C sample. Twenty atom percent Mo was detected by atomic absorption in the 600°C sample. One likely explanation for the discrepancy is that cesium oxides were formed on the sample surface, then melted. The liquid may cover the surface sufficiently to obscure the other elements from XPS analysis. XPS depths profiling of one of these samples indicated that the cesium oxide depth was approximately 40 nm. As the heating temperature further increased, all of the material melted, allowing the Mo and S to be detected, and reducing the apparent percentage of Cs. Cesium sulfate was determined by DTA to be stable up to its melting point of 1010°C [8], and it would be expected to be present in samples heated to 600°C. Between 600 and 700°C, sulfur apparently evolves, leaving behind cesium oxides. This reaction was not detected in DTA, but the absence of sulfur in the elevated temperature samples dictates that the reaction must take place.

3.5. X-ray diffraction

Fig. 5 contains XRD spectra from $2\theta = 10$ to 45° for Cs_2MoOS_3 heated in air to 800°C. Above $2\theta = 45°$, the relative intensity of the peaks was very small. Each spectrum was compared to standards and the Powder Diffraction File [7]. Fig. 6 compares Cs_2MoOS_3 to the PDF spectrum for Cs_2MoOS_3. The as-received material was different from the standard, highlighting that the Cs_2MoOS_3 used in these experiments did not have the crystal structure described in the literature [2, 3]. In

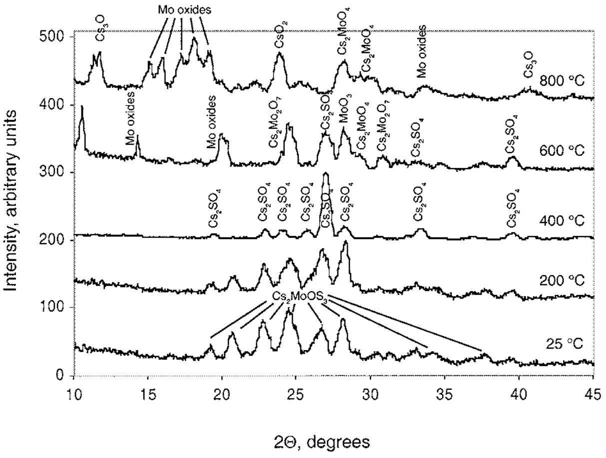

Figure 5 XRD spectra for Cs_2MoOS_3 powder heated in air.

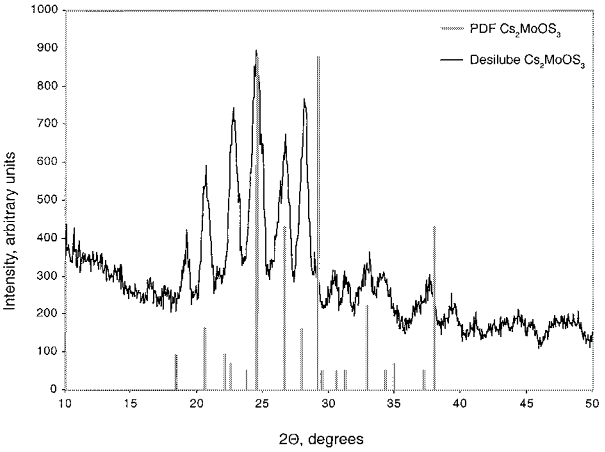

Figure 6 Comparison of XRD spectrum of Desilube's Cs_2MoOS_3 powder and Powder, Diffraction File standard diffraction pattern for Cs_2MoOS_3.

fact, analysis of the XRD patterns suggested that the as-received powder most likely also included cesium molybdates, molybdenum oxides, and Cs_2SO_4.

The XRD spectra of the room temperature and the 200°C material were virtually identical. By 400°C, the crystal structure changed, and looked nearly identical to Cs_2SO_4, with some MoO_3 present. By 600°C, some of the peaks associated with Cs_2SO_4 and MoO_3 remained, but there was also evidence of a complex cesium molybdate (most likely $Cs_2Mo_2O_7$), cesium oxides, and MoS_2. At 800°C, the materials identified included Cs_2MoO_4, cesium oxides, molybdenum oxides, and other cesium molybdenum oxides. There are 13 molybdenum oxides, 12 cesium oxides, and 10 cesium molybdenum oxides in the Powder Diffraction File [7], and the heat-treated material could be a combination of any or all of these. Therefore, an unambiguous assignment could not be made.

