Ion Plating Can Improve Coating Adhesion*

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Excellent adhesion can be obtained with electroplated coatings on many substrates, as attested to by a variety of quantitative tests, such as peel, ring shear and conical head.[1,2] Listed here are a number of substrate materials classified according to ease of coating with adherent electrodeposits:

1. *Easy to plate*: steel, copper and brass. These can be coated with adherent deposits that will not fail at the deposit-substrate interface.
2. *Special treatment*: stainless steels, aluminum, beryllium, magnesium and plastics. These can also be coated with adherent deposits that will not fail at the deposit-substrate interface.
3. *Very difficult*: titanium, molybdenum, tungsten, niobium, tantalum and glass. These often require extra steps, such as chemical etching, heating or the use of augmented energy physical vapor deposition (PVD) techniques to provide good adhesion.

The principal advantage of using augmented energy PVD techniques is that excellent adhesion can be obtained without having to resort to severe etching of the substrates and/or heating after plating.

The purpose of this report is to compare the PVD techniques of evaporation, sputtering and augmented energy deposition and to show how the latter provides superior adhesion.

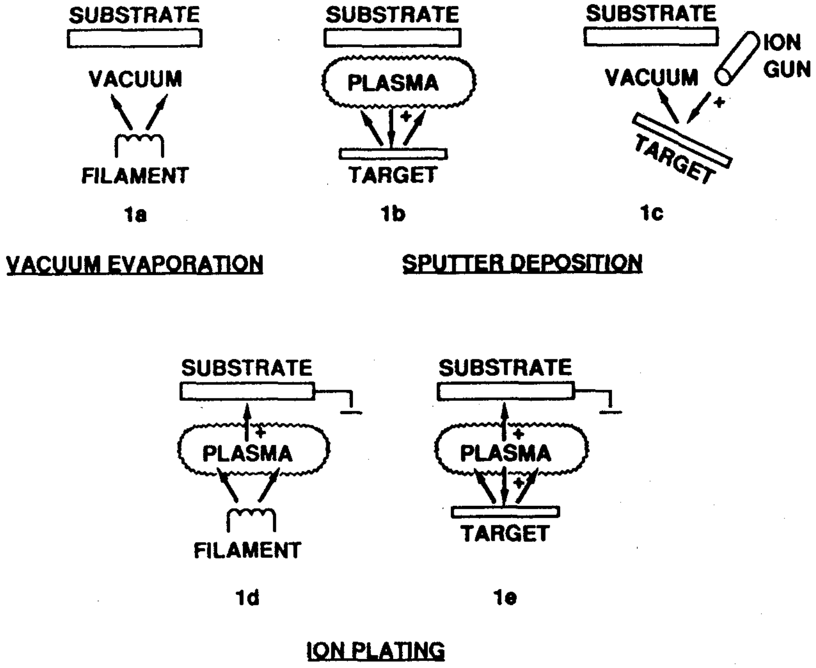

Figure 1. PVD processing techniques. (From Mattox.[6] Reprinted with permission of the American Electroplaters and Surface Finishers Society.)

PHYSICAL VAPOR DEPOSITION

In the PVD process, a material in bulk form is atomistically converted to a vapor phase in a vacuum and condensed on a substrate to form a deposit. The PVD techniques fall into three broad categories: evaporation, sputtering and augmented energy. In evaporation, vapors are produced from a material located in a source that is heated by irradiation, eddy current, electron beam bombardment, etc. The process is usually carried out in a vacuum (typically 10^{-5}–10^{-6} torr), so that evaporated atoms undergo an essentially collisionless line-of-sight transport prior to condensation on the substrate, which is usually at ground potential (not biased). Sputtering involves positive gas ions (usually argon) produced in a glow discharge that bombard the target material, thereby dislodging groups of atoms or single atoms, which then pass into the vapor phase and deposit onto the substrate. Although augmented energy techniques have been around for some 50 years,[3,4] it is only in recent times that this technology has been given renewed impetus. These techniques include ion plating,[5] thermionic plasma and formation of plasmas using hollow cathode discharge sources. Ion plating is a generic term applied to atomistic deposition processes in which the substrate is subjected to a flux of high-energy ions sufficient to cause appreciable sputtering before and during film deposition. The ion bombardment is usually done in an inert gas discharge system similar to that used in sputter deposition, except that in ion plating the substrate is made a sputtering cathode. The substrate is subjected to ion bombardment for a time sufficient to remove surface contaminants and barrier layers (sputter cleaning) before deposition of the film material. After the substrate surface is sputter cleaned, the film deposition is begun without interrupting the ion bombardment. Variations in the ion plating technique have given rise to terms such as *vacuum ion plating, chemical ion plating, bias sputtering* and others that refer to specific environments, sources or techniques. The three techniques are shown schematically in Figure 1.

