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Project Title

Magnetic Thin Films Formed in a Glow Discharge

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1. Introduction

Since this project is a continuation of a cooperative effort between UMR and General Motor Research Laboratories (GMR), it seemed fitting to provide some background information which was instrumental in the evolution of this program.

A family of filled epoxies that can be cast-to-size into sheet metal stamping dies has been developed by GMR. Advantages of this material over commercial plastic tooling materials are a fast curing rate, high strength, and negligible volume shrinkage after curing. Superior Tooling And Molding Plastic (STAMP) tooling dies are considerably cheaper and faster to make than steel tooling dies; therefore, they are currently used for prototype applications throughout General Motors. With improvement of wear resistance, STAMP dies can be used for limited production applications involving 10,000 or 20,000 parts. GMR proposed to provide a thin ($< 25 \mu\text{m}$) wear surface for the cast-to-size STAMP die to extend its wear performance.

The objective of the University of Missouri-Rolla (UMR) research effort is to technically evaluate methodologies to coat STAMP material to appreciably improve wear resistance. This does not necessarily mean that various types of coatings will be developed and evaluated. Rather, the primary responsibility is to characterize the nature of the STAMP material and design engineered films which will lead to an optimized system.

An example of this was the finding that a thin polymer layer existed on the surface of an as-cast STAMP die necessitating removal if satisfactory adherence and toughness were to be attained. The next important finding involved the influence of particle size on wear. The theme of the research approach (characterize, evaluate, correct) was maintained throughout the course of the project, with improvements being made as the causes of failure were determined and

appropriate corrections or improvements were made. These efforts would ultimately guide and assist industrial coaters (external or within GM) in providing an industrially-viable surface for STAMP dies.

It was felt that our responsibility was to point out directions and develop lab scale coatings, whose performance was fundamentally explainable. By advancing in a step-wise manner, it would be possible to advise GM as to the coating options which offered the most promise. So the major function and the primary objective were to supplement GM Research efforts in the development of the process steps necessary for a suitable coating. Obviously, some of the coatings were made to prove the various hypotheses and establish the fundamental relationships which exist.

It should be emphasized that it may not be adequate to put on one specific film by a known process, and base success or failure only on how this film performs. The nature of the composite STAMP die may require more subtle processing, with failure modes being identified along the way, before a final, acceptable coating is obtained. Different films may offer particular advantages while possessing inadequacies with regard to other aspects of performance, e.g., a very hard film may possess a very low impact strength. Thus providing a film with a proper balance of properties, giving optimum results during use, was essential.

Toward this end, development focused on two different films; one a plasma-deposited iron carbide, the other primarily electroless nickel. The iron carbide does show promise and very good progress has been made with electroless Ni as well, but only when modifications are made to the surface prior to coating.

2. Experimental Details

I. Sample Preparation

The STAMP material used in our studies is a mixture of an epoxy resin matrix filled with SiC and SiO₂ particles. The STAMP 320 die has fine SiC and SiO₂ particles (particle size $\approx 10 \mu\text{m}$) contained in the epoxy host matrix whereas the STAMP 222 die has coarse SiC and SiO₂ particles (particle size $\approx 100 \mu\text{m}$).

All as-received samples were polished with 600-grit sandpapers. A very critical step before proceeding to deposit a coating on the STAMP material is the removal of the outer layer of the as-cast material. It is essential that the epoxy resin at the surface be removed so as to expose the filler particles and provide a more favorable surface for further coating processes.

II. Design and Construction of the Plasma Processing System

In the early stage of the study, a plasma-deposited iron carbide film was proposed, hence necessitating the use of a radio frequency inductively-coupled, plasma-processing system. Later, in order to provide more surface area of the filler particles and to enhance the adhesion between the STAMP die and coatings, an oxygen plasma-etching process was proposed and applied. The deposition system can be divided into four parts, as shown in Figure 1. They are: (A) plasma reactor and vacuum system, (B) gas feed-through system, (C) power supply system, and (D) pressure monitoring system.

(A) Plasma Reactor and Vacuum System

The plasma reactor is a 5-in. diameter, 40-in. long Pyrex tube. The rest of the vacuum system consists of a pre-mixer, some stopcocks, two cold traps, and a mechanical pump. The

plasma reactor tube is made up of two sections clamped together. The mechanical pump was purchased from Marathon Electric, Inc. The entire system is evacuated to a pressure of about 0.1 mTorr before each experiment.

