

Synthesis and characterization of a high-temperature oxide lubricant

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PbMoO₄ is a potential solid lubricant for use at elevated temperatures in oxidizing environments. Pulsed laser deposition (PLD) was utilized to grow thin films of this material because it allows good control over film chemistry and crystallinity. Films were grown at different substrate temperatures in vacuum and in partial pressures of oxygen. The chemistry and crystallinity of the films were evaluated using X-ray photoelectron spectroscopy, Raman spectroscopy, and glancing angle X-ray diffraction. Friction coefficients and wear lives were measured using a ball-on-flat tribometer at room temperature and 700 °C. Films deposited in vacuum, at room temperature and at 300 °C, were oxygen deficient. To adjust chemistry and crystallinity, films were grown in a partial pressure of oxygen (i.e. 6.7×10^{-1} Pa). Stoichiometric, crystalline films of PbMoO₄ were produced when films were grown at 300 °C in this environment. PbMoO₄ films were lubricious ($\mu = 0.35$) and long lived at 700 °C, but at room temperature had high friction and failed quickly. The properties of the films grown at the different conditions are discussed.

1. Introduction

Solid lubricants are needed to meet requirements for future-generation aircraft and space vehicles that will be subjected to high temperatures in oxidizing environments. Ceramic materials are already under development for many of these applications and they will permit even higher operational temperatures than steels. Therefore, high-temperature lubricant materials must be available. Many potential solid lubricants have been identified, but over the years, MoS₂ and graphite have been used most frequently for low (–196 °C) to moderate (300 °C) temperature applications; this fact is demonstrated in a compilation of lubricants published in 1985 [1]. Other materials have found limited use for special applications (e.g. electrically conductive, high-temperature, etc.) and are also listed in the compilation. The materials for temperatures beyond 500 °C are extremely limited and further research is required to meet future needs. About 33 years ago, Peterson *et al.* [2] evaluated a variety of solid lubricant materials for high temperatures. The authors identified PbMoO₄ as a promising candidate, but no additional work on this material could be located.

Recently, pulsed laser deposition (PLD) was used to grow lubricious films from a mixture of MoS₂ and

PbO [3]. It was reported that heating the films in air at 500 °C produced PbMoO₄ along with smaller concentrations of MoO₃ and residual MoS₂. PbMoO₄ was also formed by rubbing the films in air at room temperature via a tribochemical reaction. The films were excellent lubricants and lasted up to ten times longer than pure MoS₂ films grown by PLD. These observations lead to the concept of adaptive lubricants. The tribological properties of adaptive lubricants change with changing environment to provide lubrication over an extended temperature range. For example, MoS₂/PbO provides lubrication at room temperature and, as the temperature increases, PbMoO₄ forms to provide continuous lubrication. To understand better the potential lubrication qualities of PbMoO₄, pure films were synthesized by pulsed laser deposition and then evaluated. PLD was selected for film deposition because it permits precise control of chemical and physical properties of lubricant materials [4–13]. In addition, films grown by PLD are usually fully dense. High-energy species produced during PLD [14] are considered to promote interfacial reactions and, therefore, good film adhesion.

Research reported in this paper was directed towards identifying the conditions necessary for growing crystalline, stoichiometric PbMoO₄ and then

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determining its friction and wear properties at high temperature. For this study, substrate temperature and oxygen partial pressure were used to control film stoichiometry, crystallinity, and chemistry. These properties were evaluated using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and glancing angle X-ray diffraction (GAXRD). Friction coefficients and wear lives were measured in air at room temperature (RT) and 700 °C using a ball-on-flat tribometer.

This paper reports the chemistry, crystallinity, and tribological properties of films grown at several conditions and those of the successfully grown stoichiometric and crystalline PbMoO₄.

