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ADHERENCE OF ION BEAM SPUTTER DEPOSITED METAL FILMS ON H-13 STEEL

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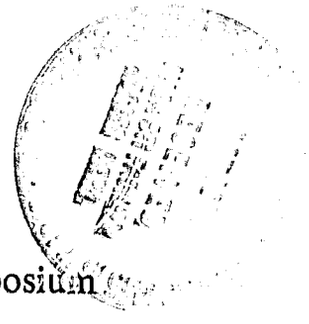

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ADHERENCE OF ION BEAM SPUTTER DEPOSITED METAL FILMS ON H-13 STEEL

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INTRODUCTION

Dies used to make aluminum castings have a limited lifetime depending upon materials properties and casting conditions. A typical die can usually be used to make between 30 to 50 thousand castings. At a cost of 50 to 70 thousand dollars per die, doubling or tripling the useful lifetime of a die could result in significant financial, manpower and energy savings. Shown in Fig. 1 is an H-13 die steel surface after numerous castings. The surface cracks appear after many cycles of exposure to molten aluminum and cold water, used to cool the die. This cracking phenomenon is known as heat checking[1] and is multifaceted - ranging from thermal stress to attack or soldering to the die by molten aluminum. It has been suggested by die manufacturers that a protective coating of either Mo or Cr or a precious metal might negate this problem. With this in mind, a program was developed at NASA Lewis Research Center in cooperation with the Die Casting Research Foundation to improve die lifetime by sputter depositing coatings on a die surface using ion beam developed technology. Although this program consists of three overlapping phases only the results of the first phase will be represented in this paper.

In phase I, coatings of various candidate metal and metal oxides were sputter deposited on flat surfaces of H-13 steel (die material) for a preliminary evaluation of the adherence of films of various thicknesses. During this phase the sputter technique, sputter rate, deposition energy level and maximum thickness were determined for each candidate coating mate-

rial. Some of these coated substrates were also exposed to elevated temperature levels, and the adherence of the coating was again evaluated. A few substrates were coated with films using RF and ion plating techniques. Comparisons in bond strength of the films using these techniques and ion beam deposition were also made and presented herein.

APPARATUS AND PROCEDURE

A 30 cm diameter argon ion beam source[2] with its ion optics masked down to an ion beam diameter of 10 cm, was used to sputter deposit metal and metal oxides onto H-13 steel substrates. The source, developed from electric propulsion technology, uses a hollow cathode to provide the discharge for the ion beam source. Ion beam extraction is accomplished by a dished, two-grid ion optics system. Neutralization of the beam is achieved by the use of a plasma-bridge neutralizer,[2] using an argon gas cathode. The ion source has a capability of operating at beam energies between 100 and 1500 eV. For these studies the source was operated at an energy level of 1000 eV.

The vacuum facility, 1.5 m in diameter and 7.3 m long, is sufficiently large to minimize backsputtered facility material from contaminating the deposited films. To further prevent contamination, a liquid nitrogen cooled baffle was used in the vacuum tank. While the ion source was operating, the pressure in the region of the experiment is about 3×10^{-4} torr (3.9×10^{-2} Pa). This pressure was maintained for most of the depositions. The partial pressure of N_2 or air in processing nitride or oxide compounds was about 1×10^{-3} torr. It should be noted that at 10^{-3} torr about 50 percent of the ions become neutralized through charge exchange[3] and a majority of the sputtering is done by 1000 eV neutrals rather than ions.

The substrate disks 2.54 cm in diameter and 1.5 mm thick were made of the same material used to make dies, that is H-13 steel. The disks were

vacuum heat treated, in a similar manner as performed on functional dies to achieve a Rockwell C hardness of 47. After heat treatment the substrates were polished to either a 16 or 32 microinch RMS finish.

The target materials were commercially purchased, most of which were 15 cm diameter disks, except for Au and Pt which were strips 2.54 cm wide. These strips were pieced together and overlapped to form a square target 12.7 cm by 12.7 cm. The strips were then mounted on a 12.7 cm by 12.7 cm steel substrate for support.