(B) Gas Feed-through System

The gas feed-through system is composed of gas cylinders, mass flowmeters, control valves, and flow controllers. The mass flowmeters are connected to control valves and then electrically hooked up to flow controllers. The flow control system is then connected to a multi-channel digital display. Each flow controller is calibrated according to the specific gas that flows through the particular channel. The components of the flow control system were purchased from MKS Instruments, Inc.

(C) Power Supply System

The power supply system consists of a rf power generator with 300 watts output capability, a matching network composed of a control unit and a tuning unit, and a 17-turn, 1/4-in. copper coil. This copper coil acts as the coupling element between the generator and the glow discharge. The induction valve of the tuning unit needs to be adjusted by changing the inductor strap to match the design of the coupling element and the plasma reactor. The rf generator is connected to the matching network and the matching network is then connected to the copper coil using 50-ohm coaxial cables. The copper coil is wound around the plasma reactor. The rf generator and the matching network were purchased from ENI Power Systems, Inc.

(D) Pressure Monitoring System

The pressure monitoring system is composed of a pressure gauge and a digital readout. The pressure gauge is equipped with an absolute transducer and capable of monitoring a pressure range of 10^{-4} - 1 Torr. Both the pressure gauge and digital readout were purchased from MKS Instruments, Inc.

III. Plasma Deposited Films

Different types of substrates were placed on a heating plate inside the plasma reactor for the purpose of controlling temperature. The starting materials used were iron pentacarbonyl [$\text{Fe}(\text{CO})_5$], hydrogen, methane (CH_4), or a combination of the three. The typical rf power was ca. 30 W and a substrate temperature of 50 °C. The film thickness was determined by the Nomarski interference method using a Reichert Nomarski polarization interferometer. The morphology of the films was examined by SEM and the crystal structure was determined by X-ray diffraction. The composition of the films was determined by Auger electron spectroscopy using a PHI Model 545 Auger spectrometer operated at pressures below 5×10^{-9} Torr. The depth profiling was carried out by sputtering with argon ions at a pressure of 5×10^{-5} Torr, a voltage of 2 kV, and a current of 10 mA. The hardness of the deposited films on the STAMP dies was measured with a Tukon microhardness tester (Model 300). Film adhesion was measured with an Instron tensile tester using a direct pull method. The main components of the apparatus for the pull test are shown in Fig. 2.

III. Wear-Resistance Test

All wear-resistance measurements are performed at GMR. These include the drawbead test, Falex test, block-on-disc test, and cylinder-on-block test. A drawbead test sample has dimensions of approx. 9 mm square x 69 mm. A Falex test sample has dimensions of 15 mm x 10 mm x 6 mm. A block-on-disc sample has dimensions of 47.5 mm x 47.5 mm x 3 mm. A cylinder-on-block sample has dimensions of 6 mm dia. x 10 mm.

3. Results and Discussion

I. Plasma Deposited Films

Initially an amorphous film was deposited onto STAMP substrates at ambient temperature using $\text{Fe}(\text{CO})_5$ and H_2 as the starting materials. The film, however, had a microhardness of only 40 HV (Vickers hardness scale, kg/mm^2) compared with a STAMP die microhardness of 20 HV. Figs. 3 and 4 show the surface morphologies of the original STAMP die and the film deposited at ambient temperature, respectively.

In order to increase the microhardness of the film, the deposition temperature was raised to 50 °C. A typical experimental run is shown in Table I. The Auger spectra of carbon peaks show the characteristic satellite peaks of iron carbide films. A compositional depth profile of the film is shown in Fig. 5. The particle size of this film is apparently larger than that deposited at ambient temperature as evidenced in Fig. 6. The film adheres to STAMP substrates very well according to the pull test results given in Table II. More importantly, the film has an average microhardness of ca. 125 HV. However, after the drawbead tests performed at GMR, a certain degree of cracking was observed within the film due, probably, to the buildup of compressive

stresses within the layer.

To increase the toughness and hopefully relieve the stresses in the film, a graded coating beginning with a soft (graphitic) layer at the interface grading to a hard layer with a thin final graphitic coating using a combination of $\text{Fe}(\text{CO})_5$, H_2 , and CH_4 as the starting materials. The flow rates of methane and hydrogen were varied with that of $\text{Fe}(\text{CO})_5$ to generate a chemical gradient in the coating. The flow rate of $\text{Fe}(\text{CO})_5$ was set at $\text{ca. } 1 \times 10^{-3}$ cc/sec and those of methane and hydrogen were changed as shown in the Appendix. The rf power was 30 W and the substrate temperature was 50°C . The microhardness of the graded coating was measured to be 70 kg/mm^2 , which was lower than that of the original ungraded iron carbide film deposited at 50°C , 125 kg/mm^2 . This was expected inasmuch as the finish coating was designed to be softer (to minimize cracking upon impact and to be somewhat lubricous). The variation of carbon content in the graded coating is shown in Fig. 7.