2. Experimental procedure

2.1. Deposition system

The methods used for pulsed laser deposition have been described earlier [4–6]. Briefly, films were grown in a stainless steel vacuum system having a base pressure of 9×10^{-7} Pa; the system pressure typically rose to about 6×10^{-5} Pa during film growth. The target was fabricated by cold pressing tetragonal PbMoO₄ powder (K&K Laboratories) into a 25 mm diameter disc at room temperature and 1.5×10^8 Pa.

A Lambda Physik LPX 110i excimer laser was filled with an Ne–KrF mixture to provide a beam of ultraviolet radiation at 248 nm. The beam was pulsed at a rate of 10 Hz and it was focused to a 2.0 mm × 4.0 mm rectangle on the target face providing a fluence of 1.2 J cm^{-2} . Film uniformity was maximized by (1) rotating the target and the substrate during deposition and (2) rastering the laser beam across the target face under computer control. Targets were polished prior to each deposition to minimize roughness and increase deposition rates. A calibrated quartz crystal oscillator was used to measure film thickness. Resistive heating was employed to degas and/or anneal the specimens; their temperature was measured using a calibrated infrared pyrometer. Target cleaning was accomplished using the laser with the sample shutter closed.

2.2. Sample preparation and analysis

Substrates for room-temperature tribo-tests were fabricated from 440C stainless steel (SS) coupons that were polished to 0.01 μm. Inconel 718 pins and flats were used as substrates for high-temperature tribo-testing. Materials were cleaned in soap and water and then ultrasonically washed in hexane, acetone and methanol. Immediately prior to deposition, the substrates were degassed at 300 °C for 1 h and allowed to cool to room temperature. The 440C flats were used in the exploratory research to determine the conditions required for growing stoichiometric, crystalline PbMoO₄. The conditions evaluated were (1) vacuum and room temperature (RT), (2) vacuum and 300 °C, (3) oxygen partial pressure of 6.7×10^{-1} Pa and RT and, (4) oxygen partial pressure of 6.7×10^{-1} Pa and 300 °C. The duration of each deposition was adjusted to provide films that were about 400.0 nm thick. Once

the conditions for growing PbMoO₄ were established, a film was deposited on to the Inconel substrate.

Surface chemistry was studied with a Surface Science Instruments (SSI) M-probe XPS instrument operated at a base pressure of 3×10^{-7} Pa. Using an aluminium anode, a 400 μm × 1000 μm line spot, and a 25 eV pass energy, the full width at half maximum (FWHM) of the Au 4f_{7/2} peak was 0.71 eV. Binding energy positions were calibrated against the Au 4f_{7/2} peak and energy separations were calibrated using the Cu 3s and Cu 2p_{3/2} peaks at 122.39 and 932.47 eV, respectively. Bulk chemistry and film crystallinity were investigated by Raman spectroscopy using a SPEX 1877 spectrometer and the incident light of a 514.5 nm Ar⁺ laser. An intensified 1024 element, diode array detector was used to collect the Raman signal. Crystal structures were determined using data acquired by a Rigaku D/max-1B diffractometer equipped with a thin film attachment and a monochromator. Room-temperature friction and wear data were collected using a ball-on-flat tribometer. A 1/8 in (~3 mm) diameter 440C stainless steel ball was dead loaded with a 100 g weight on to a 18 mm diameter track to create a Hertzian stress of 0.98 GPa. The high-temperature runs were made on a pin-on-disc tribometer which is described in detail by Sliney and DellaCorte [15]. Briefly, a Hertzian stress of 1 MPa was applied to the coated Inconel disc which was rotated to provide a sliding speed of 0.6 m s⁻¹. The tests were run in dry air.