The H-13 disks were cleaned prior to insertion into the vacuum facility. The cleaning procedure included cleaning the disks with a 2 percent Liquinox® soap solution, rinsing in distilled water and drying with nitrogen gas. This procedure was performed three times on each disk.

The substrates were mounted on a push-pull rod that could be retracted through a vacuum chamber gate valve. Prior to deposition, first the target and then the substrates were sputter cleaned by the ion beam for 1/2 hour at a beam energy of 1000 eV and a current density of 2 mA/cm^2. During the sputter cleaning of the substrate, the target is located in a stored position. During deposition the target and substrate surfaces are 19 cm apart and normal to each other; the target is at a 45° with respect to the incident ion beam. The distance from the ion source to the target was 19 cm.

The deposition rate of target material at the location of the substrate was measured by placing a piece of fused silica glass, masked to allow a step to form during deposition. A surface profiler (Alpha-Step) was used to measure the thickness of the film and hence a deposition rate could be derived.

Presented in Table I are the deposition rates at the substrate location for various target materials. The ion beam was larger in diameter than the area of the target, and totally filled the target material. The deposition

rates are presented in Table I for a current density at the target of 1 mA/cm^2 and an ion energy of 1000 eV.

Film bond strength tests were also performed on H-13 specimens that were ion beam sputter coated with eleven different materials by Commonwealth Scienific Corporation. At Commonwealth, the 10 cm diameter source[4] used grids dished such that the focal point was 45 cm downstream of the grid plane. The target at a 45° with respect to the ion sources was located 30 cm from the 10 cm ion source. The substrates were located normal to and 5 cm from the target. Because of the grid focusing and spacial variation in current density the ion beam did not totally illuminate the target.

Adherence measurements, of the film to the substrate, were made using a Sebastian Series Coating Adherence Tester®. Measurements are made by first baking an epoxy coated bonding stud (0.127 cm long by 0.16 cm in diam) to the deposited film surface at 125° C for 2 hours in an oven. This elevated temperature allows for a thermal cure of the epoxy coated stud to the film. After the stud is bonded to the film, the test stud is inserted into the instrument and a load is applied normal to the surface at a predetermined rate until failure of the bond ensues. This break in the bond is recorded in lb/in^2, and is considered a measure of the adherence, if the break occurs at the film-substrate interface. The maximum adherence from this test is the strength of the epoxy bond (approx. 6500-9000 lb/in^2). For most of the films tested in these experiments, the bond strength of the film to the substrate exceeded the bond strength of the stud (epoxy) to the film. The location of the break in the bond was determined by using an optical microscope or a scanning electron microscope.

RESULTS AND DISCUSSION

A film used to protect a die surface must exhibit good adherence if it is to remain in function on the die surface. Ion beam sputtering enables atomic cleaning of the surface thus permiting intimate contact between the deposited film and the actual substrate surface. Shown in Fig. 2 is the adherence in lb/in^2 of a 1 micrometer thick Cu film sputter deposited on three H-13 steel disks. In one case, the H-13 steel was not sputter cleaned by the ion beam before Cu deposition. The resulting Cu coating exhibited rather poor adherence of only 80 lb/in^2. The second and third H-13 disks shown in Fig. 2 were sputter cleaned by the ion beam at 1 keV and 2 mA/cm^2 for 20 and 30 minutes, respectively. The resulting 1 micrometer Cu film had an adherence of 6200 lb/in^2. The necessity of precleaning the substrate by ion beam sputtering before deposition to obtain adherent coatings has been shown by others in the literature,[5,6] and was a prerequisite to all deposition techniques used in these studies.

Presented in Table II are the adherence of various thickness ion beam deposited metal and metal oxide films on H-13 steel. The adherence measurements are the average of 5 measurements on each sample. Some of the depositions were done at NASA-Lewis Research Center and some under contract at Commonwealth Scienific Corp. Although both facilities used different size ion sources, the experimental procedures were the same. The use of different facilities and sources does not seem to affect the results, for Mo deposited at both LeRC and Commonwealth exhibit the same good adherence for films $\leq$4 mm thick. The symbol * used in Table II indicates a break in the bond at the epoxy-film interface, meaning the film-substrate bond strength was greater than the value indicated in the table. For all the metallic films $\leq$4 μm, the bond strengths between the film and the substrate were

greater than the epoxy-film bond. The only exception was B_4C, which formed a poor bond on H-13 for all thicknesses. Films of Au, Ag, Mo and Ta_5Si_3, 8 μm thick, exhibit as good an adherence as a 1 μm coating of the same material. For the other materials, film-substrate bonds could be broken at 8000 lb/in^2 or less. It was also found that the adherence of the films were independent of the substrate surface finish (16 or 32 μin. finish).