II. Electroless Ni Coatings

Since the ultimate goal of the research project with GMR was to develop a coating with a microhardness of 200 kg/mm^2 or above, an electroless Ni coating process was proposed in combination with the plasma-deposited iron carbide film or to be used as the sole coating on STAMP substrates. The electroless Ni coating system is commercially available. The electroless Ni coating deposited on a polished STAMP substrate exhibited a microhardness of 207 kg/mm^2 , while the same Ni coating formed on an iron carbide film, which had been plasma-deposited on a polished STAMP die, exhibited a microhardness of 225 kg/mm^2 . The adhesion between the Ni coating and the iron carbide film was excellent according to the pull test

(>3,000 psi).

The research objective was to evaluate and apply coatings on STAMP materials to improve wear resistance and toughness of the material. Another concern of the studies was the adhesion between the STAMP material and coating. The coating is useless unless it adheres strongly to the substrate. To improve the adhesion and hence avoid delamination, a plasma etching process was applied to the polished STAMP surfaces prior to the coating process. An electroless Ni-P system was then used to provide a wear-resistant coating.

The following initial Falex test (ring-on-block wear test) results show the effects of the oxygen plasma etching process as well as that of the filler particle size on the wear resistance of electroless Ni films.

	Time to Failure (Minutes)
STAMP 222 - uncoated (coarse filler particles, $\sim 100 \mu\text{m}$)	23
STAMP 222 - electroless Ni only	24
STAMP 222 - O ₂ plasma + electroless Ni	29
STAMP 320 - uncoated (fine filler particles, $\sim 10 \mu\text{m}$)	27
STAMP 320 - electroless Ni only	35
STAMP 320 - O ₂ plasma + electroless Ni	43
STAMP 320 - graded iron carbide coating	43

From these results, it is apparent that STAMP materials with fine filler particles (STAMP 320) provides a surface for a better wear-resistant Ni coating and that oxygen plasma-treated

surfaces provide better adhesion between the substrate and the Ni coating. The oxygen plasma etching process predominantly removes the soft polymer matrix at the surface and hence exposes not only more filler particles but also more surface area of these particles. This creates a microroughness on the surface and thus provides an interlocking effect between the substrate surface and the Ni coating. Figure 8 shows the surfaces of a STAMP 320 sample before and after oxygen plasma treatment. The operating parameters for the plasma treatment are as follows: flow rate of $O_2 = 7 \times 10^{-3}$ cc/sec (STP); rf power output = 30 watts; system pressure = 55-70 mTorr; and duration = 30 minutes. A preliminary study on the nucleation of electroless Cu on the STAMP surface indicates that these filler particles are the preferable sites for nucleation.

However, when samples of as-received STAMP 320 and 222 were further polished with fine alumina particles ($1 \mu m$) before applying the electroless Ni coating, the results were:

	Time to Failure (Minutes)
STAMP 222 - fine polish + electroless Ni	17
STAMP 320 - fine polish + electroless Ni	67

Excellent improvements was obtained over previous results for STAMP 320 dies with the polishing step being identified through SEM evaluation of previously failed samples as a potential source of improvement on the finer particle STAMP die. Therefore, it is very important to optimize the degree of microroughness of the polished surfaces for an excellent

wear-resistant coating to be achieved.

III. Applications of Electroless Cu, Electroless Ni-B and Electrodeposited Ni Coatings

The coated STAMP material not only needs to sustain wear but also provide impact toughness. Therefore, an electroless Cu system was introduced prior to the Ni coating process to act as an intermediate layer and provide impact toughness. In addition to the electroless Ni-P system mentioned in the previous section, an electroless Ni-B system using dimethyl amine borane (DMAB) as the reducing agent was also applied over the Cu layer. An electrodeposited Ni coating was also applied for comparison with the electroless Ni coatings. A series of samples (STAMP 320) with these different Ni coatings on electroless Cu layers were tested for wear using the block-on-disc method. Current results indicate that the electrodeposited Ni coating had the greatest resistance to wear among the three Ni coating systems.

