DEVELOPMENT AND QUALIFICATION OF NEW SOLID LUBRICANT COATINGS. A TRIBOLOGY EXPERIMENT AT THE TRIBOLAB ONTO EUTEF.

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ABSTRACT - *A recent study has identified that a significant number of satellite failures and anomalies, including those caused during qualification testing of mechanisms, were caused by lubrication related problems. Solid lubrication is, owing to lower vapour pressures, better boundary lubrication properties, relative insensitivity to radiation effects and wider temperature range of operation, still a preferred option for a number of space mechanisms. However, actual solid lubricants wear out and do not provide effective protection for long life mechanisms. A longer life and reduced wear debris is desirable to improve mechanism reliability.*

The present work reports on early results on the development of a new generation of solid lubricant coatings by the use of state of the art magnetron sputtering technology and thermal spraying processes. These coatings after a proper qualification procedure under laboratory ground conditions will be finally tested at the TriboLAB instrument that will be integrated onto the EuTEF facility at the International Space Station (ISS).

Metal alloyed MoS_2 solid lubricant films have been produced by a magnetron sputtering PVD process. Tribotests carried out under vacuum in a ball-on-disc tribometer with MoS_2 coated AISI 440C steel discs have shown very low friction coefficients of 0.01 and long endurance, in excess of 300,000 revolutions at about a max. 0.8 GPa contact stress. These films also exhibited low friction coefficients (about 0.10) and good durability under atmospheric conditions at RT and up to 50 to 60 % RH. The thick composite lubricant coatings consisting of AlCoFeCr, NiCr, Ag and BaF_2-CaF_2 were deposited by plasma spray and HVOF on X-750 Ni-base superalloy. These coatings have been characterised by EDS-SEM as well as hardness measurements. The best coatings from preliminary experiments have been produced by HVOF process; these show very low porosity, a more uniform phase distribution and hardness levels of 635 $HV_{0.2}$. Anticipated high temperature applications of former coatings might include elevon hinges for re-usable space planes.

1. INTRODUCTION

It has been recognised that failures in space have been often caused in recent years not to a malfunction in complex electronics, but to breakdowns in mechanical systems. A study carried out at the Lewis Research Centre - NASA [1] revealed that a significant number of satellite failures and anomalies during operation and qualification testing were caused by tribological problems. Many of these problems have been reviewed in a recent work by Borrien [2]. The demands placed on lubricants continue to multiply since mission duration, as well as size and complexity of space vehicles and systems have increased in a way that today space lubricants are being pushed to their limits, and many aerospace application requirements exceed the available lubrication and wear reduction technologies. Therefore, today the challenges are to develop lubricant systems that can

survive not only longer mechanism lifetimes but also increased levels of ground testing and tighter pointing control to name a few [3]. These requirements demand, in the case of solid lubrication, coatings that are longer lasting in both vacuum and atmospheric conditions.

MoS_2 has been the most widely used lamellar compound solid lubricant film for space applications, since the pioneering work of Spalvins [4] and subsequent developments of magnetron sputtered MoS_2 thin films [5]. In particular when this coating is deposited by PVD (e.g. by magnetron sputtering) it is highly suitable for application on precision mechanisms and a uniform coverage, excellent adhesion and low friction properties can be guaranteed [6]. However, there has been an interest in further improving MoS_2 films by enhancing their endurance life and resistance under atmospheric humid conditions. This would also extend their ground test capability and alleviate storage conditions without undue performance or degradation of the coating. Additionally, it would extend spin off applications in a range of ground industrial situations; such as in wear components or tooling [7, 8]. Possible ways or achieving this goal are by film densification to reduce porosity, hence avoiding large-scale film debris generation early in wear of space mechanisms, and incorporation of getter materials to inhibit oxidation of MoS_2. Modern PVD technology allows the production of metal alloyed MoS_2 coatings with or without the combination of inner layers of harder ceramic materials that can increase wear resistance and endurance life whilst maintaining low friction coefficient values [9].

