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Thermal chemistry of a high temperature solid lubricant, cesium oxythiomolybdate

Part II *Thermo-oxidative stability of Cs_2MoOS_3/Si_3N_4 mixtures*

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Cesium oxythiomolybdate (Cs_2MoOS_3) may be an excellent high temperature lubricant, providing a friction coefficient below 0.2 at 650°C. However, oxidation products provide the lubrication above 400°C. Lubricant effectiveness depends strongly on the composition of the substrate materials in contact, such as Si_3N_4, suggesting that tribochemical and/or thermal reactions at the interface produce new compounds. The thermo-oxidative stability of Cs_2MoOS_3/Si_3N_4 and Cs_2MoOS_3/SiO_2 mixtures have been evaluated between room temperature and 1000°C in air. The transition temperatures and oxidation products were identified. The thermal chemistry of Cs_2MoOS_3/Si_3N_4 mixtures was significantly different than that of Cs_2MoOS_3 alone, largely due to the oxidation of Si_3N_4 to glassy SiO_2. Cesium oxythiomolybdate formed cesium oxides, which melted below 600°C. As SiO_2 is formed, the cesium oxides diffused into it, creating a cesium silicate glass. Also, Cs_2MoO_4 was preferentially formed over complex cesium molybdates and molybdenum oxides. In a tribological application, Cs_2MoO_4, oxides, and cesium silicate glass may be formed at contacting interfaces from Cs_2MoOS_3 films deposited on Si_3N_4 substrates. Lubrication would be provided as the shear strength of these compounds decreases with increasing temperature.

1. Introduction and background

Ideally, it would be desirable to operate a silicon nitride bearing at temperatures up to 815°C with a coefficient of friction below 0.2 for several hours, but conventional solid lubricants such as graphite and MoS_2 are not capable of performing at that temperature for an extended period of time. Cs_2MoOS_3 has been shown to be an effective lubricant, providing a friction coefficient below 0.2 at 650°C [1]. However, it has been noted that the material oxidizes and decomposes during high temperature testing.

Oxidation of Cs_2MoOS_3 alone has been studied by us previously [2]. It was discovered that the commercial grade Cs_2MoOS_3 powder used in this and previous studies was impure, consisting of approximately 1/2 Cs_2MoOS_3, 1/4 Cs_2SO_4, with the remainder cesium molybdates, molybdenum oxides and MoS_2. Between 300–400°C, Cs_2MoOS_3 began to decompose, forming Cs_2SO_4 and MoS_2. Between 400–600°C, the Cs_2MoOS_3 continued to oxidize, also forming cesium molybdates and molybdenum oxides. The Cs_2SO_4 began to oxidize to cesium oxides and SO_x gas. The cesium oxides melted almost immediately upon formation. Also, MoS_2 oxidized to MoO_3. The complex cesium molybdates partially oxidized to additional Cs_2MoO_4 and molybdenum oxides. At 650°C, the material began to melt, but some solid material was present up to approximately 750°C, where the material was completely liquid. Starting at 700°C, MoO_3 sublimed. Upon cooling from 800°C, the mixture consisted of approximately 1/2 cesium oxides, 1/4 Cs_2MoO_4, and the remaining components were complex cesium molybdates and molybdenum oxides (e. g. $Cs_2Mo_2O_7$ and Mo_9O_2).

Some researchers have concluded that Cs_2MoOS_3 may oxidize by a different mechanism in the presence of Si_3N_4 substrates. King and Forster theorized that there may be some lubricant/substrate interaction, based on detection of SiO_2 in wear scars of Cs_2MoOS_3 applied in a Na_2SiO_3 binder on silicon nitride substrates [1]. Other investigations have found superior performance of similar cesium-based lubricants on silicon nitride substrates as compared to high temperature steels [3].

An understanding of the oxidation of Si_3N_4 is important to the study of its interaction with Cs_2MoOS_3. Generally, Si_3N_4 reacts with oxygen at temperatures above 700°C to form a protective scale of SiO_2 [4–7]. Below 1350°C, the reaction occurs at the nitride/oxide interface with the formation of amorphous SiO_2 and nitrogen gas:

$$Si_3N_4(s) + 3O_2(g) \rightarrow 3SiO_2(s) + 2N_2(g) \quad (1)$$

Nitrogen diffuses to the surface and is lost to the atmosphere. The scale is amorphous at the beginning of the oxidation and at low temperatures, and tends to crystallize at longer times, higher temperatures, and in the presence of impurities [6]. To make a structural ceramic, pure Si_3N_4 is typically combined with a few percent metal oxides such as yttria or magnesia to aid in sintering and improve high temperature mechanical properties [8]. Therefore, pure Si_3N_4 oxidizes more slowly than a structural silicon nitride. Cristobalite (a crystalline form of SiO_2 which can be formed by devitrification of SiO_2 glass) has been observed on Si_3N_4 surfaces at temperatures as low as 750°C. This suggests that additive cations reduce the viscosity of the glassy layer, lowering the devitrification temperature. In summary, any lubricant used on Si_3N_4 below 1350°C could interact with the smooth, amorphous silica layer on the surface, and reduce the devitrification temperature of the amorphous silica.