3. Results

Surface chemistry and stoichiometry were determined from analyses of the Pb 4f_{5/2-7/2}, Mo 2p_{1/2-3/2}, and O 1s XPS spectra. The PbMoO₄ target was an insulator, so an electron-flood gun was employed for charge neutralization. Peak positions were referenced to carbon. Charging did not have a significant effect on the determination of stoichiometry. To provide additional certainty to the chemical analysis, energy separations amongst the different peaks were recorded. XPS spectra are shown in Fig. 1. Peaks were fitted to Voigt functions by minimizing the chi-squared value; binding energies and FWHMs determined by the fitted data are presented in Table I. Carbon and oxygen contamination were present on the surface of all specimens due to handling in air. The features due to oxygen contamination were easily deconvoluted from metal oxides so atomic ratios could be calculated accurately. Crystal structure and the degree of crystallinity were determined by analysis of Raman spectra and GAXRD scans which are shown in Figs 2 and 3.

Friction and wear data collected from the different films are presented in Fig. 4. The number of revolutions the substrate disc traverses before film failure was used as a measure of wear life; failure was defined as an increase in the friction coefficient above 0.6. The films deposited on 440C stainless steel had friction coefficients near 0.6 at the start of the test and were not considered to be lubricious. The PbMoO₄ film deposited on to Inconel provided an erratic friction trace at

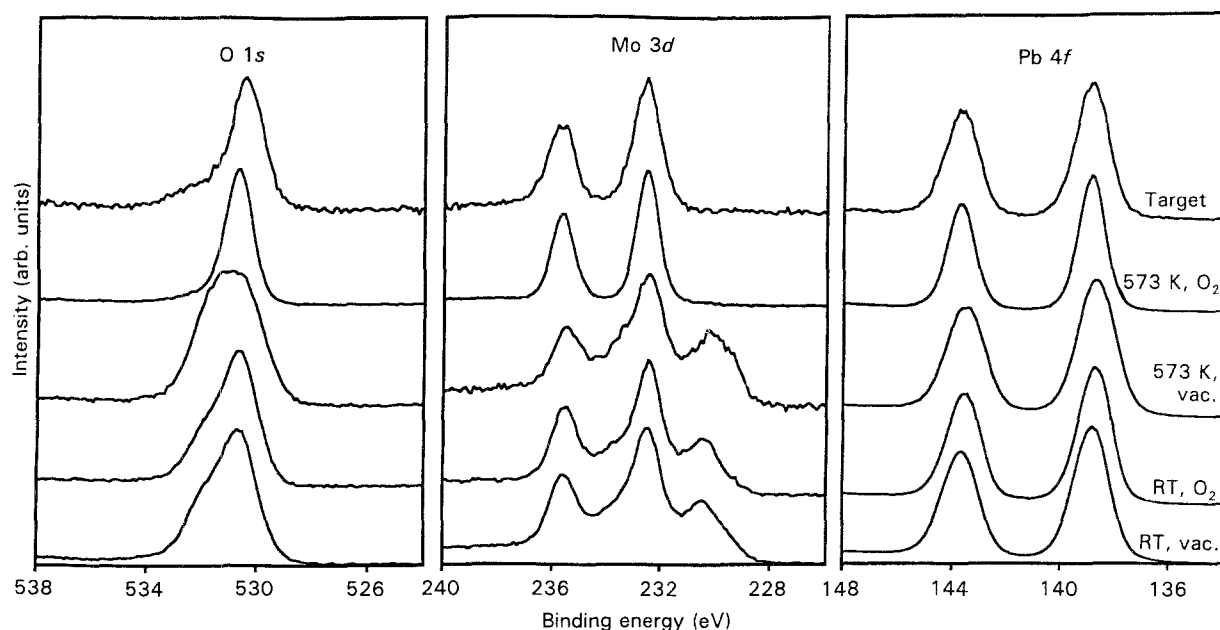


Figure 1 XPS spectra collected from the PbMoO_4 target and the different films.