When there is a need of improving lubrication at high temperatures (e.g. in hot gas valves on launcher engines, control surface rub seals, turbo-pump bearings, elevon hinges and actuator gearboxes on re-usable space planes, among others [10]); the only practicable approach is by means of solid lubrication. Thermal sprayed self-lubricating composites, such as those developed over 10 years ago by NASA´s Lewis Research Centre [11] perform well tribologically, offering a good combination of wear and friction properties over a wide temperature range. Another new family of coating materials with promising tribological behaviour is that of quasicrystalline alloys (QC), that exhibit a combination of low friction coefficient, high hardness and high yield strength under compression [12]. Among these QC alloys, AlCoFeCr has a high hardness (~700 $HV_{0.1}$), a thermal expansion coefficient close to that of metals, high thermal stability, low thermal conductivity and good oxidation and hot corrosion resistance [13]. The aim of this work is to produce thick composite coatings by thermal spraying processes based on a combination of AlCoFeCr, NiCr, Ag and the BaF_2-CaF_2 eutectic. These should have enhanced tribological properties and excellent adhesion to substrate, to be useful in elevon hinges for re-usable space plane applications, where temperatures of 700 ºC are reached during re-entry into the Earth's atmosphere [14]. These coatings should also be capable of providing effective lubrication at lower temperatures since "cold start" operation may be necessary, even in the space environment.

This work reports on the first series of laboratory experiments conducted with metal alloyed MoS_2 solid lubricant films and the former composite alloys, that after ground qualification will eventually be tested in the TriboLAB – Tribotester instrument [15] onto the EuTEF at the International Space Station (ISS). The TriboLAB is designed to perform tests at basic tribometer and component level by having two axles equipped with ball-on-disk and angular bearing tests respectively.

2. EXPERIMENTAL

2.1. Magnetron sputtered films.

Films were deposited on previously hardened and tempered AISI 440C bearing steel discs of 45 mm diameter and 5 mm thick with a surface finish of 0.01 µm Ra. A CemeCon CC800/8 magnetron sputtering PVD unit was used for the deposition work. The Ti doped MoS_2 was deposited by dc magnetron sputtering from four targets (1 to 2 targets of MoS_2 and 1 to 2 targets of Ti) in a 99.999 % pure Ar discharge at a pressure of 0.5 to 0.7 Pa at a variable Ar flow of 200 to 300 sccm. The Ti cathode power varied from 160 to 1500 W and the MoS_2 cathode power from

100 to 300 W. The substrate bias voltage induced by a RF power operating at a frequency of 13.56 MHz was varied from 0 to 75 V.
Hardness of MoS_2 thin films was measured with a Fischerscope H100 dynamic microprobe apparatus using a conventional Vickers indentor at loads up to a maximum of 10 mN [16]. Electron probe microanalysis (EPMA) and Small Area X-ray photoelectron spectroscopy (SAXPS) combined with 4 keV Ar^+ sputtering were conducted to obtain compositional and chemical analysis. The EPMA experiments were carried at 7.5 kV to account for the limited film thickness. SAXPS analysis were performed in a Microlab MKII VG spectrometer with Al Kα radiation at 34 mA and 13 kV under a pressure of less than 2×10^{-9} mbar (without Ar). For each sample, survey and detailed spectra (Ti 2p, Mo 3d, S 2p, O 1s and C 1s) were recorded.
Wear and friction tests were performed in two types of ball-on-disk tribotesters. The first one was a Falex ISC 320 tribometer under atmospheric conditions with a controlled humidity cabinet. A 1 N load was applied to an AISI 52100 steel ball of 10 mm in dia. with a constant sliding speed of 0.1 m/s. These experiments were performed as a preliminary screening method to select MoS_2 films with good dry lubricant characteristics. CSEM equipment was the second tribometer to carry out tests under vacuum ($< 10^{-5}$ mbar), applying a load of 5 N to an AISI 440C steel ball of 6 mm dia. at a constant sliding speed of 0.5 m/s. A calculated estimate of Hertzian contact stress under these conditions is 0.75 GPa. Each tests run until a friction coefficient of 0.2 was reached.