With PVD films, adhesion has been reported to vary from poor to excellent.[7–9] Results clearly show much better adhesion for sputtering than for evaporation. This is attributed to the

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Table I. Quantitative Adhesion Comparisons for Physical Vapor Deposition Films on Various Substrates

Coating	*Substrate*	*Adhesion Test*	*Results*			*Ref.*
			Evaporated	*Sputtered*	*Ion Plated*	
Gold (4000 Å)	Glass	Scratch	3 g	1.5 kV, 2.5 g	–	14
	Glass	Scratch	–	2.0 kV, 3 g	–	14
	Glass	Scratch	–	2.5 kV, 13 g	–	14
Gold (8000 Å)	Glass	Scratch	6.5 g	1.5 kV, 7.5 g	–	14
	Glass	Scratch	–	2.0 kV, 17.5 g	–	14
	Glass	Scratch	–	2.5 kV, 32 g	–	14
Nickel and platinum-group metals	Glass/quartz/glazed tile	Pull	<0.7 MPa	7–10.4 MPa	–	15
Beryllium	Molybdenum	Pull	31 MPa	–	–	16
Copper	Molybdenum	Pull	–	–	>71 MPa[a]	17
	Molybdenum	Ring shear	–	–	216 MPa	17
	Tungsten	Ring shear	0	0	173 MPa	18
4 µm	6061-T6 Al	Pull	–	26–46 MPa	>71 MPa[a]	19
2.5 µm	304L Stainless steel	Ring shear	–	193 MPa	–	20
4000 Å	316 Stainless steel	Pull	<0.7 MPa	–	>71 MPa[a]	22

[a] Failed in epoxy used to adhere the pull test pin to the coating.

higher energy of the deposition species in sputter deposition compared with that of evaporated atoms (1–10 eV versus 0.1–0.2 eV).[10,11] Sputtered atoms are energetic enough not only to clean the surface of adsorbed gas atoms but also to remove oxide layers. They are also energetic enough to penetrate the substrate lattice.[12] An added benefit with sputtering is that substrate biasing has a tendency to resputter the adsorbed or weakly adhered material, thus promoting film adherence.[13] Ion plating provides even better adhesion than that obtained with sputtering. This is attributed to the highly energetic depositing ions (50–100 eV) as well as to the in situ substrate precleaning and the simultaneous deposition and substrate sputtering due to the continuous bombardment of the substrate during deposition.[7,11]

QUANTITATIVE ADHESION COMPARISONS

Quantitative adhesion data have been obtained by using scratch tests, pull tests and ring shear tests on substrates, such as glass, quartz, glazed tile, aluminum, stainless steel, molybdenum and tungsten. All of the data are summarized in Table I, which clearly shows that ion-plated coatings provide superior adhesion. Sputtered films adhere better than those produced by evaporation, but even these are noticeably inferior to those obtained with ion plating.

Chopra[14] measured the scratch test critical load for gold films deposited on glass by evaporation, glow discharge sputtering and argon ion beam sputtering. The results, presented in Figure 2, show that (1) in all cases the critical load was found to increase rapidly with the film thickness above approximately 2000 Å; (2) sputtered films applied at sputtering voltages above 1.5 kV were noticeably more adherent than evaporated films; and (3) adhesion was higher and increased more rapidly for increasing accelerating voltages.

Belser and Hicklin[15] used a pull test to measure adherence of metal films deposited on glass, quartz and glazed-tile surfaces. Headed brass pins were soldered to the coated substrate with Cerroseal (50% tin–50% indium) or tin-lead solder. The force to pull the film perpendicularly from the surface of the substrate was measured by a spring balance and winch system. Pull values of 7–10.4 MPa were obtained for sputtered nickel and the platinum metals, except palladium, deposited after bombardment with positive ions (50–100 mA at approximately 3000 V for 5–10 min). Occasionally, glass substrates fractured near the upper values without breaking the bond between them and the film. By contrast, values of less than 0.7 were obtained for evaporated gold films.