TABLE I XPS data for the PbMoO_4 target and the different films

Specimen	$\text{Pb } 4f_{7/2}$ (eV)	$\text{O } 1s$ (eV)	$\text{Mo } 3d_{5/2}$		$\text{Mo}^{6+}\text{-Pb}$ (eV)	O-Pb (eV)	O-Mo^{6+} (eV)	Pb-Mo-O
			Mo^{4+}	Mo^{6+}				
RT, vac					93.60	391.75	298.15	$\text{PbMo}_{0.8}\text{O}_{2.8}$
BE	138.88	530.63	230.51	232.48				
FWHM	1.51	1.48	1.90	1.13				
300 °C, vac					93.65	391.94	298.29	$\text{PbMo}_{0.8}\text{O}_{3.0}$
BE	138.72	530.66	230.22	232.37				
FWHM	1.57	1.91	1.86	1.15				
RT, O_2					93.69	391.93	298.20	$\text{PbMo}_{0.5}\text{O}_{2.6}$
BE	138.76	530.65	230.55	232.45				
FWHM	1.40	1.44	1.67	1.09				
300 °C, O_2					93.66	391.82	298.16	$\text{PbMoO}_{4.2}$
BE	138.90	530.72	-	232.56				
FWHM	1.15	1.08		0.99				
Target					93.75	391.88	298.13	PbMoO_4
BE	139.02	530.90	-	232.77				
FWHM	1.36	1.35		1.19				

^a BE, binding energy; FWHM, full-width-half-maximum.

RT; a much smoother friction trace was observed at 700 °C with the friction coefficient at about 0.35.

4. Discussion

4.1. Chemistry and crystal structure

The objective of this study was to grow a stoichiometric crystalline PbMoO_4 film and determine its friction and wear properties. Several different deposition environments were selected for film growth. The first approach was to grow the film in vacuum on a substrate at room temperature. The film grown under these conditions was oxygen and molybdenum deficient; the stoichiometry, determined using XPS data, was $\text{PbMo}_{0.8}\text{O}_{2.8}$. The lead peaks were fit to a single broad doublet whereas the molybdenum peaks were clearly representative of two chemical states. The doublet to higher binding energy is representative of

Mo^{6+} possibly from an amorphous and oxygen deficient PbMoO_4 or MoO_3 component. The doublet to lower binding energy arises from molybdenum in a lower oxidation state, close to that from Mo^{4+} (e.g. MoO_2 - 229.3 eV). This suggests that some MoO_2 type bonding is present. It is noted that Raman and XRD scans demonstrate that the film is amorphous, at least to the limits of detection for these techniques, which is about a 2 and 5 nm diameter crystalline domains, respectively. No additional information is provided by analysis of the O 1s spectra. The oxygen deficiency is likely caused by recombination of oxygen atoms in the plasma or at the film surface and subsequent removal of the oxygen molecule through pumping. Residual gas analysis measured by a mass spectrometer in a non-line-of-sight geometry confirmed that the background concentration of oxygen increased during deposition.

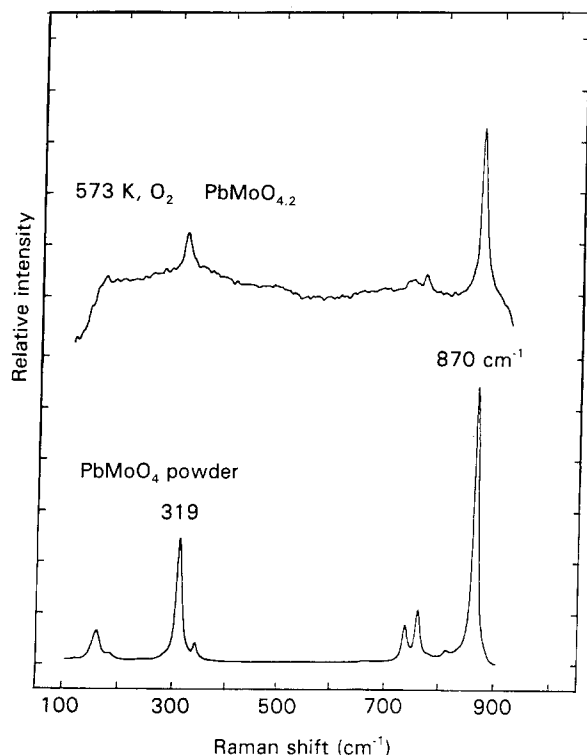


Figure 2 Raman spectra collected from the PbMoO_4 target and the film grown at 300°C in oxygen. Note: the other films (i.e. RT-vacuum, RT- O_2 , and 300°C , vacuum) do not produce Raman spectra.