2.2. Thermal spray coatings

Coatings were deposited by a PC controlled plasma-spraying unit (SNMI) and by HVOF equipment (Diamond Jet Hybrid from SULZER-METCO). The selected substrates were low-C steel for the first runs and X-750 Ni-base superalloy for the optimisation runs. The coatings consisted of a series of AlCoFeCr/NiCr/Ag/BaF_2-CaF_2 composites named TH100.
Microstructures of the coatings were observed by SEM (JEOL JSM-840 equipped with a KEVEX EDS micro-analyser). Indentation hardness measurements were made with a Vickers indentor under a 200 g load on polished cross-sections.

3. RESULTS AND DISCUSSION

3.1. Magnetron sputtered films

Dynamic hardness values obtained from the films demonstrated that a wide range of results could be obtained dependant on deposition conditions. The hardness oscillated in these films from 3600 to 10000 N/mm^2 at the max. load of 10 mN. These values still correspond to typical data of a soft material such as a MoS_2 film. Hardness of the films increased with Ti content in agreement with the results of Teer et al [8]. A summary of mechanical properties and chemical compositions obtained is presented in Table I.
The EPMA analyses show for all the coatings a S/Mo atomic ratio varying from 1.3 to 1.6 and a Ti content that varies from 7.26 to 11.46 % at. In a previous study conducted by Moser et al [17] on the effect of MoS_x composition on tribological behaviour, the authors concluded that films exhibiting lubricating characteristics had a composition of $x > 1.2$. Therefore, it can be anticipated that films produced in this work should also have a lubricating behaviour.
XPS analysis showed a preferential sputtering of S making difficult an accurate stoichiometric determination of the S/Mo ratio. Anyway, similar S/Mo ratios to those obtained by EPMA have been obtained applying, at the outermost analysis, the linear relationship between S/Mo and (Mo 3d5 – S 2p3) binding energy determined by M.A. Barker et.[18]. XPS spectra obtained from the Mo 3d, S 2p and Ti 2p region at selected sputtering times (0, 1, 8, 108 and 144 min) in sample MoS_2/Ti 25939 (Fig. 1.A and 1.C) demonstrated that a high Mo-S bonding contribution is created. For instance, the peak positions of the S 2p3 spectra (Fig. 1.B) stays around 162.1 eV through all the thin film, which mainly correspond to Mo-S bonds (MoS_2: S 2p3~ 162.35 eV). Furthermore,

the Mo 3d spectrum for the outer layer (0 m, Fig. 1.A) shows three main contributions: Mo-S bonds ($3d_{5/2}$ ~ 228,6 eV; and $3d_{3/2}$ ~ 231,8 eV), M-O bonds (MoO_3: $3d_{5/2}$ ~ 232.8 eV; and $3d_{3/2}$ ~ 236 eV; low MoO_2 contribution could not be disregarded) and S 2s. Due to the film stoichiometry (S/Mo ~ 1.5) the Mo-S peak contribution has a lower binding energy (BE) than in MoS_2 (Mo $3d_{5/2}$ ~229.25 eV). After sputtering a shift to lowest BEs is produced and a steady value is quickly achieved without noticeable oxide contribution. The shift in the Mo 3d peak position to lower binding energies reflects the changing electrostatic environment around Mo atoms caused by the loss of neighbouring S atoms to which is bonded. On the other hand, the Ti 2p spectra (Fig. 1.C), where Ti $2p_{3/2}$ lines for TiO_2 (~ 458.7 eV), TiS_2 (~ 456.4 eV) and Ti^o (~ 454.0 eV) are drawn, show two possible contributions inside the coating: Ti-O and Ti-S bonds. Furthermore, TiO contributions (Ti ~ 454.9 eV) are found, maybe due to the preferential sputtering of the oxygen. When the titanium interlayer is reached (144 m) a metallic contribution is found.