The purpose of this research was to study the thermal chemistry of Cs_2MoOS_3/Si_3N_4 mixtures to determine the reaction products in the presence of air, and to assess the products as potential high temperature lubricants.

2. Experimental

In order to study the thermal reactions between cesium oxythiomolybdate and silicon nitride in air, the powders were mixed and heated together in an oven and analyzed using x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), and Raman scattering. Mixtures of Cs_2MoOS_3 and SiO_2 were also evaluated since it is likely that the lubricant would interact with the oxide on the surface of a Si_3N_4 substrate. Cs_2MoOS_3 powder was obtained from Desilube Corporation, mixed in a 50/50 ratio by atomic weight with either Si_3N_4 or SiO_2 from Alfa Products, with a reported purity of 99.9%. As discussed in a prior report, the Cs_2MoOS_3 powders were not pure [2]. Other powders used as standards (Cs_2SiO_3, MoS_2, MoO_3, Cs_2SO_4, Cs_2MoO_4) were also obtained from Alfa Products and were 99.9% pure.

Cold-pressed pellets of mixed powders of Cs_2MoOS_3 and Si_3N_4 were placed in a porcelain crucible and heated to 200, 400, 600, and 800°C for 6 hours in a Ney 3-550 programmable oven. Samples were held in ambient conditions until analysis was performed. In order to drive any possible chemical reactions to completion, some Cs_2MoOS_3/Si_3N_4 and Cs_2MoOS_3/SiO_2 mixtures were heated in porcelain crucibles to 1000°C for 40 hours. All samples were analyzed with XPS, XRD, and Raman spectroscopy.

X-ray photoelectron spectroscopy was performed in a Surface Science Instruments M-probe XPS instrument 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. 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, and had an accuracy of ±2 atom%. Molybdenum was analyzed with atomic absorption, and had 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 [9]. 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.

Differential Thermal Analysis (DTA) was performed on a DuPont Instruments 910 DSC fitted with a DTA 1600 unit. Samples of Cs_2MoOS_3, Si_3N_4, SiO_2, and mixtures of Cs_2MoOS_3/Si_3N_4 and Cs_2MoOS_3/SiO_2 were heated from room temperature to 1000°C at a rate of 10°C per minute, unless otherwise noted. The analysis was performed in ambient air.

3. Results

3.1. X-ray photoelectron spectroscopy

XPS was performed on all mixed powders before and after heating to determine the chemical composition. Determining the atomic concentrations of N, Mo, and S was difficult due to peak overlap. The Mo $3d_{3/2}$ and $3d_{5/2}$ peaks (230 and 227 eV) nearly overlap the Cs 4s peak (231 eV) and the S 2s peak (229 eV). Also, the S 2p peaks at 164/165 eV are between the Cs $4p_{3/2}$ and $4p_{1/2}$ peaks at 162 and 172 eV, respectively. The S peak chosen for analysis was the 2p peak. The peaks were deconvoluted knowing that the cesium peaks remained a constant 10 eV apart. The N 1s peak at 399 eV is close to the Mo $2p_{3/2}$ peak at 393 eV, complicating the analysis of N and Mo. The Mo peak chosen for analysis was the $3p_{1/2}$ peak at 410 eV. Peak shifting, broadening, and asymmetry toward lower binding energy were common due to sample charging and charge neutralization with the electron flood gun.

