TRIBOLOGICAL PERFORMANCE OF ENVIRONMENT FRIENDLY SURFACE MODIFIED DIES IN DEEP DRAWING

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ABSTRACT

The present paper investigates the characteristics of well deposited surface coating of tool steel. By the right choice of surface coating processes, process parameters, coating material and coating properties like coating thickness and possibly multiple layer configurations, a mechanically well functioning coating can be obtained. MoS_2 was used as a source material in thermal evaporation process to deposit a thin film of Molybdenum of thickness in submicron on high speed steel substrates and their coating characteristics were analyzed.

Keywords: surface coating, deep drawing, friction.

INTRODUCTION

Deep drawing is one of the most widely used sheet metal forming processes in the production of automotive components, LPG bottles and cooking utensils. The formability of a blank depends on process parameters such as blank holder force, lubrication, punch and die radii, die- punch clearance, material properties and thickness of sheet metal. Deep drawing is a process that is characterized by severe sliding contact between blank and die. The tribological system designed for a deep drawing process should impede the direct contact between die and the blank. The separation of die and blank surfaces minimizes the adhesion thereby reducing tool wear. Lubrication which is required to realize the die-blank separation and friction reduction depend strongly on the tribological loads that appear in the process.

Contact normal stresses, surface enlargement, relative velocity between die and blank surfaces, initial temperature and sliding distance are some of the parameters that characterize the tribolgical loads in the deep drawing process [1].Contact normal stresses and sliding distance can be very significant in designing a tribological system for deep drawing process. These parameters illustrate the need for special lubricants, antifriction surface coatings on die surfaces and use of anti seizure tool materials to maximize life of die. Deep drawing is therefore often lubricated by effective but environmentally hazardous (chlorinated) lubricants to increase the life time of die and punch.

Mineral oil without additives is often used in simple deep drawing operations. Friction modifiers are added to mineral oil for heavy duty applications. Lubricants with extreme pressure (EP) additives containing chlorine, phosphorous, zinc and sulphur are specially developed for deep drawing process. These EP additives form a reaction layer at severe friction conditions and at high temperatures. Although these lubricants are effective in reducing the wear of die, they are extremely hazardous. Chlorinated paraffin often form dioxins, zinc based additives give problems in waste water treatment and sulphur based additives are incompatible with non ferrous components of machinery.

In addition to the lubricants, unhealthy degreasing agents are used to remove lubricating oil from deep drawn parts. The disposal, recycling and handling of these residual lubricants and degreasing agents is a problem faced by metal forming industries.

In the die curvature region, contact pressures between die and blank can achieve high values so even low coefficient of friction will lead to relatively high shear stresses. At the punch radius, however, the material flow should be suppressed, so the coefficient of friction should be as high as possible. As a result, the material flow is suppressed and the friction stresses help to transfer the punch force to the blank. Hard solid lubricant coatings deposited on specific areas of dies can be useful in increasing the life of dies. Due to production costs and environmental issues it is more desirable for deep drawing process to be carried out in minimized oil based lubrication or substitute oil based lubrication with hard solid lubricant coated dies.

The deposition of suitable solid lubricating coatings on deep drawing dies may result in an environment friendly “greener metal forming operation”. Deposition of a protection coating, preferably a hard coating is necessary to prevent failure of the system caused by wear of die, especially caused by material transfer from sheet to die. Titanium carbide, Titanium nitride, Diamond like carbon, Molybdenum Disulfide and chromium nitride are the coating substances that have been successfully applied to dies to reduce wear in unlubricated deep drawing process [2].

Wear resistance and hardness of forming tools, being surface properties, can be improved by various surface modification methods and to extend the service life of the components [2]. Coating techniques are currently implemented to improve deep drawing die life though it is difficult to meet the many coating requirements of excellent bonding, adequate thickness, and absence of flaws, suitable mechanical properties, thermal shock resistance and high temperature stability [3]. Reactive coating and Deposition coating are the two methods that can be used to improve the surface of deep drawing dies and tribological performance of deep drawing process. Even though reaction coatings are able to increase the wear resistance of die material, they will not be able to eliminate or reduce lubrication.