Another type (cylinder-on-block) of wear testing was introduced after the above-mentioned two types (Falex and block-on-disc) of wear testing were used. Only electroless Ni-P coatings have been deposited on the cylindrical shaped substrate. Although the wear resistance of the Ni-P coating on the STAMP cylinder looked promising, blistering appeared after the wear test. A possible remedy was to provide either mechanical or ultrasonic agitation in order to drive off hydrogen gas bubbles from the growing film during the electroless deposition.

IV. Application of a Plasma-deposited Sn Film as the Initial Undercoat

Cylindrical shape specimens (for cylinder-on-block type wear test) made of STAMP 320 with dimensions of 6 mm (diameter) x 10 mm (length) were polished and cleaned as mentioned

previously. Figure 9(a) shows the morphology of a polished specimen. The specimens were placed inside the plasma reactor and plasma-treated as follows:

Gas: oxygen

Flow rate: 7.0×10^{-3} cc/sec

Pressure: 70 - 75 mTorr

RF power: 30 Watts; SWR ~ 1

Temperature: ambient

Duration: 30 minutes

The plasma-treated samples were then immediately coated via plasma deposition of tin (Sn) films without breaking the vacuum. The precursors of the plasma-deposited Sn films were tetramethyltin[(CH₃)₄Sn] and oxygen. The tetramethyltin is the source of tin particles and oxygen acts as the scavenger for the decomposed hydrocarbon species. The flow rate of oxygen has to be carefully controlled so that it is enough to consume hydrocarbon species but not so excessive as to cause the oxidation of tin. The operating parameters of the tin deposition are as follows:

Tin precursor: tetramethyltin(TMT), (CH₃)₄Sn

Gas: oxygen

Flow rate of TMT: 1.15×10^{-3} cc/sec

Flow rate of O₂: 1.60×10^{-4} cc/sec

RF power: 30 Watts; SWR ~ 1

Temperature: ambient

Duration: 6 hours

The plasma-deposited Sn films are approximately $1.5 \mu\text{m}$ thick. Figure 9(b) shows an SEM micrograph of a Sn film deposited on the plasma-treated specimen. The tin film exhibits the characteristics of columnar and granular crystal growth.

The purpose of applying this plasma-deposited Sn films was to provide a more adherent coating to the substrate surface, part of our efforts to continue to improve the adhesion between the coating and the substrate. Because of the extreme difference in the nature of the material between the coating and the substrate, care must be taken in choosing an appropriate coating technique to obtain an adherent coating. Plasma deposition techniques provide an opportunity to create a transitional boundary layer between substrate and coating due to the characteristics of the plasma. Particles as well as the electrons generated in the plasma constantly bombard the surfaces of the substrate and the growing film. The bombardment results in not only the deposition of the particles from the plasma volume but also the ejection of the particles from either the substrate surface or the growing film. It is this "mixing" effect that enhances the adhesion.

Another advantage of applying this plasma-deposited Sn film is that it is self-catalytic in the electroless Cu deposition that follows the tin coating process. The tin-coated specimens were

electrolessly coated with 5 μm of Cu and 15 μm of Ni as described in the previous section for the processing of the die simulator insert. The morphologies of the Cu and Ni coatings are shown in Fig. 10 and Fig. 11 respectively.

V. Processing of Die Simulator Inserts

A die simulator insert made of STAMP 320 (approx. 3" square x 8") was mechanically polished with 600 grit sandpaper to remove the outer layer of the as-cast insert. The importance of the removal of the epoxy resin at the surface is described earlier. After being cleaned in an ultrasonic cleaner, the die simulator insert was placed inside a plasma reactor as shown in Fig. 1. The plasma system was evacuated to a vacuum of 0.1 mTorr before plasma processing. Oxygen gas was introduced through a flow control unit to the system and rf power was applied from an rf generator. The die simulator insert was then plasma-treated under the following conditions:

Gas: oxygen

Flow rate: 0.3 sccm ($=5.0 \times 10^{-3}$ cc/sec)

Pressure: 101.5 - 102.1 mTorr

RF power: 75 Watts; SWR ~ 1

Temperature: ambient

Duration: 70 minutes

The plasma-treated die simulator insert was immersed in distilled water prior to further processing. After immersion, the die simulator insert was electrolessly coated with a 5 μm Cu coating followed by a 15 μm electroless Ni coating. Both Cu and Ni solutions used were commercial products from Shipley Company. Mechanical agitation was provided during both Cu and Ni coating processes to eliminate blistering by driving off hydrogen gas formed on the surfaces of the growing films. The purpose of the initial immersion was to avoid air being trapped in the pores which were formed on the surface of the die simulator insert during casting. If air was trapped in the pores, during the Ni coating process at elevated temperatures, the trapped air could expand and force the coating to break away from the substrate surface and hence cause delamination.