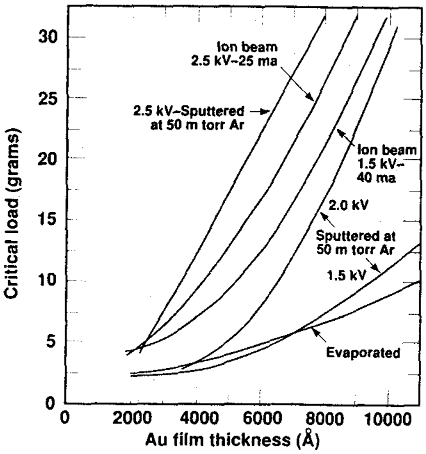

Figure 2. Critical load in a scratch test as a function of the thickness of polycrystalline gold films deposited on glass at an average rate of approximately 1 Å/sec by evaporation at 10^{-6} torr and glow discharge sputtering at 50 mtorr and argon ion-beam sputtering at 10^{-4} torr with different accelerating voltages.

With molybdenum, evaporated beryllium coatings failed in the Sebastian pull test at 31 MPa,[16] whereas ion-plated copper coatings failed at 71 MPa,[17] and this was the maximum value obtainable from this test because failure occurred in the epoxy holding the pin to the coating. Ring shear tests with ion-plated copper on molybdenum showed failure in the copper deposit at 216 MPa when ion plating was used.[17] With tungsten, ion-plated copper coatings provided bond strengths of 173 MPa in ring shear tests, whereas values of zero were obtained for evaporated and sputtered coatings.[18]

Vasofsky and Corbett[19] evaluated sputtering and ion plating of copper on 6061-T6 aluminum as a substitute for the numerous aqueous processing steps, including zincating, that are required prior to subsequent electrodeposition or electroless coating. Their goal (waste minimization) was to eliminate the aqueous processing steps and replace them with a nonaqueous process that would provide a base for subsequent electroless nickel deposition. Coupons were glow discharge cleaned at 1500, 2000 and 2500 V and ien coated with 4 μm of copper by ither sputtering or ion plating. Results iowed that the adhesive strength of ie copper coating, determined by the ebastian pull test method, was greatst for those coupons cleaned at 2500 and ion plated. In fact, the adhesive rength exceeded the maximum test ull strength of 71 MPa for the ionlated coupons. Porosity testing, done y placing a drop of 10% sodium ydroxide on the copper coatings, evealed that specimens cleaned at 500 V were pore free, whereas those eaned at lower voltages (e.g., 1500 nd 2000 V) were porous.

The ion-plating process was accomished without exceeding the 171°C recipitation temperature of the 6061-6. By either slowing down the depotion rate or simply halting the depositon process and allowing the substrate cool before additional coating, the mperature of the aluminum never ceeded 154°C. No difficulties were countered in plating electroless ckel on the ion-plated copper; hower, this step was not characterized in ly detail.

Vasofsky and Corbett[20] also evalued magnetron sputtering of copper on 04L stainless steel with the objective using this process to prepare stainss steel for thick electroplating witht having to use the numerous aqueis pretreatment steps usually reired. They used a ring shear test herein 2.5 μm of copper was sputred onto a 0.5-in.-diameter rod. Afrward, approximately 1 mm of copr was electroplated onto the rod. The d was then machined to produce veral test specimens with a ring ickness of 0.065 in. These specimens ere then tested to failure by pushing em through a hardened steel die.

Results revealed that failure ocrred in the bulk of the deposited pper at 193 MPa. Typically, with ueous cleaning and activating prior copper plating, ring shear tests show ilure in the copper at approximately 8 MPa.[21] Although the results obined with magnetron sputtering were od, even better results would be tained if ion plating were used stead of the sputtering process.