Table I: Hardness, elastic recovery and chemical composition of Ti alloyed MoS_2 films

Sample Ref.	Hardness at 10mN (N/mm^2)	% Elastic recovery	Ti (% At.)	S/Mo ratio
MoS_2/Ti 25932	5120 +/- 386	31.51 +/- 2.30	7.261	1.628
MoS_2/Ti 25935	3748 +/- 061	27.26 +/- 0.24	8.767	1.498
MoS_2/Ti 25936	4642 +/- 118	28.14 +/- 0.43	7.395	1.336
MoS_2/Ti 25939	7961 +/- 247	34.09 +/- 1.42	11.432	1.525
MoS_2/Ti 25940	5799 +/- 255	32.17 +/- 1.29	7.820	1.368

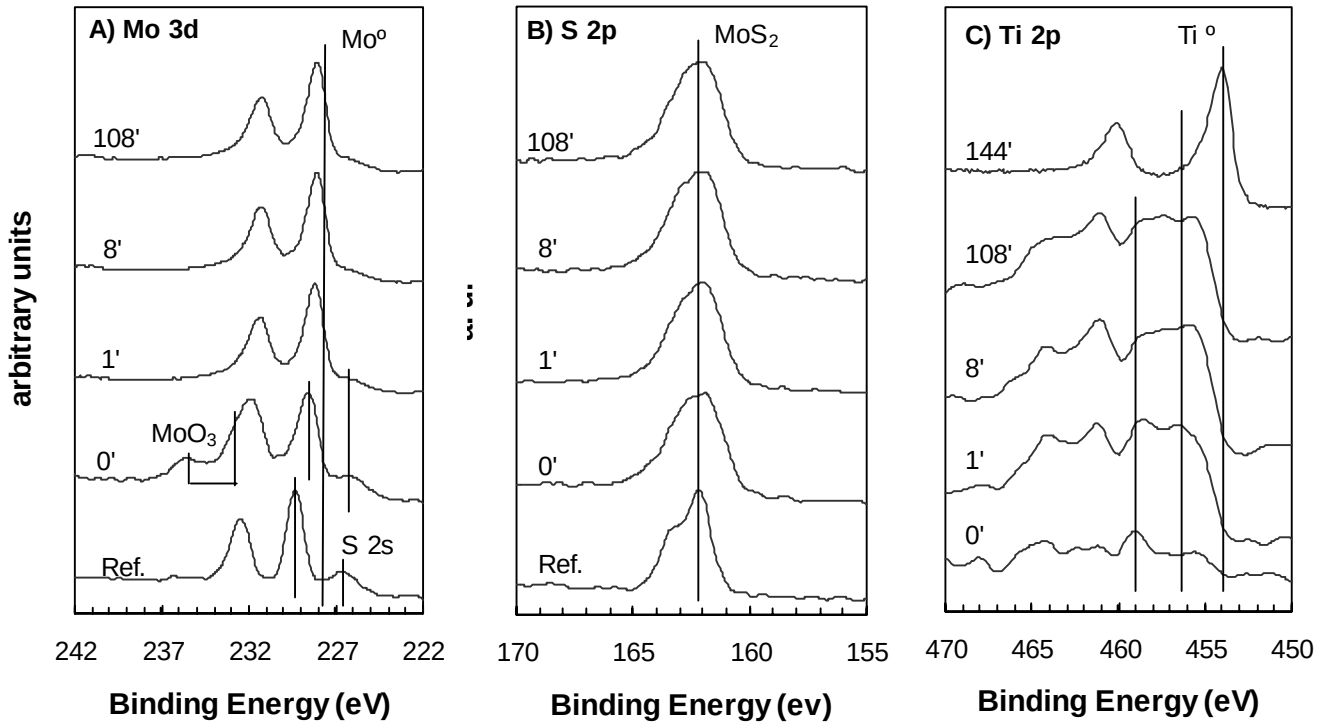


Fig. 1 .- XPS spectra from sample 25939 at different sputtering times (0, 1, 8, 108 and 144 min): A) Mo 3d; B) S 2p and C) Ti 2p. A reference spectrum from MoS_2 is included in A and B.