The chemical compositions of Cs_2MoOS_3/Si_3N_4 mixtures heated to various temperatures as determined by XPS are shown in Table I. Also included in the table are the results from chemical analysis by the other

TABLE I Atom percent compositions of Cs_2MoOS_3, Cs_2MoOS_3/Si_3N_4 mixtures, and Cs_2MoOS_3/SiO_2 mixtures heated in air to 1000°C, as determined by XPS

		Atomic percent composition					
Material	Temperature, °C	Cs	Mo	O	S	Si	N
Cs_2MoOS_3	calculated, stoichiometric	28.6	14.3	14.3	42.9	–	–
Cs_2MoOS_3	25	29.1 (51)	17.1 (20)	26.8	27.0 (18)	–	–
Cs_2MoOS_3	200	36.0	12.0	43.1	8.9	–	–
Cs_2MoOS_3	400	41.4 (53)	6.1 (20)	51.0	1.5 (18)	–	–
Cs_2MoOS_3	600	45.0 (54)	5.3 (20)	49.7	0 (17)	–	–
Cs_2MoOS_3	700	32.5 (57)	7.1 (24)	60.4	0 (4)	–	–
Cs_2MoOS_3	800	14.8 (29)	17.9 (37)	67.4	0 (0)	–	–
Cs_2MoOS_3/Si_3N_4	25	6.7	11.5	29.0	1.6	25.6	25.6
Cs_2MoOS_3/Si_3N_4	200	5.4	9.2	31.1	1.1	27.4	25.9
Cs_2MoOS_3/Si_3N_4	400	9.9	7.0	39.6	0	22.0	21.5
Cs_2MoOS_3/Si_3N_4	600	14.9 (20)	5.7 (9)	48.8	0 (3)	9.8	20.8
Cs_2MoOS_3/Si_3N_4	700	12.7	7.1	73.5	0	6.7	0
Cs_2MoOS_3/Si_3N_4	800	9.2	7.2	47.2	0	16.0	20.5
Cs_2MoOS_3/Si_3N_4	1000	9.9	4.9	62.5	0	22.7	0
Cs_2MoOS_3/SiO_2	25	7.6	2.2	68.7	0	21.5	–
Cs_2MoOS_3/SiO_2	1000	9.0	2.0	65.7	0	23.3	–

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

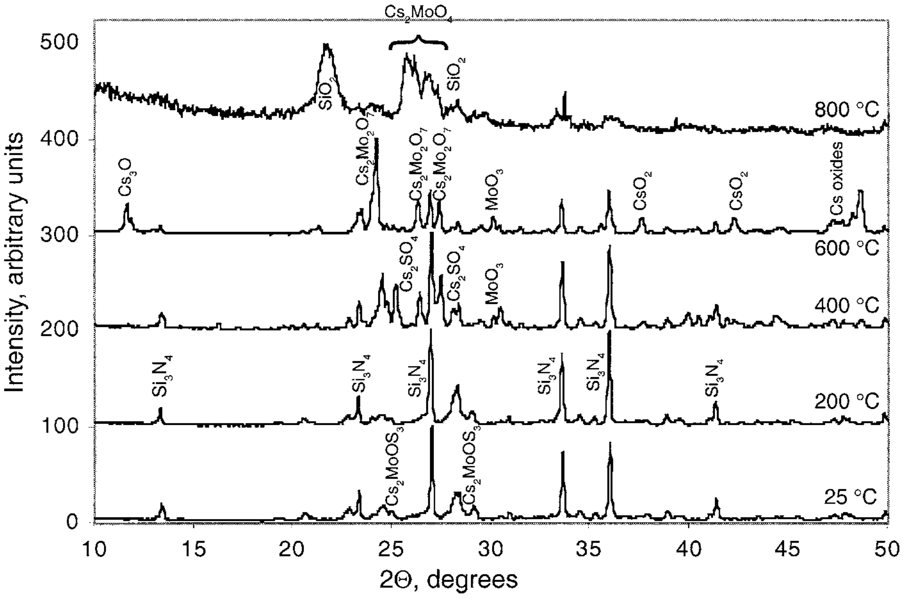

Figure 1 XRD spectra of Cs_2MoOS_3/Si_3N_4 mixture heated in air.

methods. The data is reported without inclusion of C, 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 is extremely difficult to differentiate O contamination from oxygen contained in Cs_2MoOS_3.

Above 200°C the percentage of oxygen generally increased, and S was undetectable with XPS. The amount of Cs increased to 600°C, then decreased to 800°C. This effect was also seen for Cs in the pure powders [2]. It was discovered that as the cesium oxides were formed at the surface of the pellet, they melted, obscuring the other elements below. This premise was confirmed with bulk chemical analysis of the mixture after heat-treatment at 600°C. Sulfur and Mo were present in higher amounts than detected by XPS (3% and 9%, respectively). However, the amount of S should have been higher (about 9%) if oxidation of the mixture was identical to that of the pure powder. Nitrogen was not detected with XPS for the mixture heated to 1000°C for 40 hours. It is likely that the surfaces of the silicon nitride particles oxidized completely to SiO_2 when kept at temperature for this length of time.