Igata et al.[22] reported that the adheon of copper on type 316 stainless eel was at least 100 times higher with n plating than with conventional aporation. They attributed this increased adhesion to a change from physical adsorption to chemical adsorption, resulting in the formation of copper oxide at the interface. They did not sputter clean the stainless steel prior to depositing the copper, so the oxide film on the stainless was available to form copper oxide (approximately 300 Å thick). For all deposition conditions, the thickness of the copper film was 5000 Å, and adhesion was measured by a pull test using epoxy resin glue. When ion plating was used, the copper film did not separate at the interface before the epoxy resin glue was peeled.

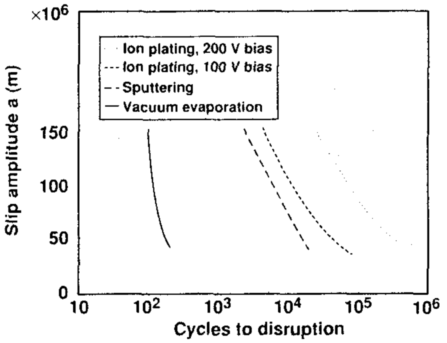

Figure 3. Durability of PVD gold films against fretting. (Adapted from Ohmae.[24])

TRIBOLOGICAL APPLICATIONS

Comparisons of PVD Films

Tribological applications involve not only friction, lubrication and wear, but also mechanical properties, such as fatigue and tensile strength. Ion-plated films offer three distinct advantages over vapor-deposited or sputtered coatings for tribological applications: (1) increased life, (2) lower coefficient of friction and (3) avoidance of catastrophic failure.[23] Figure 3 shows the durability of vacuum-deposited gold films (3000 Å) against fretting. The good resistance to fretting of the ion-plated gold film at 200-V bias is most likely due to its good adhesion and to the uniformity of the deposit. Vacuum-evaporated films were torn away at the outer region of contact as well as at the contacting surface, and sputtered films separated on the periphery of the contacting region.[24]

Friction data were obtained for the vacuum-deposited gold films against a spherical indenter of low carbon steel in controlled air.[24] Ion-plated films exhibited a much lower friction coefficient when the normal load was less than 8 N. By comparison, evaporated or sputtered films fractured at low loads and exhibited as high a frictional coefficient as bulk steel. The gradual increase in frictional coefficient for ion-plated films at higher loads may be explained by their good adhesive properties, as reported by Spalvins[25] in his work on friction experiments in ultrahigh vacuum. Friction curves for ion-plated and vapor-deposited gold films (2000 Å) on nickel-chromium and 440C stainless steel substrates were also developed.[13,23] For both substrates, the ion-plated film exhibited a lower coefficient of friction, and this continued for almost twice the sliding distance as that obtained with vacuum-evaporated films. Comparison of the slopes of the curves after the films had been worn through revealed that the

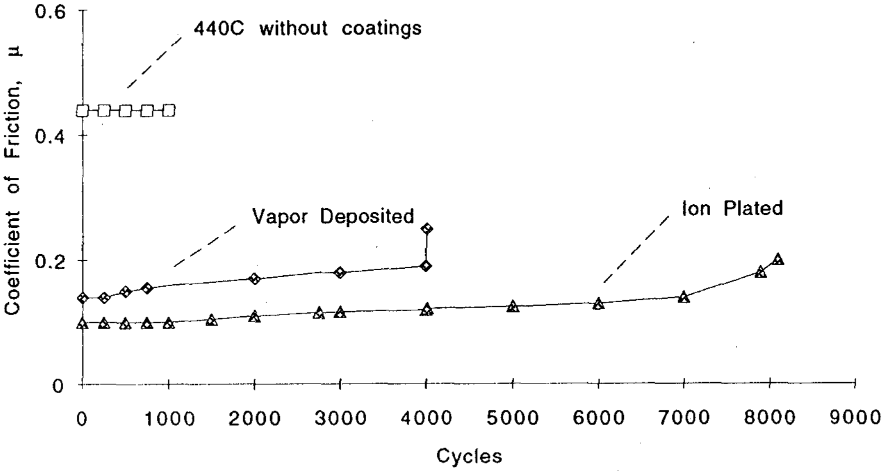

Figure 4. Comparison of coefficient of friction of ion-plated and vapor-deposited gold films on 440°C steel. (Adapted from Antler and Spalvins.[23])