Deposition coatings can be obtained by depositing a thin film of coating substance to the surface. Hard chrome plating, Physical vapor deposition, chemical vapor deposition and laser surface modification are some of the important deposition processes used in deep drawing. Hard chrome plating, even though widely used in forming industry is not environment friendly. PVD and CVD Coatings are preferred by metal forming industry because of their ability to minimize die wear. The thickness of the coating by PVD and CVD is around 5µm or less. Laser surface modification can be an important development used in deep drawing to coat the surface of die to improve the life time of dies.

The coating needs a minimal thickness to reduce risk of plastic deformation of the substrate because the spot where the maximum von mises stress occurs has to be in the coating and not in substrate or at coating substrate interface [4]. A coating with high elastic modulus acts in fact as a stress barrier. This means that after deposition of coating, higher mechanical loading of forming tool is in principle possible. It is important to select right choice of coating properties. For this, factors like coating thickness, roughness, elastic modulus and internal stresses which are in a complex way interrelated have to be optimized. If this is not done, failure of coating, interface or substrate can occur.

Solid lubricants are solid materials that exhibit low friction and/or low wear during sliding in the absence of external supply of lubricants. Solid lubricant can be attractive alternative to oil based lubricants in can forming for food industry, because of their superior cleanliness. The crystal structure of MoS_2 is a hexagonal layered structure similar to that of graphite. It consists essentially of planes of Molybdenum atoms alternating with planes of sulphur atoms in the sequence S:Mo:S:S:Mo:S:. The atomic arrangement in each layer is hexagonal and each Molybdenum atom is surrounded by trigonal prism and S atoms at a distance of 0.241 nm. Adjacent planes of S atoms are 0.301 nm apart. Thus the forces holding the atoms together in each group of S:Mo:S layer are relatively strong covalent bonds whereas the forces between adjacent planes of S can slide readily over each other and this is believed to be responsible for low frictional resistance. MoS_2 is often used in the form of dry powder [5].

The effect of moisture on molybdenum disulphide is to increase both friction and wear rate; however, the effect of moisture on the coefficient of friction is generally reversible. Usually moisture is not encountered in metal forming process. The general effect of increased temperature on molybdenum disulphide films is to reduce both friction and life. The friction is at its lowest for fully ordered surface films in dry air or vacuum at high load and highest for randomly-oriented films in the presence of water vapor or certain other vapors at low load.

Kenneth Holmberg *et al*., [6] presented the fundamentals of coating tribology by using a generalized holistic approach to the friction and wear mechanisms of coated surfaces in dry sliding contacts. It is based on a classification of the tribological contact process into macro mechanical, micromechanical, nano mechanical and tribo chemical contact mechanisms, and material transfer. The use of thin multilayer offers an excellent possibility for surface design to achieve the required properties at the surface. Increased coating/substrate adhesion, improved load support, surface stress reduction and improved crack propagation resistance can be achieved by different concepts of multilayer surface design.

G. Wiese *et al*. deposited MoS_x films with interlayer of Cr on steel substrates by means of magnetron sputtering [4]. The coating parameters such as working pressure, target substrate distance, rf power and deposition mode were varied. It was observed that the microstructure of MoS_x films is found to be nano structured and is very strongly influenced by sputtering process conditions. Good wear properties were achieved when the films were deposited on coating conditions with large target substrate distance. It was reported that rf magnetron sputtering of MoS_x films on deep drawing die ring was not promising because of lack of adhesive strength. The coating technique needs to be investigated for optimizing wear resistance of deep drawing die material by varying the coating parameters, structure and tribological properties.

Table-1. Properties of MoS_2.

S. No.	Property	Units
1	Density	5.06 g/cm^3
2	Hardness	60 kg/mm^2
3	Thermal conductivity	0.13 W/m °K

EXPERIMENTAL PROCEDURE

Sample preparation

The material investigated in this study was High speed steel with a composition of 18% W, 4% Cr, 1% V, 0.7% C and rest Fe. The substrates were made with dimensions of 50 x 12 x 1 mm and hardness of HRC 60. The substrate samples were cut from a HSS single point cutting tool using a wire cut EDM machine. The substrates are ground and polished using silicon carbide emery paper. Then the substrates were cleaned with acetone prior to coating. The substrate samples were then etched in Nital solution.