3.2. X-ray diffraction

XRD spectra of Cs_2MoOS_3/Si_3N_4 mixtures heated to various temperatures are shown in Fig. 1. The peaks observed at temperatures as high as 400°C are either Si_3N_4, the starting Cs_2MoOS_3 powder, or Cs_2SO_4. Analysis revealed that at 600°C, the mixture most likely contained cesium molybdates, Si_3N_4, cesium oxides, Cs_2SO_4, and MoO_3. After heating to 800°C, SiO_2 and Cs_2MoO_4 were the only constituents detected. The composition of Cs_2MoOS_3 alone after heating to

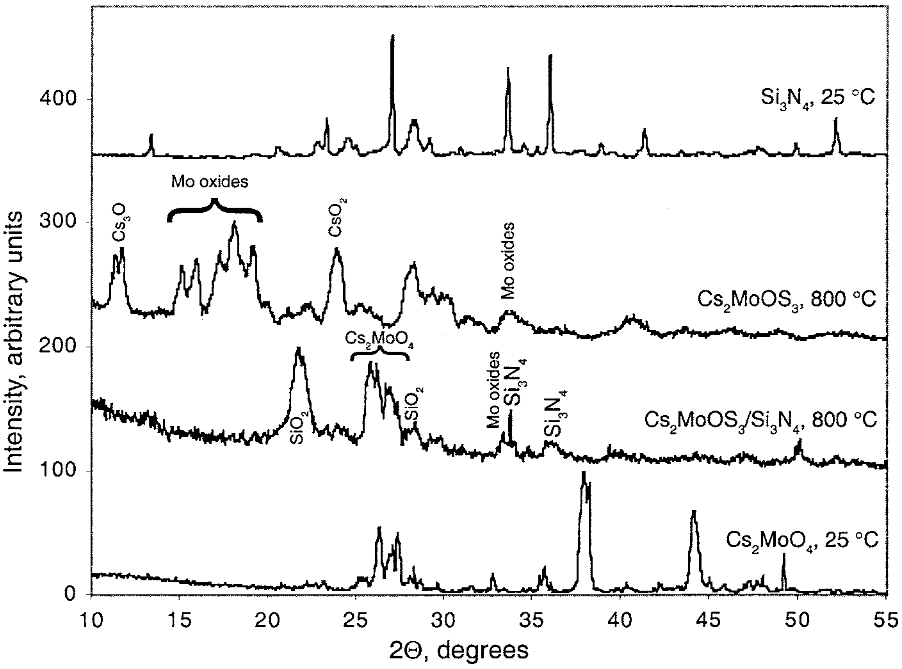

Figure 2 Comparison of XRD spectra of Cs_2MoOS_3 powder and Cs_2MoOS_3/Si_3N_4 mixture heated in air.

800°C and cooling to room temperature was similar except crystalline cesium oxides and complex cesium molybdates were also present [2]. Comparing spectra of Cs_2MoOS_3/Si_3N_4 mixtures, Cs_2MoOS_3, and Si_3N_4 after heat-treatment at 800°C, it is clear that the mixture was not simply a superposition of the individual components, as shown in Fig. 2. Formation of Cs_2MoO_4 over crystalline molybdenum oxides and cesium oxides is favored in the mixture at 800°C. The spectra of heated Cs_2MoOS_3 and Cs_2MoOS_3/Si_3N_4 mixtures are complicated, and therefore compound identification may not be unique. Also, the presence of an amorphous phase would not be detected with XRD.

3.3. Raman spectroscopy

Raman spectra of Cs_2MoOS_3/Si_3N_4 mixtures heated to 800°C were compared to Cs_2MoOS_3 and pure Si_3N_4. All of the spectra at 400°C and above were dominated by a strong peak at 520 cm^{-1}. The Raman spectrum of the Si_3N_4 powder alone also showed this peak, but it was not present in the Raman spectrum of a commercial Si_3N_4 solid disk. It was due to elemental Si, which could remain after incomplete reaction during the manufacture of the Si_3N_4 powder.

To examine the impact of the elemental Si on the mixed powder results, additional analysis was undertaken on the Si_3N_4 powder. XPS revealed that the atomic composition of the powder was 47.6% Si and 52.4% N, close to the stoichiometric composition (42.8% Si and 57.1% N) and with less excess Si than a commercial Si_3N_4 solid disk (54.6% Si and 45.4% N). In addition, the Si 2p peak would ordinarily occur at approximately 102 eV for Si_3N_4, and at 99 eV for elemental Si [10]. The Si 2p peak appeared at 101.6 eV, indicating that the sample was nearly pure Si_3N_4. Finally, elemental Si was not identified in XRD spectra of the mixtures at room temperature. This evidence led to the conclusion that a small amount of Si, probably less than 2 atomic%, was present in the Si_3N_4 powder, and would not significantly impact the results.