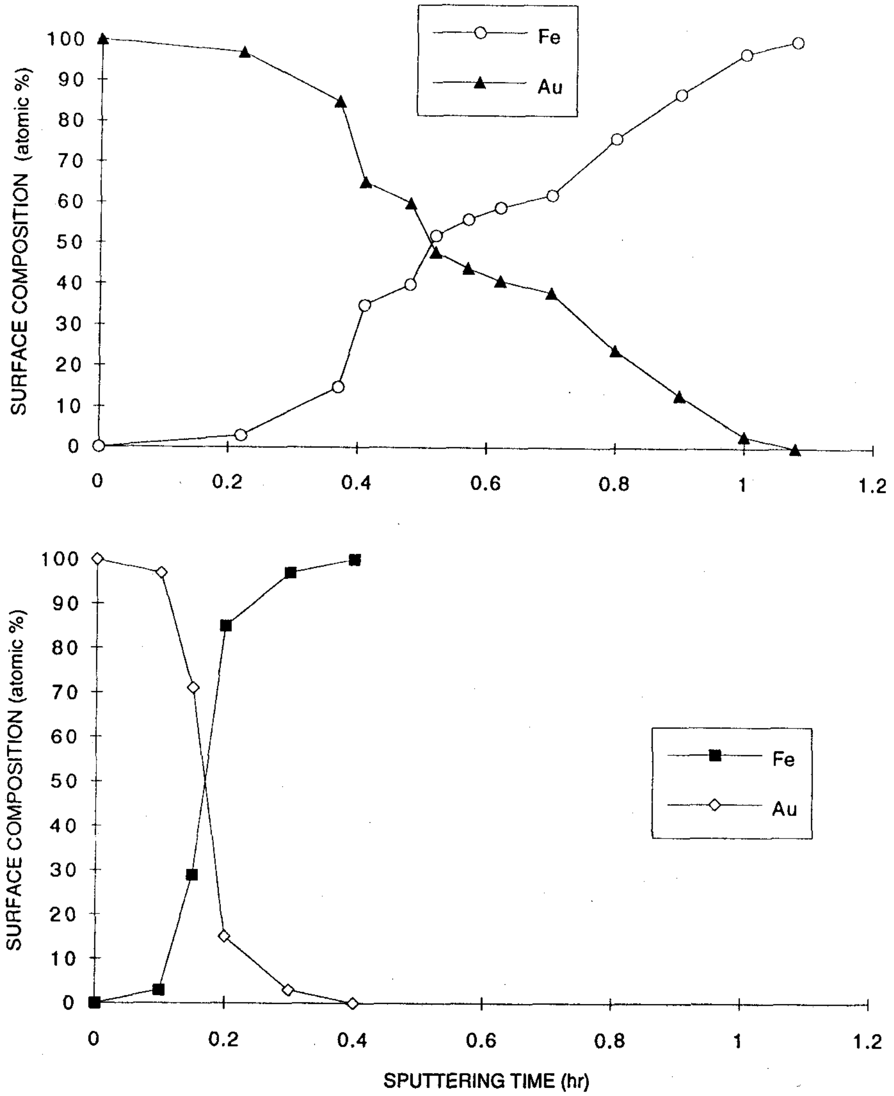

Figure 5. Elemental depth profiles for ion-plated (top) and vapor-deposited (bottom) gold on iron. (Adapted from Antler and Spalvins.[23])

ion-plated films increased gradually, whereas the vacuum-deposited films rose abruptly. The curves for the 440C stainless steel substrate are shown in Figure 4.

The gradual increase in friction coefficient for the ion-plated films is due to their graded interface, which is also responsible for their superior adhesion.[13,23] This graded interface provides a gradual transition between the properties of the substrate and the coating. With films produced by conventional means, such as vapor deposition, there is an abrupt transition in the structure and composition of the layer and substrate. This is shown very effectively in Figure 5, which presents elemental depth profiles for ion-plated and vapor-deposited gold on iron substrates. X-ray photoelectron spectroscopy depth profiling was used to obtain composition as a function of sputter removal time. In the case of ion deposition (see Fig. 5, top), the surface composition did not change during the first 20 min of sputtering, and then gradually decreased in gold content, whereas the iron level increased. The thickness of the graded interface was approximately 1.5 μm. By comparison, the vapor-deposited film exhibited an abrupt interface wherein the gold content rapidly decreased with sputtering time (see Fig. 5, bottom).