Wear and friction testing results of representative films are presented in Table II. This table includes data obtained of the mean coefficient of friction when tested under air at a relative humidity of 50%. The friction coefficient was about 0.1 and in some cases 0.07 under these humidity conditions. These friction results appear to be better than those obtained by Matsumoto et al [19] when testing pure MoS_2 under different humidity conditions. Tests at higher relative humidity than 50% RH were also performed for some of the coatings. These showed a higher friction coefficient of about 0.2 for a relative humidity of 70% and a value of 0.6 for 85% RH.
Table II also presents the vacuum tribology data, including the mean coefficient of friction, wear rate of disc and ball as well as the endurance life in wear cycles of films before the onset of failure. The failure was determined when the test reached a friction coefficient higher than 0.2 for a prolonged time, due to delamination or depletion of the film and its lubricating protection.
The evolution of the friction coefficient in most cases was similar, with a marginal higher friction at start up and during the running in process. A steady state low friction value was then achieved until the friction coefficient raised to the cut off value set up at 0.2. Figure 2 shows a characteristic plot of the variation of the friction coefficient of a MoS_2 film as a function of turns. This graph depicts the evolution of three curves of the maximum, mean and minimum coefficient of friction. In some cases, a sudden rise of the friction coefficient up to 0.05 or 0.1 is observed soon returning to the lowest value. This might correspond to entrapped harder wear debris or film starting to break, but the transferred MoS_2 film to the counterface ball material acts as a lubricant reservoir, reducing again friction values. The transfer film on the ball surface was clearly seen by SEM analyses.
The morphology of the films, as seen by SEM, was very smooth without showing the typical columnar structure of more conventional films produced by sputtering.

Table II. Summary of representative tribology results of Ti alloyed MoS_2 thin films.

Sample Ref.	**Friction under air RH 50 % μ_{mean}**	**Friction and wear under vacuum**			
		Endurance (m)	**Friction μ_{mean}**	**Ball wear rate (mm^3/Nm)**	**Disc wear rate (mm^3/Nm)**
MoS_2/Ti 25932	0.14	19980	0.02	8.5×10^{-7}	4.5×10^{-7}
MoS_2/Ti 25934	0.1	2	0.07	1.9×10^{-9}	2.3×10^{-4}
MoS_2/Ti 25935	0.07	29025	0.01	0	3.5×10^{-7}
MoS_2/Ti 25936	0.07	43950	0.01	3.8×10^{-7}	2.7×10^{-7}
MoS_2/Ti 25938	0.15	1410	0.02	5.5×10^{-7}	3.1×10^{-6}
MoS_2/Ti 25939	0.1	19890	0.01	6.3×10^{-9}	1.7×10^{-7}
MoS_2/Ti 25940	0.07	26475	0.01	2.9×10^{-7}	6.2×10^{-8}
MoS_2/Ti 25941	0.13	8400	0.03	3.2×10^{-9}	5.2×10^{-7}