Vacuum coating unit

The basic unit of thermal evaporation system consists of a cabinet containing a vacuum pumping system together with all the electrical components necessary for coating process. The chamber is fabricated from polished stainless steel with a circular window for visual inspection of coating process.

VOL. 9, NO. 5, MAY 2014 ISSN 1819-6608
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The chamber is evacuated by a diffpack pump and backed by a 250 litres/min double stage direct driven rotary vacuum pump. A hand operated high vacuum valve isolates the chamber from the pumping system so that the chamber can be brought to atmospheric pressure without switching of the pumping system. Two numbers of butterfly valves are connected in pipe line, one for roughing and other for backing.

A boat type filament holder is fixed to L.T. live electrode and a earth electrode. The filament is normally positioned vertically below the centre of work holder to give uniform distribution of the evaporation. This resistance filament heater is used to evaporate the source material. A substrate heater of heating element Super khanthal and size 3 inches diameter and 35 mm thickness is used. A thermocouple of K type is used. A quartz crystal of 6 MHz is used for digital thickness monitor. The thickness monitor allows improved manual control of the vacuum film deposition process by providing a direct display of film thickness and deposition rate.

Semi automatic control of film thickness can be accomplished by utilization of the shutter control relay in the monitor. The shutter control relay allows for direct control of the system shutter and will also automatically close the shutter when the deposition thickness equals a pre programmed value.

Coating of MoS_2

The deposition of hard thin films by thermal evaporator consists of the following steps (1) Transition of a condensed phase, which usually is solid, into the gaseous state by heating the source material in a resistance-heated vessel or, with an electron-gun (2)Vapor traversing the space between the evaporation source and the substrate at a reduced gas pressure (in the order of 10^{-4} Pa for non-reactive, or 10^{-2} Pa in cases of reactive evaporation) and (3) Condensation of the vapor onto the substrate upon arrival (if required, at an elevated temperature, e.g. 300°C).

The thermal evaporator is started up by turning on the power supply and vacuum. The preprogrammed option on the deposition selection meter is selected. The coating thickness of 1 µm is set. Then the density and impedance slots are selected and values set. For Molybdenum density value is 10.8 and impedance is 34.36 (as given by coating equipment manufacturer). The bell jar is opened and HSS samples are inserted in to the substrate holder and 15 grams of MoS_2 powder is loaded in to filament boat. The bell jar is closed and the chamber is pumped on. The filament heater is turned on and the selector switch is on 8 amperes. The substrate heater is also switched on. When the deposition has begun, the open shutter is pressed on deposition meter by flipping shutter switch down. The current is adjusted to maintain the ideal deposition rate. At the desired thickness the shutter is closed. The current is slowly ramped down. The equipment is turned off and the jar is opened and coated sample removed.

Purity of the film depends on the purity of the source material and the quality of the vacuum. Thicknesses of the film vary due to the geometry of the chamber. The working pressure in the vacuum chamber was kept at 5 x 10^{-6} Pascal. The substrate was heated to 160°C. Quartz crystal is used to monitor the thickness of the deposited film and also to control the rate of evaporation. A thin film of MoS_2 of approximately 1 µm was deposited on HSS substrate.

Coating characterization

The metallographic study and chemical composition analysis of thermally evaporated MoS_2 coatings were conducted using scanning electron microscope integrated with energy dispersive x-ray spectroscopy. The samples were observed using the scanning electron microscope while the EDXS detector was used to collect composition data from the sample. The focusing distance was set less than 14 mm to allow the EDXS detector to collect the information from the sample surface. Identification of elements on the sample cross-sectional surfaces was carried out using the integrated software.

RESULTS AND DISCUSSIONS

The SEM images of uncoated HSS sample are shown in Figure-1. The microstructure consists of carbides in a martensite matrix. These carbides are probably the types M6C (where M is either molybdenum or tungsten) and vanadium carbide. The SEM image of MoS_2 coated sample is shown in Figure-2 and a homogenous microstructure is seen. A significant difference in microstructure is seen in the SEM images of coated and non coated sample.