3.4. Long term heat-treatment of Cs_2MoOS_3/Si_3N_4 and Cs_2MoOS_3/SiO_2 mixtures

XPS results for Cs_2MoOS_3/Si_3N_4 and Cs_2MoOS_3/SiO_2 mixtures heated to 1000°C for 40 hours are shown in Table I. Primarily Si and O with a small percentage of Cs and Mo were observed for both mixtures. This was not surprising, considering that Si_3N_4 begins to oxidize in air at temperatures above 700°C, or lower in the presence of impurities [8]. The XRD data for these mixtures after heating to 1000°C were also nearly identical. The mixtures revealed the presence of only the cristobalite form of SiO_2 and Cs_2MoO_4. Fig. 3 shows these spectra. It is interesting to notice that the materials did not completely melt at temperatures as high as 1000°C; however, the powders sintered into a solid piece at temperatures as low as 600°C, indicating that some melting or diffusion was taking place. Pure Cs_2MoOS_3 powders melted completely at 750°C.

Raman analysis of powders heated to 1000°C was quite different than that of the powders heated to lower temperatures for shorter times. The spectra are shown in Fig. 4. Raman spectra of both the Cs_2MoOS_3/Si_3N_4 and Cs_2MoOS_3/SiO_2 mixtures were, again, nearly identical. The dominating silicon peak at 520 cm^{-1} disappeared, and was replaced by several broad peaks between 200–450 cm^{-1} and 800–1000 cm^{-1}. While standards for comparison were limited, the heated mixtures most closely resembled Cs_2MoO_4. The small peaks at 292, 777, and 1077 cm^{-1} closely matched those found in the literature for β-cristobalite [11], which is stable above 266°C. At fast cooling rates, metastable β-cristobalite would be observed at room temperature.

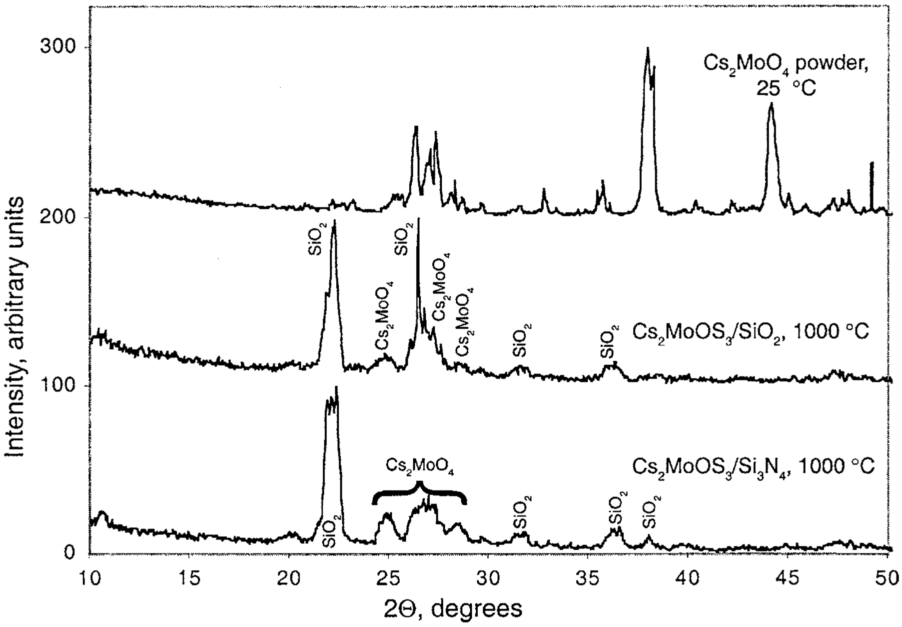

Figure 3 XRD spectra of Cs_2MoOS_3 mixtures heated in air to 1000°C.