Hardness measurements were also used to evaluate the interface formation, and the results are shown in Figure 6. The ion-plated film was initially low in hardness but gradually increased in the interface region because of alloying and finally decreased again as it reached the nickel substrate (Fig. 6A). A constant hardness was obtained with the vapor-deposited film (see Fig. 6B), and this is indicative of a sharp interface.[23]

Comparison of Lead-Tin Films Deposited by PVD and Electrodeposition

A systematic study of lead-tin alloys deposited by ion plating, vacuum deposition and electrodeposition was reported by Gupta et al.[26] The effects of sliding distance and load on friction coefficient and wear for lead-tin coatings (10–40 wt % tin) deposited on polished steel disk substrates were measured. Typical results are shown in Figure 7, which presents variations of disk wear volume on load for lead/10% tin films. Ion-plated films exhibited the least wear, increasing slightly from 13 × 10^8 to 25 × 10^8 μm^3 linearly as the load increased from 15 to 145 N. In the case of electroplated films, the disk wear volume increased significantly from 18 × 10^8 to 60 × 10^8 μm^3 and for vacuum evaporated films from 18 × 10^8 to 80 × 10^8 μm^3. The conclusions drawn from this study were that ion-plated films exhibited minimum coefficient of friction and maximum endurance life. Material loss due to wear was minimum in ion-plated films and maximum in less adherent vacuum-deposited films, where several failure mechanisms, such as plucking, peeling and film detachment, were observed.[26]

INFLUENCE ON FATIGUE

Ion-plated gold films improve the fatigue property of low carbon steel.[24] This is shown in Figure 8, which also

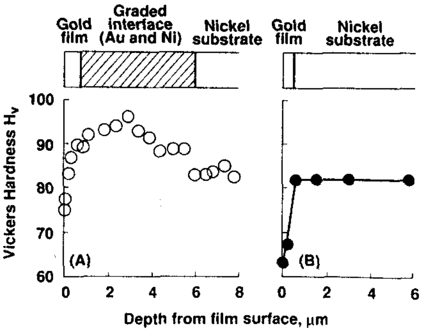

Figure 6. Hardness-depth profiles for ion-plated (A) and vapor-deposited (B) gold on a nickel substrate: Hardness measuring load was 0.1 N. (Adapted from Antler and Spalvins.[23])

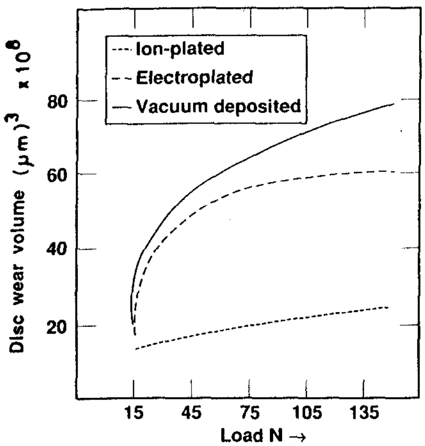

Figure 7. Disk wear volume versus load for lead-tin (10 wt % tin) films on a stainless steel surface (Ra ~ 0.06 μm; sliding speed = 0.4 m/sec). (Adapted from Gupta et al.[26])

reveals that electroplated gold films have little or no effect on fatigue. It is speculated that the graded interface obtained with ion plating is responsible for this improved performance. This is somewhat verified because heating the electroplated specimens in vacuum for several hours improved their performance close to that of ion-plated specimens, and this step undoubtedly caused a graded layer at the interface. Ion-plated iron films did not improve fatigue properties of low carbon steel, but this is not surprising, since a graded interface is not expected in this case.[24]

COMBINING ELECTROPLATING AND PVD

Some metals and alloys (such as those listed earlier as "very difficult") that require thick coatings for corrosion resistance and other engineering purposes are among the most difficult to electroplate with sound, functionally acceptable deposits. The origin of the problem is typically a thin, naturally forming oxide film that is often difficult to remove and that reforms quickly when a clean surface is exposed to air or water. Techniques that have been used by electroplaters to prepare difficult-to-plate substrates for coating include etching to allow mechanical keying between the substrate and plated deposit; mechanical roughening, such as glass bead or sand blasting to roughen the substrate surface; replacing the oxide film with a displacement coating; heating to allow for interdiffusion between the substrate and coating; anodic oxidation of the substrate; and intermediate strike coatings to minimize the coefficient of thermal expansion mismatches.