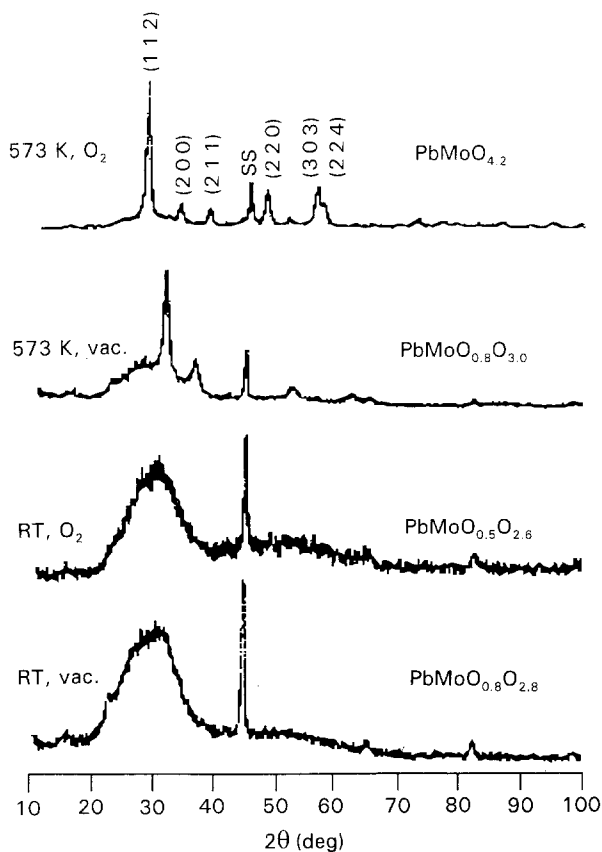


Figure 3 Glancing angle XRD scans of the different films.

To address the oxygen deficiency and increase crystallinity, a film was grown at 300°C in vacuum. It was anticipated that this would alter the reaction kinetics to favour the formation of PbMoO_4 by increasing

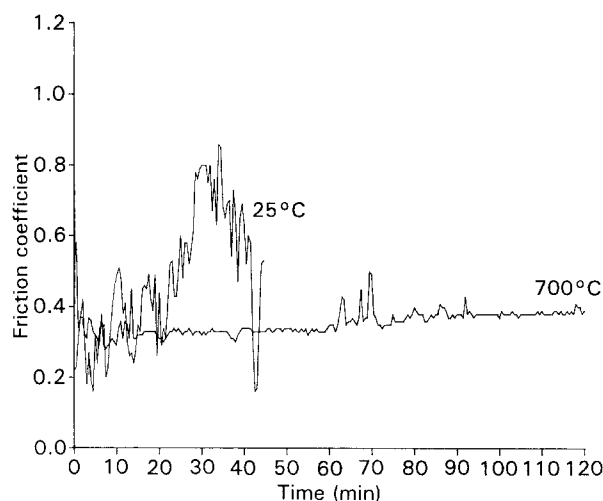


Figure 4 Friction trace of the PbMoO_4 film tested at room temperature and at 700°C .

the reaction rate of oxygen with metal atoms. XPS data shown in Fig. 1 indicated that the film was quite similar to the one grown at room temperature and was still oxygen deficient – its stoichiometry was $\text{PbMo}_{0.8}\text{O}_{3.0}$. XRD data confirmed that the film had a crystalline component but comparison of the film to the PbMoO_4 JCPDS file demonstrated that it was not PbMoO_4 . The XRD peaks were broad, which indicates that there is much disorder in the crystalline domains and/or that the domains are small.