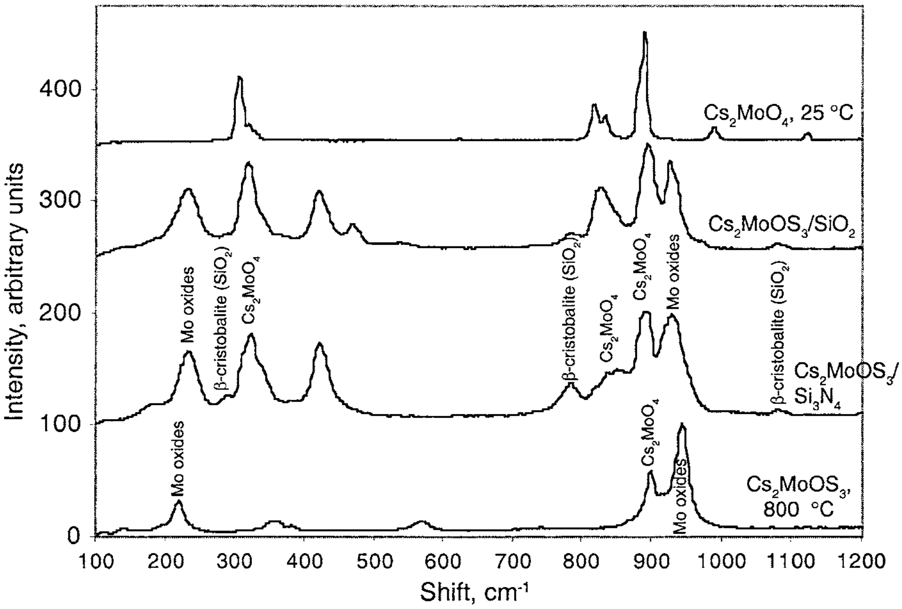

Figure 4 Raman spectra of Cs_2MoOS_3 and mixtures heated in air to 1000°C.

The presence of various impurities, e.g. Ca, Mg, Na, K, etc., cause devitrification of the glass to β-cristobalite [12]. By analogy, Cs might also stabilize β-cristobalite. Other standards which were used for comparison were Cs_2SiO_3, MoS_2, MoO_3, Cs_2SO_4, and Si_3N_4 powder. The 1000°C powder mixtures did not match any of these well. There were two peaks at 229 and 925 cm^{-1} which also occurred in Cs_2MoOS_3 after it was heated to 800°C alone. These are probably associated with complex molybdenum oxides. There was a peak at 418 cm^{-1} which was unidentified. It was not due to Si_3N_4 or any common crystalline form of SiO_2. Nor was it likely due to a known decomposition product of Cs_2MoOS_3 alone, since it did not appear in the high temperature Raman spectrum of that material. Therefore, the peak must be due to a product made only when Si_3N_4 and Cs_2MoOS_3 are heated together and for which references and literature data were not available. The peak is most likely due to a substoichiometric crystalline form of cesium silicate.

The presence of cristobalite after heating to 1000°C for 40 hours indicates that at shorter times at lower temperatures, glassy SiO_2 exists in Cs_2MoOS_3/Si_3N_4 and Cs_2MoOS_3/SiO_2 mixtures. We surmise that in air at temperatures of less than 800°C for up to 10 hours, Cs_2MoOS_3 in combination with Si_3N_4 oxidizes to Cs_2MoO_4, cesium silicate glass, and molybdenum oxides.

3.5. Differential thermal analysis

Fig. 5 shows the results of DTA for SiO_2, Si_3N_4, Cs_2MoOS_3, Cs_2MoOS_3/Si_3N_4, and Cs_2MoOS_3/SiO_2. The arched shape of the spectra was a function of the

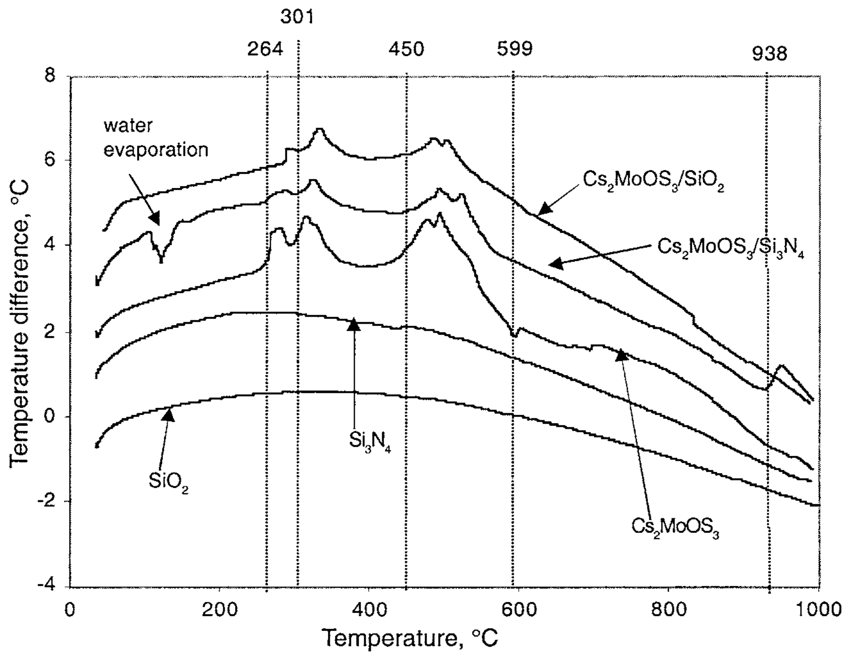

Figure 5 DTA spectra of Cs_2MoOS_3 and mixtures (heating rate 10°C/min).