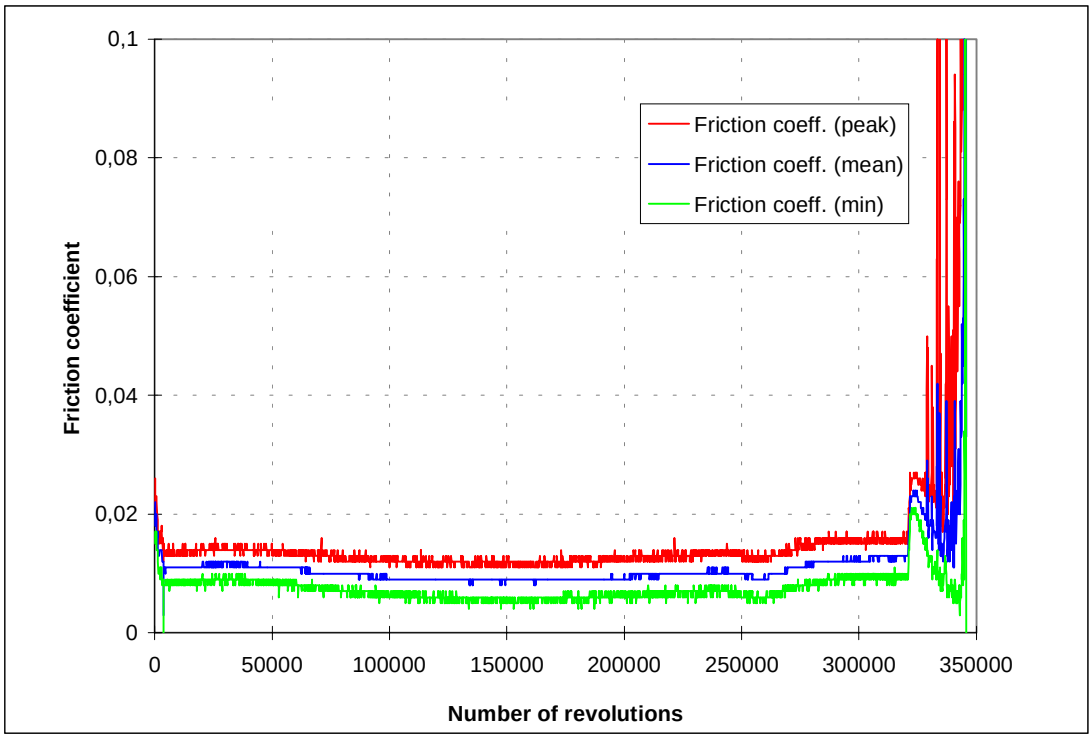
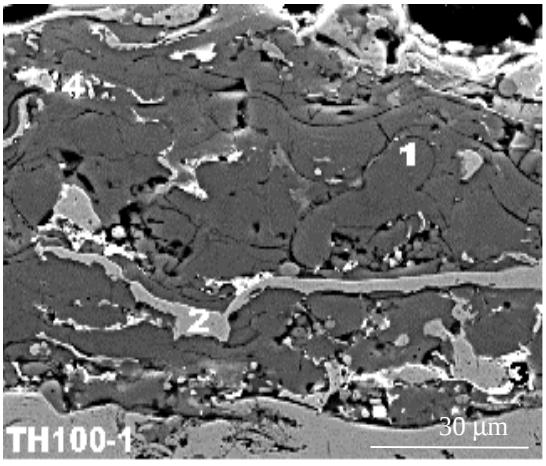


Fig. 2: Variation of friction coefficient as a function of number of revolutions for a MoS_2 film (Sample AISI 440C + MoS_2/Ti 25936)

3.2. Thermal spray films

Several series of samples were coated with both HVOF and APS to optimise the microstructure. SEM images of polished cross-sections of as-sprayed coatings, corresponding to both deposition techniques, are shown in Figures 3 (APS, TH100-1) and 4 (HVOF, TH100-2).

The TH100-1 coating, with a thickness of about 100 µm, shows pores and many cracks and oxidation lines along the splat boundaries (Figure 3). The TH100-2 coating is denser than its APS analogue, with a level of porosity close to 0 and very good adhesion to the substrate. It was also very uniform and about 400 µm thick (Figure 4). EDS analyses carried out on each different phase observed in coatings corresponded with AlCoFeCr (1), NiCr (2), Ag (3) and the BaF_2-CaF_2 eutectic (4) for both layers (Figures 3 and 4).



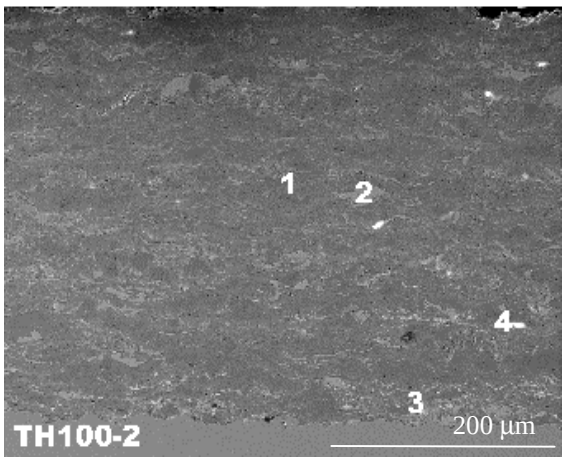


Fig. 3: SEM image of APS coating

Fig. 4: SEM image of HVOF coating

Note: (1) AlCoFeCr, (2) NiCr, (3) Ag, (4) BaF_2-CaF_2 eutectic.