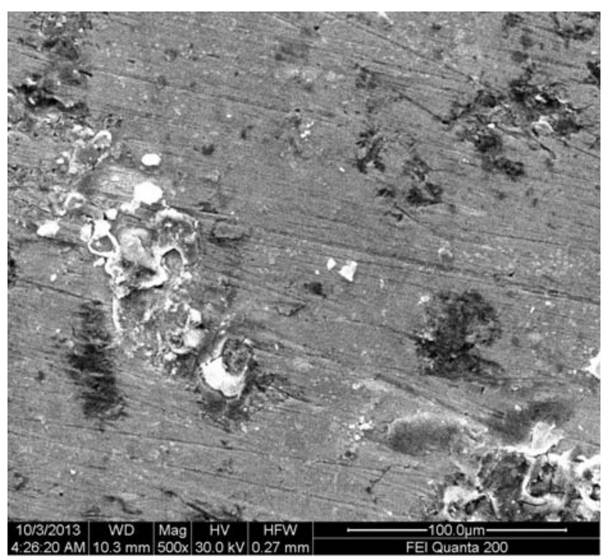

Figure-1. SEM image of non coated sample.

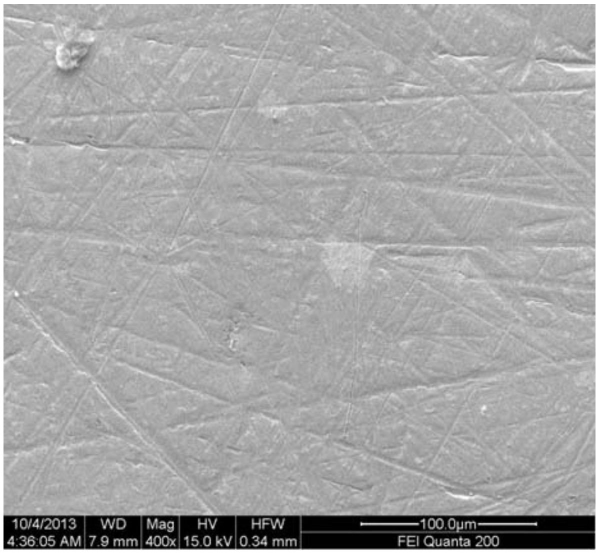

Figure-2. SEM image of coated sample.

The EDXS qualitative analysis spectrum of phases detected in the selected area of non coated sample is given in Figure-3. Figure-4 shows the spectrum of MoS_2 sample. A High Mo peak was observed in spectrum of coated sample and Fe peak was observed in non coated sample.

The Chemical composition of coated sample was compared with non coated sample (Figure-5 to Figure-8). In Figure-5, eight elements were detected in the selected region of coated sample. The content of all the elements were lower when compared with non coated sample.

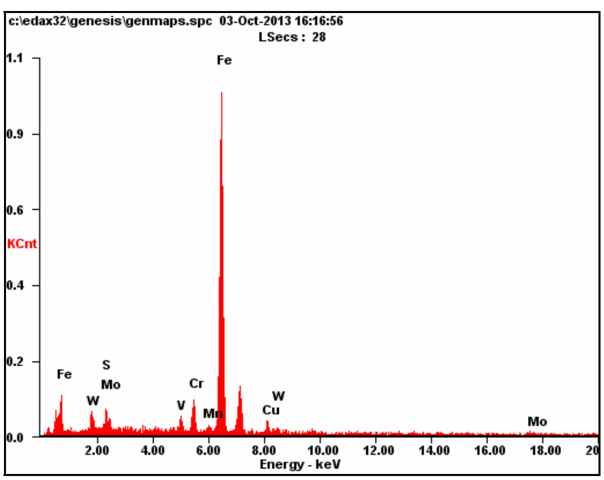

Figure-3. EDX spectrum of non coated sample.

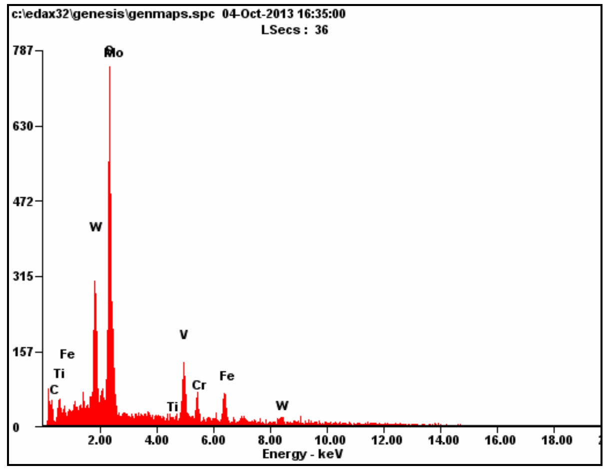

Figure-4. EDX spectrum of MoS_2 coating.