equipment and the reference material, and had no significance. Neither SiO_2 nor Si_3N_4 appeared to undergo any phase changes or chemical reactions in air over the temperature range of 25 to 1000°C. As discussed earlier, Si_3N_4 begins to oxidize at approximately 700°C. That reaction was not observed in this spectrum for two reasons. First, the heating rate was too high and the oxidation rate was too low for observation. Secondly, oxidation takes place at the Si_3N_4 particle surfaces, and the extent of that reaction was too small to observe.

Cesium oxythiomolybdate alone undergoes five transformations, at 264, 301, 450, 490, and 599°C. The first four were oxidation reactions, which include the formation of Cs_2MoO_4, Cs_2SO_4, molybdenum oxides, other cesium molybdates. But the final transition at 600°C was melting. We attributed this melting to cesium oxides, which have melting points between 400 to 600°C [2, 13].

The scans for the mixtures were nearly identical to the pure material, with the exception that the melting of cesium oxides was not detected. Cesium oxides are present, as seen in XRD, but the high heating rate and low concentration in the mixture may prevent the melting from being observed. Also, an exotherm at an onset temperature of about 938°C was seen for the silicon nitride mixture, which may be a chemical reaction or phase transition. The endotherm shown between 110 and 150°C in that scan was evaporation of water which was introduced into the sample holder before the test. While DTA did not show a chemical reaction taking place in the mixtures over the proposed application temperature range (25 to 800°C), it is important to note that the heating rate of 10°C/minute is not an equilibrium condition, and thermal transition temperatures appear higher than they would at thermal equilibrium.

To further investigate any possible melting or chemical reaction between Cs_2MoOS_3 and Si_3N_4, DTA was performed at 1°C/minute for this mixture. Fig. 6 shows the 10°C/minute and the 1°C/minute scans of the mixture, and compares them to pure Cs_2MoOS_3. The background for the slower scan is different since the reference material was changed, but does not effect the results. All of the peaks for the mixture were observed at lower temperature at the slower heating rate. The cesium oxide melting peak was discernible at 548°C. Also apparent was a transition which is likely to be a glass transition, at approximately 700°C. The high temperature exotherm seen at the faster heating rate (at 938°C) was significantly lower at 826°C, which is nearer tribological application temperatures. Assuming a glass was formed, the transition at 826°C is likely to be devitrification.

4. Discussion

As reviewed in the introduction, the commercially available Cs_2MoOS_3 powder produced by Desilube was previously found to be impure. We also discovered that oxidation of this material alone was complicated, leading to the formation of cesium oxides, molybdenum oxides, and Cs_2MoO_4. In this study, we found that oxidation of Cs_2MoOS_3 in the presence of Si_3N_4 was even more complex. The reaction path is postulated as follows. Starting at about 300°C, Cs_2MoOS_3 began to oxidize to Cs_2SO_4 and, most likely, MoO_3 since MoS_2 was not detected by XRD. In contrast, MoO_3 was *not* detected in the powder alone at this temperature. At about 450°C, the Cs_2SO_4 oxidized to cesium oxides and SO_x gas. The cesium oxides melted below 600°C. Between 450–550°C, the remaining Cs_2MoOS_3 oxidized to complex cesium molybdates. At 600°C, the materials present were complex cesium molybdates, cesium oxides, and MoO_3. Between 600–800°C, the complex cesium molybdates oxidized further to Cs_2MoO_4 and molybdenum oxides. Starting near 700°C, the Si_3N_4 oxidized to amorphous SiO_2. Cesium ions diffused into the SiO_2 glass as soon as it was formed. Also, at about 700°C, MoO_3 sublimed. At approximately