3.6. Raman spectroscopy

Raman spectra of Cs_2MoOS_3 heated in air to 800°C are shown in Fig. 7. Individual spectra were compared to standards: Cs_2SO_4, Cs_2MoO_4, MoO_3 and MoS_2. The room temperature spectrum indicated that the as-received powder contained Cs_2SO_4, MoS_2, and Cs_2MoO_4, confirming that the as-received material was not pure. Only the peaks at 913 and 941 cm^{-1} were unique to Cs_2MoOS_3. Again, the 200°C spectrum was nearly identical to that of the room temperature material. Raman confirmed that the 400°C material was nearly identical to Cs_2SO_4, with some residual MoS_2. Upon close inspection, peaks associated with Cs_2MoO_4 were also visible in the 400°C spectrum, but were very small compared to those of Cs_2SO_4 and are not apparent in Fig. 7. The material heated to 600°C showed peaks for Cs_2SO_4 and MoS_2, but displayed the presence of Cs_2MoO_4 more clearly. At 700°C, the Raman spectrum resembled that of Cs_2MoO_4 with some residual Cs_2SO_4, but the MoS_2 spectral features were no longer apparent. Finally, by 800°C, a peak was present at approximately 900 cm^{-1} which is a possible match to Cs_2MoO_4, but the remaining peaks could not be identified. Based on the XRD results, these could be cesium oxides, molybdenum oxides, and complex cesium molybdenum oxides, for which neither standards nor literature values were available.

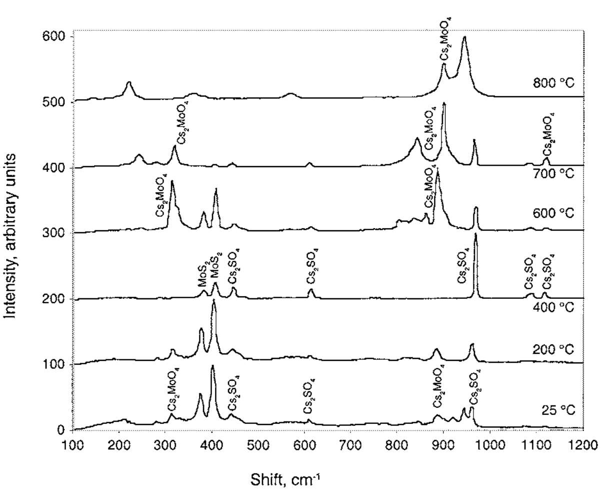

Figure 7 Raman spectra for Cs_2MoOS_3 powder heated in air.

4. Discussion

Based upon the reaction temperatures identified by thermal analysis, the colors of the resulting compounds, and the oxidation products identified by XPS, micro-Raman scattering, and XRD of the heated powders, the following reaction path is postulated for Desilube's Cs_2MoOS_3. The starting material was likely a mixture of approximately 1/2 Cs_2MoOS_3, 1/4 Cs_2SO_4, and the remainder was cesium molybdates, molybdenum oxides, and MoS_2. Between approximately 300 and 400°C, Cs_2MoOS_3 began to decompose, forming Cs_2SO_4 and MoS_2, which is black and would account for the black color observed after heating to 400°C. Although TGA showed a weight loss to 300°C, primarily Cs_2SO_4 was identified by XRD and Raman at 400°C, and little loss of S was detected by the titration method. Therefore, the weight loss must be entirely due to loss of water vapor. This is substantiated by the loss of water observed by FTIR when the material was heated above the boiling point of water.