The EDS mapping carried out on these samples (see Figs. 5 and 6) show that HVOF coating has a more uniform phase distribution of NiCr, Ag and the fluorides eutectic in an AlCoFeCr matrix, as well as lack of intergranular oxidation typical of APS deposited coatings. Indentation Vickers hardness results ($HV_{0.2}$) were 200 and 635 for the APS and HVOF coatings respectively, which can probably be explained by the difference in the coating density and homogeneity. The hardness of HVOF coating is close to that of QC alloy or coating (~700 $HV_{0.1}$) and higher than that of the NASA PS212 coating (~ 300-400 HV) [20]. Tribology tests are in progress with these coatings.

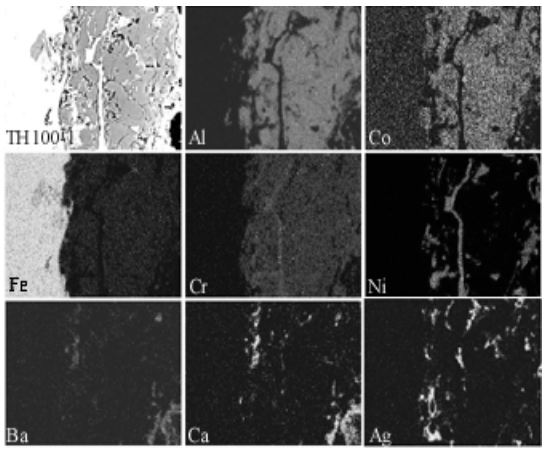


Fig. 5. EDS mapping of APS coating

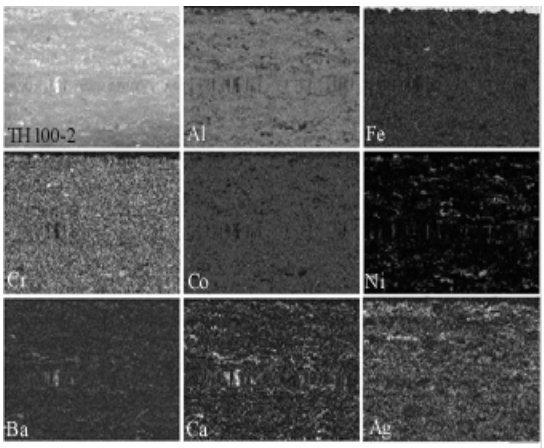


Fig. 6. EDS mapping of HVOF coating

5. CONCLUSIONS

The following conclusions can be drawn from the work performed on alloyed MoS_2 thin films:

- The initial results presented in this work show that MoS_2 films alloyed with titanium are dense and smooth, with a hardness value under load up to about 10000 N/mm^2, for max. loading of 10 mN, which still corresponds to the hardness value of a soft lubricant film. The elastic recovery of the indentation on these thin films is about 30%. Hardness of films increases with Ti content.
- Ti alloyed MoS_2 films present a relatively low and stable friction coefficient of about 0.07 - 0.1 when tested under atmospheric conditions and relative humidity below 50-60 %. Higher relative humidity conditions led to degradation in the performance of these films, raising the friction coefficient up to values of 0.2 to 0.6.
- When tested under vacuum the best MoS_2 films exhibit very low and stable friction coefficients near 0.01 for long periods of time. Endurance life of these films at contact stress 0.75 GPa can be as high as about 350,000 wear cycles, before the onset of failure.
- As it occurs with other MoS_2 films, there is transference of material to the counterface ball during wear testing, therefore providing low friction behaviour during tribological tests.

Concerning the work done on thermal spray coatings:

- QC alloy matrix composite coatings have been deposited by APS and HVOF. The HVOF deposited layer exhibits excellent microstructural quality and a promising hardness level, which is higher than in the case of other high T solid lubricant coatings, such as NASA PS212.
- Tribo-tests are in progress to determine the usefulness of these coatings for the intended high T space application. More detailed characterisation including XRD analyses of the starting powders and the coatings is being carried out in order to determine if the different phases as well as their orientation (in particular, the quasicrystalline one) are maintained in the coating.

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