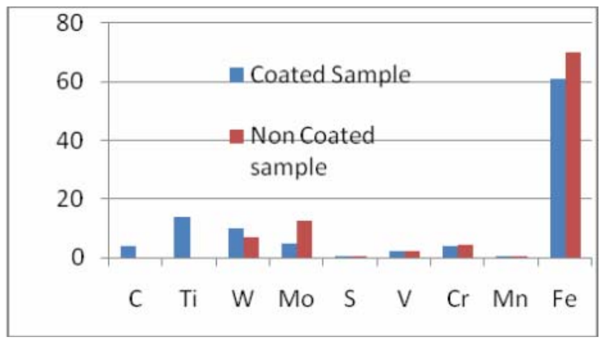

Figure-5. Comparison of chemical composition of coated and non coated samples (wt%)-Spectrum-1.

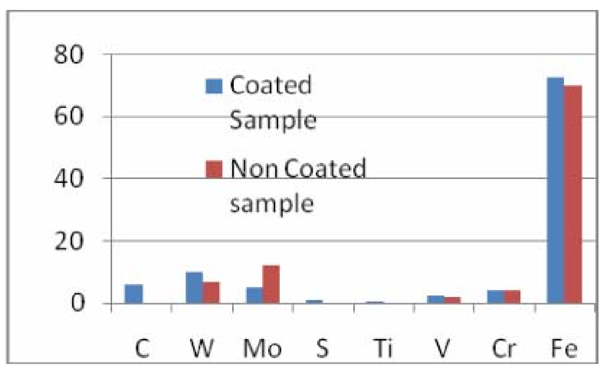

Figure-6. Comparison of chemical composition of coated and non coated samples (wt%)-Spectrum-2.

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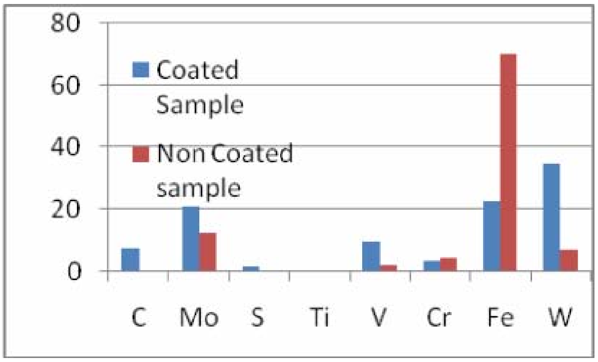

Figure-7. Comparison of chemical composition of coated and non coated samples (wt%)-Spectrum-3.

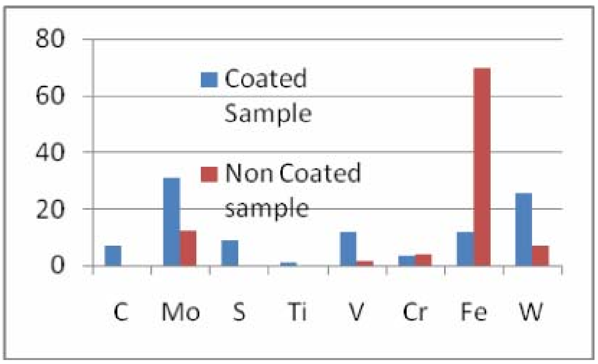

Figure-8. Comparison of chemical composition of coated and non coated samples (wt%)-Spectrum-4.

The Chemical composition of coated sample was compared with non coated sample (Figure-5 to Figure-8). In Figure-5, eight elements were detected in the selected region of coated sample. The content of all the elements were lower when compared with non coated sample.

The same pattern is observed in the selected region of Figure-6. In Figure-7, the Mo and W content of coated sample is higher than that of non coated sample. The Fe content of coated sample is lower when compared with non coated sample. The Cr content remain unchanged in all selected regions of coated and non coated samples.
In Figure-7, the Mo and W content (weight %) is substantially higher in coated sample when compared with non coated sample. The Fe content (weightt %) has lowered considerably after coating. In Figure-8 also the Mo and W content has increased and Fe content decreased after coating. The weight % of S is considerably lower in almost all the coated samples.