An approach that works very well and that also eliminates the severe pickling, mechanical roughening or heating required of the processes just discussed is the use of augmented energy PVD to provide an initial adherent coating and then electroplating over this to the required final thickness. Ion plating and hot hollow cathode deposition have been used successfully for providing the initial, adherent coating. Ring shear data for three very difficult-to-plate metals—tungsten, molybdenum and titanium—are presented in Table II. The results clearly show that use of an augmented energy PVD process for the initial stage of the coating cycle provided extremely good adherence. In all cases, the adherence was considerably improved over that obtained without use of PVD. For example, the wet chemical process for tungsten consisted of etching parts in a hydrofluoric acid/nitric acid concentrated solution, followed by anodic treatment in 300 g/L potassium hydroxide. Adhesion with this process was only 48 MPa, whereas, with ion plating as the initial step, adhesion was 173 MPa. With molybdenum, the plating process included two firing operations at 1000°C in dry hydrogen, and the resulting adhesion of the gold electrodeposit was good enough that failure occurred in the gold at 125 MPa. By comparison, use of magnetron ion plating to provide the initial coating (60,000 Å of copper) followed by thick electroplated copper resulted in a bond that failed in the copper deposit at 216 MPa. Last, the same type of result was obtained with titanium. The wet chemical process included an anodic etch in hydrofluoric acid/acetic acid and a heating step at 480°C for 2 hr, and this provided a bond with a shear strength of 148 MPa. Use of ion plating provided a bond with a shear strength of 252 MPa. Clearly, coupling augmented energy PVD processes with electroplating provides better adhesion than that obtained with the wet processes while eliminating the need for roughening the surface chemically or mechanically or heating after coating.

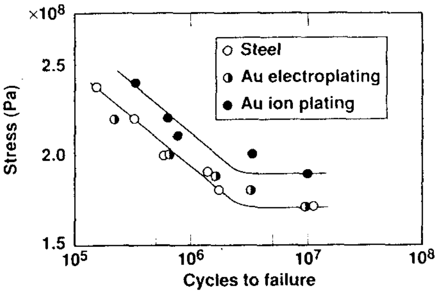

Figure 8. Effect of ion plating and electroplating of gold on the fatigue property of low carbon steel. (Adapted from Ohmae.[24])

SUMMARY

The PVD techniques of evaporation, sputtering and ion plating are compared in this report. Quantitative adhesion data obtained by using scratch tests, pull tests and ring shear tests on substrates, such as glass, quartz, glazed tile, aluminum, stainless steel, molybdenum and tungsten, clearly show that ion plating provides superior adhesion. This improved adhesion is attributed to highly energetic deposition ions, in situ substrate precleaning and the simultaneous deposition and substrate sputtering due to the continuous bombardment of the substrate during deposition. With ion-plated gold on nickel, a graded interface approximately 1.5 μm thick is obtained, whereas no graded interface is obtained with vapor-deposited gold on nickel. Ion-plated films offer a variety of advantages over other PVD coating methods for tribological applications: (1) increased life, (2) lower coefficient of friction and (3) avoidance of catastrophic failure. Combining ion plating with electroplating allows for the coating of difficult-to-plate substrates with thick, adherent

Table II. Ring Shear Data Show the Value of Combining Physical Vapor Deposition (PVD) with Electroplating for Plating on Difficult-to-Plate Metals

Metal	*Electroplating (MPa)*	*PVD + Electroplating (MPa)*
Tungsten	48 (Cu)	173 (Cu)
Molybdenum	125 (Au)[a]	216 (Cu)
Titanium	148 (Cu)[b]	252 (Cu)

[a] This included two firings in a dry hydrogen operation at 1000°C.
[b] This included an anodic etch in hydrofluoric acid/acetic acid and heating at 480°C for 2 hr.

deposits without having to resort to severe pickling, mechanical roughening or heating to obtain adherence.

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