Between 400–600°C, the Cs_2MoOS_3 continued to oxidize, also forming cesium molybdates and

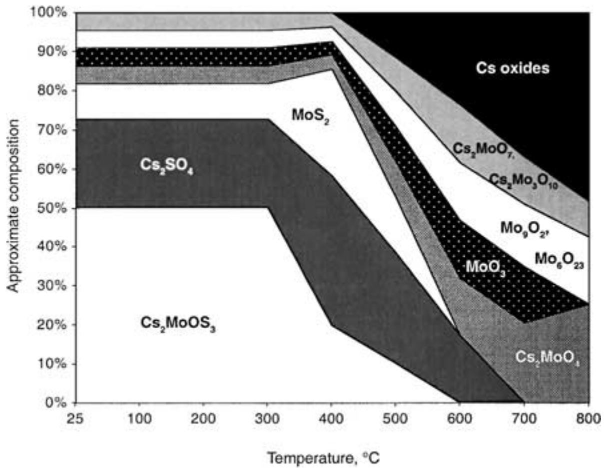

Figure 8 Thermal model for Cs_2MoOS_3 oxidation.

molybdenum oxides. In this temperature range, Cs_2SO_4 began to oxidize to cesium oxides and SO_x gas. The cesium oxides melted almost immediately upon formation, and these are likely the yellow liquid observed at 625°C and above. Also, MoS_2 oxidized to MoO_3, which is also yellow. As the temperature rose, complex cesium molybdates partially oxidized to additional Cs_2MoO_4 and molybdenum oxides. Above 600°C, the oxidation of Cs_2SO_4 was complete, and starting at 700°C, MoO_3 sublimed. Upon cooling form 800°C, the mixture consisted of approximately 1/2 cesium oxides (which can be light-colored), 1/4 Cs_2MoO_4 (which is white), and the remaining components were complex cesium molybdates and molybdenum oxides. Fig. 8 contains a schematic of the probable oxidation products of Desilube's Cs_2MoOS_3 after heating in air to the designated temperature.

Previous researchers have questioned whether MoS_2 was a decomposition product of Cs_2MoOS_3 and if it contributes to lubrication [16]. MoS_2 is a superior lubricant from room temperature to approximately 400°C, where it begins to oxidize to MoO_3 [9]. This research confirmed the presence of MoS_2 in the starting powder. It is also a likely decomposition product starting above 300°C. However, it is present in small quantities which may not be sufficient to provide lubrication.

Between approximately 500–700°C, several compounds were identified which are lubricious in this temperature regime. Molybdates, such as Cs_2MoO_4, and soft oxides, such as MoO_3, are known to have increasing lubricity as the temperature approaches their respective melting points [17]. For example, $PbMoO_4$, which has a melting point of 1065°C, has a coefficient of friction of approximately 0.50 at room temperature on high temperature alloy substrates. The friction coefficient drops to 0.33 at 704°C. Molybdenum trioxide has a coefficient of friction of about 0.2 near 700°C. Some of the cesium oxides could also act as lubricants between the formation temperature and the melting temperature between approximately 400–500°C. Assuming there is no chemical interaction with the substrate, these oxides are the likely lubricants at elevated temperature.

The as-received material appeared to melt over a range of temperature between 650–750°C as the various oxidation products reach their melting points. The liquid could have Cs_2MoO_4 and other high melting point solids dissolved or suspended in it. It is likely that lubrication is provided by a liquid at 750°C or greater, and would be relatively ineffective for boundary lubrication.

5. Conclusion

In-depth study of the thermo-oxidative stability of Cs_2MoOS_3 has clarified the complicated oxidation reactions of this potential high temperature lubricant. The as-received powder did not have the stoichiometric composition nor the crystal structure published in the literature for Cs_2MoOS_3. In addition, Cs_2MoOS_3 is slightly hygroscopic. At moderate temperatures (300 to 600°C), the primary reaction products were Cs_2MoO_4 and other cesium molybdates, Cs_2SO_4, cesium oxides, and MoO_3 and other molybdenum oxides. The cesium oxides melted between 400–600°C, coating the samples and making analysis more difficult. The lubricant was at least partially liquid at about 650°C and above. At temperatures of 700°C and above, the compounds present were cesium oxides, molybdenum oxides, Cs_2MoO_4, and other cesium molybdates. Cesium molybdate and MoO_3 may be good lubricants at temperatures between 500–700°C. Above 750°C, the material is likely to be completely liquid and a poor lubricant, assuming there is no interaction with the substrate. Since interaction with silicon nitride substrates has been indicated, analysis of the thermal chemistry of Cs_2MoOS_3 in the presence of Si_3N_4 will be addressed in future research.

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