The At % of various elements in the coating is shown in Table-2.The At % of C and Fe has been higher in the coating when compared with non coated sample and this is probably due to thermal evaporation. One important observation is that the elements can be controlled by optimizing the thermal evaporation parameters such as Vacuum pressure and substrate temperature.

Matthinj de Rooij investigated the deep drawing process, operating under unlubricated conditions using dies with a hard protective coating [7]. Under conditions of static contact, material and roughness of sheet dominate the contact between the sheet and die. Therefore a hard coating on die does not significantly influence the static contact behavior. The micro geometrical properties of die are important in case of sliding contact between die and sheet blank. Under unlubricated conditions the material is transferred from sheet to die and lumps can initiate on die surface, grow during production and at a certain moment grow large enough to scratch the sheet blank. Material transfer preferably occurs at surface extrema (high heights and steep slopes).

A theoretical model has been developed describing the growth of lump initiated on the die surface. The tribological behavior of hard surface coated dies under conditions of unlubricated deep drawing are investigated experimentally and the results are in agreement with lump growth model.

Francis Clarysee [8] investigated the effect of applying PVD coatings on forming tools for forming of galvanized steel identifying the response of coating to galling. Three different PVD coatings, a typical hard CrN coating, a tungsten doped DLC (WC/C) Coating and a Ti N/MoST composite coating were compared with uncoated tool by tribological characterization of various coatings.

Table-2. At % of elements in coating from EDX spectrum.

	I	II	III	IV	V	VI	VII
C	16.7	23.6	18.8	22.9	34.9	31.2	45.4
Ti	14.7	0	0	0	0	0	0
W	2.7	2.5	2.5	2.6	11.0	7.56	9.9
Mo	2.5	2.4	2.7	3.5	12.7	17.6	13.0
S	0.9	1.0	1.0	0.16	2.54	14.8	0.5
V	2.0	0.3	0.5	0.67	11.0	12.4	11.2
Cr	3.6	2.2	1.8	2.15	3.43	3.58	3.79
Mn	0.5	3.8	4	4.04	0	0	0
Fe	56.0	63.7	68.4	63.8	23.6	11.7	15.6

In the multifrottement test, a steel strip ia clamped between a flat and cylindrical die (both coated) and pulled several times (typically 10) at a given velocity under dry condition. The standard output of this test is the evolution of coefficient of friction, calculated from pulling forces as a function of passage (stroke number). It was observed that WC/C Coating performed very well when compared with other coatings. Topographical Surface Analysis for four different tool surfaces (three different coated tools and one uncoated tool) was performed. In case of uncoated systems very large bumps of Zn (coming out of steel) were identified. The adhesive build up of Zn is much smaller for tool surfaces with CrN and TiN/MoST coatings, while for WC/C coating cold welding is not observed. The improved behavior of WC/C coating found out from results on laboratory scale have been verified and confirmed in industrial environment.

A Molybdenum disulphide/titanium surface coating (MoST) is developed for forming applications and its performance is evaluated [9]. The composite MoST coatings of 1.2µm thick were deposited by DC Magnetron sputtering. Scratch testing of MoST coating showed failure of coating at 120 N which is much better than other hard tool coatings. Reciprocating wear tests were conducted at 100 N loads with 5 mm WC-6%Co ball moving at 150 mm/min. At 41% humidity the MoST coating survived for 9999 cycles. The friction Coefficient is 0.043 and the wear rate after 9999 cycles is 0.5µm. The hardness value for MoST coating is is found to be in the range of 15 GPa to 21 GPa.

The effectiveness of MoST coating is confirmed by metal forming industry. The surface of ejector pins used for plastic moulds was modified by MoST coating and compared with uncoated ejector pins. The uncoated ejector pins produced 2000 shots before failure whereas MoST coated pins produced 1, 00, 000 shots. MoST surface coatings has improved productivity when compared with conventional hard coatings and has a great potential for success in dry and greener metal forming.