To grow a more oxygenated film, the deposition chamber was backfilled with oxygen to a pressure of 6.7×10^{-1} Pa to promote the formation of PbMoO_4 and reduce the fraction of the oxygen-deficient phase observed by XPS. The first attempt was made with the substrate held at room temperature. Earlier work by the authors [9] demonstrated that these conditions were sufficient to permit the growth of stoichiometric PbO when attempts without excess oxygen failed. These conditions had little effect for PbMoO_4 . Raman spectra were featureless and the XRD data appeared unchanged from the RT, vacuum deposition. The stoichiometry determined from XPS was $\text{PbMo}_{0.5}\text{O}_{2.6}$.

The film grown in an oxygen background (i.e. 6.7×10^{-1} Pa) on a substrate heated to 300°C was stoichiometric, crystalline PbMoO_4 . The binding energies of the film and target material matched quite closely and only one chemical state of molybdenum was observed. By comparison in Table I, the FWHMs from this specimen are smaller than from the other films indicating a more uniform chemical environment (note, the target peaks are broad due to charging). In addition, the binding energy separations of the Pb-O and Mo-O peaks are very close to those obtained from the target, confirming the chemical bonding is similar. The XRD pattern from this film shown in Fig. 3 matches the pattern listed in the JCPDS files [16] for tetragonal PbMoO_4 . The intensity ratios are somewhat different because the JCPDS data are for a powder specimen. All peaks in the XRD scan were accounted for by PbMoO_4 and the 440C substrate. The intensity and d -spacing of the dominant planes

TABLE II Glancing angle XRD data from PbMoO₄ [16] and the 300 K, oxygen film. Only the most prominent lines from the diffractogram are listed

PbMoO ₄ powder		Plane	300 K, oxygen film	
<i>d</i> (nm)	<i>I</i> / <i>I</i> ₀	(<i>hkl</i>)	<i>d</i> (nm)	<i>I</i> / <i>I</i> ₀
0.4960	12	101	0.4907	5
0.3240	100	112	0.3219	100
0.2718	25	200	0.2702	19
0.2383	8	211	0.2366	16
0.1920	14	220	0.1914	28
0.1787	18	116	0.1786	9
0.1653	25	303	0.1646	30
0.1622	12	224	0.1621	17
0.1308	12	316	0.1307	8

are listed in Table II along with those of PbMoO₄ from the powder diffraction files. Comparison of the Raman spectrum from the target to that from the film in Fig. 2 confirms that PbMoO₄ is produced by these deposition conditions. It is noted that these same deposition parameters produced PbO from a PbO target [9]. In that earlier study, films grown in oxygen at room temperature and at 300 °C were PbO; however, the RT runs produced orthorhombic PbO and the HT runs produced a mixture of the orthorhombic and tetragonal phases. It is likely that the high temperature is necessary to permit crystallization and that the film oxidizes during or after deposition in the oxygen background.

4.2. Friction and wear

The films grown on 440C substrates, including the PbMoO₄ specimen, were poor lubricants at room temperature; the films failed immediately. The PbMoO₄ film grown on Inconel also did not perform well at room temperature. However, the film displayed good tribological properties at 700 °C. Its friction coefficient dropped to between 0.3 and 0.4 and lasted for over 2 h, at which time the test was terminated before film failure. This drop is likely due to the decrease in shear strength of the material as the temperature approaches the melting point as suggested earlier by Peterson *et al.* [2]. It is noted that the friction coefficient they reported for PbMoO₄ powder, using a low-speed reciprocating apparatus at 704 °C, was about 0.37.