Both immersion and agitation contributed significantly to improving the integrity of the coating and preventing the formation of blisters as shown in Fig. 12. The photographs of the coated die simulator insert clearly show the difference in surface quality obtained as a result of processing variations. A smooth adherent coating was obtained on the surfaces prepared by polishing prior to electroless coating processes as described previously. In contrast, if the essential process of polishing was not applied to the substrate surface, blistering would develop even when immersion and agitation were applied during the electroless coating processes. The results of the coated die simulator insert tests is now needed to evaluate how the wear resistant films can be optimized. It will also improve the flexibility of processing alternatives for the surface modifications as the situation requires.

4. Conclusions

Major improvements to the adhesion of coatings on STAMP were made primarily by eliminating the thin polymeric layer on the as-cast samples and subsequently applying an oxygen plasma etch. Judging from the wear test data collected to this point, it is vital that the combination of polishing and plasma treatment be applied prior to the deposition of wear resistant coatings. According to the proposed goal of wear resistance specified by GMR, it is believed that the goal of providing a wear resistant coating with a microhardness of 200 kg/mm² has been exceeded, using either electroless Ni-P coating or a electrodeposited Ni coating, to increase the wear performance of the STAMP die. In the course of the studies, the delamination of the coatings appeared to be the major problem. However, by applying the above-mentioned effective surface modification measures, the integrity of the coatings (i.e. reduced possibility of delamination) has been improved markedly. To date, neither the stamp test results of the die simulator inserts nor the wear test results for the most recent samples that were sent to GMR have been received. Several attempts have been made to inquire as to the situation of the test results and hopefully this would lead to the conclusion of the study. A patent disclosure is in the process of being submitted to the Patent and License Office of the University of Missouri System.

TABLE I

Operating Conditions for Glow Discharge Film Formation

Pressure before experiment	1.5 μmHg
Argon ion cleaning of substrates	10 min; 37 μmHg ; r. f. power 30 W
Starting monomer	$\text{Fe}(\text{CO})_5$
Flow rate of $\text{Fe}(\text{CO})_5$	8.39×10^{-4} cc(STP)/sec
Flow rate of H_2	2.46×10^{-2} cc(STP)/sec
r.f. operating parameters	30 W (SWR = 1); 3.9 MHz
System pressure	108-110 μmHg
Duration	8 hours and 40 minutes
Maximum deposition rate	57.7 $\text{\AA}^*/\text{min}$
Temperature of substrate	50°C

TABLE II

Pull Tests of Glow Discharge Films

Film Thickness (μm)	Substrate	Adhesion Strength (F/A, psi)*
1.6	STAMP	>2,978
1.6	STAMP	>2,755
2.6	STAMP	>3,433
2.6	STAMP	>2,410

* All breakages occur between the rod and the cement. This indicates that the adhesion between the film and the substrate is even better than the values listed here.

Fig. 1. Schematic diagram for the inductively-coupled rf glow discharge system.

Figure 2. The main components of the apparatus for the pull test.

(a)

(b)

Figure 3. SEM micrographs of original STAMP. (a) 1,000X ; (b) 10,000X.

Figure 4. SEM micrographs of plasma coating using $\text{Fe}(\text{CO})_5$ and H_2 at ambient temperature. (a) 1,000X ; (b) 10,000X.

(b)

(a)

Figure 5. Depth profile of iron carbide film deposited at 50°C (sputtering rate = 25 Å/min).

(a)

(b)

Figure 6. SEM micrographs of iron carbide film deposited at 50 °C. (a) 1,000X ; (b) 10,000X.

Figure 7. Depth profile of the graded coating (sputtering rate = 35 Å/min).

(a)

(b)

Figure 8. SEM micrographs of STAMP 320. (a) before oxygen plasma treatment (b) after oxygen plasma treatment.

(a)

(b)

Figure 9. SEM micrographs of (a) polished cylindrical specimen. (b) plasma-deposited Sn film on polished cylindrical specimen.

(a)

(b)

Figure 10. SEM micrographs of electroless Cu coating on cylindrical specimen.
(a) 5,000X ; (b) 20,000X.

(a)

(b)

Figure 11. SEM micrographs of electroless Ni coating on cylindrical specimen.
(a) 2,000X ; (b) 5,000X.

(a)

(b)

Figure 12. A die simulator insert coated with electroless Ni.

APPENDIX

Specific Flow Rates and Times Used to Prepare the Graded Coatings