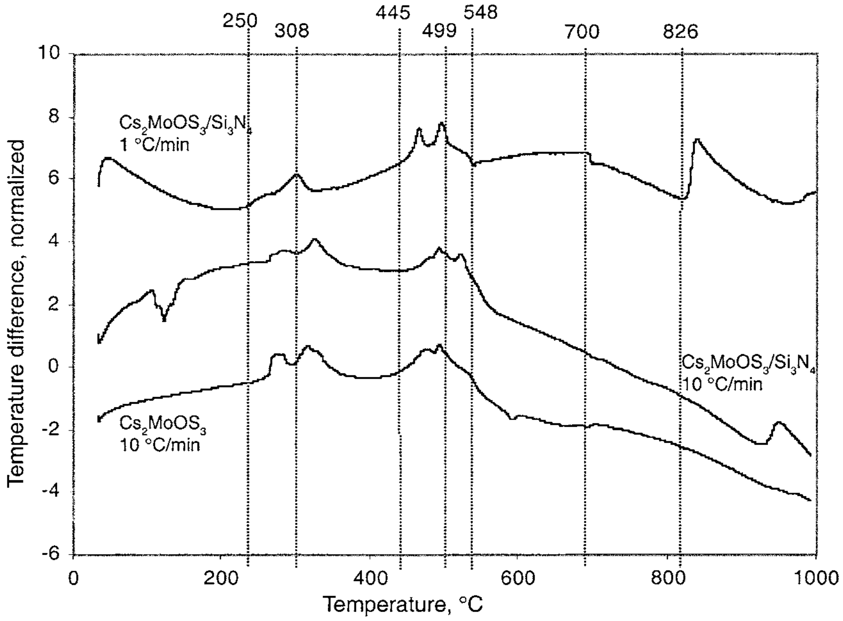

Figure 6 DTA spectrum of Cs_2MoOS_3/Si_3N_4 mixture (heating rate 1°C/min).

825°C, the cesium silicate glass devitrified. This was confirmed with the XRD and Raman scattering results of the mixtures heated to 1000°C for 40 hours, in which crystalline SiO_2 (β-cristobalite) was identified. In addition, the similar behavior of Cs_2MoOS_3/Si_3N_4 and Cs_2MoOS_3/SiO_2 mixtures verified that the SiO_2 on the surface of Si_3N_4 is the material with which the Cs_2MoOS_3 interacts when heat treated.

The presence of Si_3N_4 significantly altered the thermal chemistry of Cs_2MoOS_3 in air. One important difference was the absence of cesium oxides at 800°C. The cesium oxides produced reacted with SiO_2 and were then contained in the cesium silicate glass. The lack of melting of the mixed powders at temperatures as high as 1000°C was different than the Cs_2MoOS_3 powder alone, which was completely liquid at 750°C. This difference could be due to the cesium oxide/silica reaction, which eliminated the liquid components in the mixture. However, the diffusion associated with the reaction could be the cause of the observed sintering. For tribological applications, low viscosity melted materials do not provide lubrication or wear protection, and the absence of cesium oxide in the system could enhance lubrication. The amount of S present at 600°C detected by the titration method was about half of what would be expected from the results for the pure powder, indicating that the oxidation of Cs_2SO_4 was accelerated. This was confirmed by the absence of S–containing compounds identified by XRD in the 600°C spectrum. In addition, Cs_2MoO_4 was preferentially formed in the Cs_2MoOS_3/Si_3N_4 mixtures at 800°C. Cesium oxides and molybdenum oxides, which were present in the heated pure powder, were not detected in the heated mixtures at this temperature.

Formation of molybdates, MoO_3, and cesium silicate glass is significant for tribological applications. Molybdates are glass-forming materials under heat and pressure and have been shown to have low coefficients of friction at 704°C by Peterson *et al.* [14]. Peterson also found that oxides near their melting points have low coefficients of friction. At temperatures above 600°C, MoO_3 is known to be a good lubricant [15]. The silicate itself is also a likely lubricant at elevated temperature. Alkali ions are typically added to break up the three dimensional network of an SiO_2 glass, reducing the softening point and shear strength significantly [16]. It is likely that, at elevated temperature and in the presence of cesium ions, the oxidized silicon nitride forms a low shear strength glass film which could provide lubrication. For example, Peterson *et al.* have found that borate glass (B_2O_3) has a coefficient of fiction of 0.10 at 650°C [15].

5. Conclusions

In the present study, we have shown that oxidation of Cs_2MoOS_3 was different in the presence of Si_3N_4 than alone, resulting in the formation of less cesium oxide, more Cs_2MoO_4, and a cesium silicate glass in the temperature range of 600–800°C. If the glass has a low shear strength at elevated temperature, it may be a good lubricant. Since the cesium oxides diffuse into the SiO_2 formed by the oxidation of Si_3N_4, the material does not melt at temperatures as high as 1000°C. Together, Cs_2MoO_4, MoO_3, and the cesium silicate glass may create a low shear strength film which could be an excellent lubricant in the temperature range of about 450 to 800°C.

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