Molybdenum is coated on AISI1045 steel substrates using a novel technique known as electro-thermal explosion directional spraying (EEDS) [10]. The foils were prepared for deposition of coating using EEDS system with a applied voltage of 4850 V and a spraying distance of 100-200 mm. The thicknesses of the coatings ranged from 20 µm to 40 µm. Lamellar microstructure was not found in the Molybdenum coatings deposited by EEDS. A compact microstructure is found and this is possibly due to high temperature and high speed of molten particles during the deposition process and rapid solidification under non equilibrium conditions. The tribological tests reveal that the friction coefficient increases with the increase of the applied load. The wear loss of the Mo coatings increases with the increase of the applied load or the micro hardness of the counterpart. The main wear failure mode is micro-plowing.

Due to the strength and surface texture difference between the component blank, different friction conditions persists between the Tailor welded blanks and the tools during deep drawing process [11-13]. The friction at the interface between blank holder and TWB was found to be moderate and the friction at interface between die and TWB was found to be normal and the friction at interface between punch and TWB was found to be high. Fairly uniform thickness distribution is observed in all combinations of Al-steel tailor-welded blanks by adopting different friction condition in different regions in the deep drawing dies.

Laser processing has been proven to be capable of producing adherent, hard, wear, corrosion, fatigue and fracture resistant coatings on a diverse range of materials [14-15]. The crystal structure of metals' surfaces can actually be modified into very fine non equilibrium microstructures as a result of rapid solidification via laser surface modification [16]. Though both continuous and pulsed wave lasers may be employed for surface modification, defects such as porosity, bubbles or depressions, occur easily with a continuous wave laser [17]. Though several types of lasers are used for surface modification, CO_2 lasers have advantages over excimer lasers such as large beam size, higher laser efficiency, ease of operation, use of non toxic gases and lower costs [18].

A Mo-S-Te Composite film was grown on Inconel super alloy substrates by a hybrid pulsed laser and magnetron deposition system [19-21]. The deposition was carried out in a ultra high vacuum chamber evacuated by a turbo pump to a pressure of 1.33 x 10^{-6} Pa. An excimer laser was used to provide a pulsed beam of UV radiation of 248 nm wavelength, 20 ns duration, 50 Hz rate, and 400mJ energy. Laser targets were fabricated by mixing MoS2 and Te powders at a 75:25weight ratio (i.e., 23.5 at. % Mo; 47.0 at. % S; 29.5 at. % Te), and were cold pressed into compacted disks of 25.4 mm diameter by 6.4 mm thickness.

The SEM micrographs of Mo-S-Te composite coating showed a granular like structure. The EDS spectrum analysis revealed that some of sulphur and tellurium contents were lost because of its volatile vaporization by laser irradiation plume. The Mo-S-Te films exhibited a low friction coefficient of 0.05 at 300 °C and 0.10 at 450 °C for above 10, 000 cycles in air. The purpose of using Te additives to enhance the film durability was proposed to decrease the oxidization rate of MoS2 lubricant films at high temperatures by thermally-induced tellurium barrier formation. As tellurium migrates to the surface and oxidizes, it can protect the underlying MoS2 by being a diffusion barrier.

CONCLUSIONS

The surface modification of HSS steel was carried out using thermal evaporation with a solid lubricant coating of Molybdenum disulphide and the microstructure and chemical composition were examined. Thermal evaporation is a promising technique to deposit solid lubricant on selected areas of deep drawing surfaces so as to improve their tribological performance and eliminate oil lubrication. Excellent coating was observed on the samples. Change of elements composition in the surface modified layer of MoS2 coating was detected in the EDX analysis. A well adherent surface coating can be deposited on deep drawing die steels by controlling the coating process parameters, coating properties, coating film thickness and possibly a multi layer coating. Additional research is required so that the solid lubricant coating of deep drawing dies can be reliably practiced by sheet metal forming industries.

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REFERENCES

[1] Bay, A. Azushima, p. Groche, I. Ishibashi, M. Merlein, M. Morishita, T. Nakumara, S. schmid and M. Yoshida. 2010. Environmentally benign tribo-systems for metal forming. CIRP Ann. 59: 760-780.

[2] Francesca Borsetto. 2009. Tribolgical Performance of environment friendly solid lubricant coating for sheet metal forming, DoctoralThesis, University of Paduva.