5. Conclusion

Deposition conditions were identified for growing stoichiometric, crystalline PbMoO₄. By changing the deposition conditions, in this instance substrate temperature and oxygen partial pressure, film stoichio-

metry and crystallinity can be adjusted. PbMoO₄ films grown by PLD are poor lubricants at room temperature but become lubricious as the temperature is raised to 700 °C. The results presented demonstrated the utility of PLD to provide adherent films that have the desired chemistry and crystal structure.

References

1. E. L. McMURTRY, NASA TM-86556 (1985).
2. M. B. PETERSON and R. L. JOHNSON, *Lubrication Eng.* **13** (1957) 203.
3. J. S. ZABINSKI, M. S. DONLEY, V. J. DYHOUSE and N. T. McDEVITT, *Thin Solid Films* **214** (1992) 156.
4. M. S. DONLEY, P. T. MURRAY, S. A. BARBER and T. W. HAAS, *Surf. Coat. Technol.* **36** (1988) 329.
5. M. S. DONLEY, P. T. MURRAY and N. T. McDEVITT, in "New Materials Approaches to Tribology", edited by L. E. Pope, L. L. Fehrenbacher and W. O. Winer, Materials Research Society Proceedings, Vol. 40, (MRS, Boston, MA, 1989) pp. 277-82.
6. M. S. DONLEY, N. T. McDEVITT, T. W. HAAS, P. T. MURRAY and J. T. GRANT, *Thin Solid Films* **168** (1989) 335.
7. P. J. JOHN, V. J. DYHOUSE, N. T. McDEVITT, A. SAFRIET, J. S. ZABINSKI and M. S. DONLEY, in "Beam-Solid Interactions" Materials Research Society Symposium Proceedings, Vol. 201 (MRS, Boston, MA, 1991) pp. 117-22.
8. J. S. ZABINSKI, M. S. DONLEY, P. J. JOHN, V. J. DYHOUSE, A. SAFRIET and N. T. McDEVITT, *ibid.* (MRS, Boston, MA, 1991) pp. 195-200.
9. J. S. ZABINSKI, M. S. DONLEY, V. J. DYHOUSE and N. T. McDEVITT, in "Photons and Low Energy Particles in Surface Processing", edited by C. I. H. Ashby, J. H. Brannon and S. W. Pang, MRS Symposium Proceedings, Vol. 236, (Materials Research Society, Pittsburgh, PA, 1992) pp. 437-42.
10. A. E. DAY, S. J. P. LAUBE, M. S. DONLEY and J. S. ZABINSKI, in "Laser Ablation in Materials Processing: Fundamentals and Applications", edited by B. Braren, J. J. Dubowski and D. P. Norton, MRS Symposium Proceedings, Vol. 285 (Materials Research Society, Pittsburgh, PA, 1993) p. 539.
11. S. V. PRASAD, J. S. ZABINSKI and V. J. DYHOUSE, *J. Mater. Sci. Lett.* **11** (1992) 1282.
12. M. S. DONLEY, J. S. ZABINSKI, W. J. SESSLER, V. J. DYHOUSE, S. D. WALCK and N. T. McDEVITT, in "Photons and Low Energy Particles in Surface Processing", edited by C. I. H. Ashby, J. H. Brannon and S. W. Pang, MRS Symposium Proceedings, Vol. 236 (Materials Research Society, Pittsburgh, PA, 1992) pp. 461-6.
13. W. J. SESSLER, M. S. DONLEY, J. S. ZABINSKI, S. D. WALCK and V. J. DYHOUSE, *Surface Coat. Technol.* **56** (1993) 125.
14. P. T. MURRAY, V. J. DYHOUSE, L. GRAZULIS and D. R. THOMAS, in "Beam-Solid Interactions", Materials Research Society Symposium Proceedings, Vol. 201 (MRS, Boston, MA, 1991) pp. 513-18.
15. H. E. SLINEY and C. DELLACORTE, *Lubr. Eng.* **47** (1991) 314.
16. Powder Diffraction File: Set 8, International Centre for Diffraction Data, Swarthmore, PA (1960) No. 8-475.

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