[3] Jiang W and Molian P. 2001. Nanocrystalline TiC powder alloying and glazing of H13 steel using a CO_2 laser for improved life of die-casting dies Surf Coat Technol. 135(2-3):139-149.

[4] G. Weise, N. Mattern , H. Hermann, A. Teresiak, I. Ba¨cher, W. Bru¨ckner, H.-D. Bauer H. Vinzelberg, G. Reiss, U, U. Kreissig, M. Ma¨der and P. Markschla¨ger. 1997. Preparation, structure and properties of MoS*x* films, Thin Solid Films. 298: 98-106.

[5] Bharat Bhushan. 2013. Principles and Applications of Tribology. 2^{nd} Edition. Wiley.

[6] Kenneth Holmberg. 1998. Allan Matthews and Helena Ronkainen, Coatings tribology-contact mechanisms and surface design. Tribology International. 31(1-3): 107-120.

[7] Matthinj de Rooij. 1998. Tribological aspects of unlubricated deep drawing processes, Phd Thesis, University of Twente, Netherlands.

[8] Francis Clarysse, Walter Lauwerens and Michel Vermeulen. 2008. Tribological properties of PVD tool coatings in forming operations of steel sheet. Wear. 264: 400-404.

[9] N.M. Renevier, V.C. Fox, D.G. Teer and J. Hampshire. 2000. Performance of low friction MoS_2 titanium composite 2 coatings used in forming applications. Mater Design. 21: 337-343.

[10] Guo Jin, Binshi Xu , Hai-dou Wang , Qing-fen Li and Shi-cheng Wei. 2007. Tribological properties of molybdenum coatings sprayed by electro-thermal explosion directional spraying. Surf Coat Technol 201: 6678-6680.

[11] R. Padmanabhan, M.C. Oliveira, J.L. Alves and L.F. Menezes. 2008. Numerical simulation and analysis on the deep drawing of LPG bottles. J. mater process technol. 200: 416-423.

[12] R. Padmanabhan, M.C. Oliveira and L.F. Menezes. 2008. Deep drawing of aluminium-steel tailor-welded blanks Mater Design. 29: 154-160.

[13] Selection and identification of elastoplastic models for the materials used in the benchmarks. In: Progress Report of the Digital Die Design Systems (3DS) Project. vol. 13, University of Paris.

[14] DiMelfi RJ, Sanders PG, Hunter B, Eastman JA, Sawley KJ and Leong KH, *et al*. 1998. Mitigation of subsurface crack propagation in railroad rails by laser surface modification. Surf Coat Technol. 106(1): 30-43.

[15] Tsai H.L. and Tsai P.C. 1995. Performance of laser-glazed plasma-sprayed (ZrO_2- 12wt. %Y_2O_3)/ (Ni-22wt. %Cr-10wt. %Al-1wt. %Y) thermal barrier coatings in cyclic oxidation tests. Surf Coat Technol. 71(1):53-59.

[16] Matthews D.T.A, Ocelik V and deHosson J.T.M. 2007. Tribological and mechanical properties of high power laser surface-treated metallic glasses. Mater Sci Eng. 471(1-2):155-164.

[17] Pinkerton AJ and Li L. 2003. An investigation of the effect of pulse frequency in laser multiplelayer cladding of stainless steel. Appl Surf Sci. pp. 208-209:405-410.

[18] Dadbin S. 2002. Surface modification of LDPE film by CO_2 pulsed laser irradiation. Eur Polym J. 38(12): 2489-2495.

[19] J.J. Hu, J.E. Bultman, C. Muratore, B.S. Phillips, J.S. Zabinski and A.A. Voevodin. 2009. Tribological properties of pulsed laser deposited Mo–S–Te composite films at moderate high temperatures. Surf Coat Technol. 203: 2322–2327.

[20] Panagopoulos CN, Markaki AE and Agathocleous PE. 1998. Excimer laser treatment of nickelcoated cast iron. Mater Sci Eng A. 241(1-2):226-232.

[21] A. Nilsson, L. Kirkhorn, M. Andersson and J.-E. Ståhl. 2011. Improved tool wear properties in sheet metal forming using Carbide Steel, a novel abrasion resistant cast material. Wear. 271: 1280-1287.