To obtain proper stoichiometry it was necessary at times to bleed N_2 or air into the vacuum system when depositing a nitride or oxide compound. Introduction of air into a vacuum chamber during deposition can lead to limited lifetime of the hollow or filament cathodes used in the ion source and hence a MgO film of only 2.4 μm maximum thickness was deposited. From the data presented in Table II, it is clear that depositions of metals and metallic compounds on H-13 steel using an ion source have a bond strength much greater than the upper limit adherence measuring capabilities of the instrument used to make the measurement.

Film bond strengths were also measured on some materials that were deposited on H-13 using other deposition systems. Shown in Fig. 3 is a plot of the film adherence as a function of thickness for Mo, Cr, Ni and ZrO_2 using ion beam, radio frequency (rf) or ion plating deposition systems. Ion plating of Mo was done on contract at Hohlman plating. The open symbols indicate that the bond broke at the epoxy-film interface and the closed symbols a break at the film-substrate interface. For Mo, ZrO_2 and Cr ($\leq$3 μm thick) deposited with either an ion beam or rf sputter system, the adherence of the films were better than the epoxy bond strength. Ni film adherence on H-13 steel was greater than 8000 lb/in^2 when an ion beam source was used for film deposition. Adherence of rf sputter deposited films ranged from

about 7000 to 280 lb/in^2 depending on film thickness. The use of an ion beam or rf source appears to give better Mo film adherence than from deposition using a commercial ion plating system.

In the second phase of this program the best candidate coatings from phase I are to be coated on a thermal fatigue test specimen.[1] This coated test specimen will then be emersed in liquid aluminum and then cooled by water for 15 000 cycles, to simulate part of the environment of a die casting die. To further evaluate the adherence of the coatings in phase I at elevated temperatures some of the coated H-13 disks were exposed in an oven for 15 minutes at temperature levels of 400° and 700° C and allowed to cool to room temperature. This procedure was performed three times before another adherence measurement. Shown in Fig. 4 is film adherence as a function of exposure to elevated temperatures. Also listed in the figure are the films deposited by an ion source, whose adherence remained unchanged at 400° C and even after exposure to 700° C. For these listed materials the film-substrate bond strength was still greater than the epoxy-film bond strength. The 1 μm Cu film deposited by rf, the 8 μm M_o film deposited by ion plating and the 8 μm AlN film deposited by the ion beam show decreases in adherence after exposure to elevated temperature. Not all films were tested at elevated temperatures.

To qualitatively check the mechanical integrity of the film-substrate bond, a center punch was used to indent three coated surfaces. Shown in Fig. 5 are (1 μm, 4 μm) Mo and a 6 μm Au films that were subjected to indenting by an automatic center punch. Although there were tears in all the films at the edge of the crater, the ion beam deposited Mo and Au films experienced only a slight crack in the film at the crater edge, whereas the ion plated Mo was torn from its H-13 substrate.

CONCLUDING REMARKS

Two different Argon ion beam sources were used to sputter deposit adherent metallic films up to 8 μm thick on H-13 steel. The adherence of the coatings was in most cases greater than the upper limit of the adherence measuring device. To obtain adherent thin films, it was necessary to preclean the substrate in the ion beam before deposition. It was necessary, at times, to introduce N_2 or air to obtain the proper stoichiometry in N_2 or O_2 metallic compounds. For all pure metallic films 4 μm thick or less the bond strength of the film to the substrate were greater than the epoxy to film bond (~8000 psi). Films of Au, Ag, M_o and Ta_5Si_3 8 μm thick exhibit as good a bond strength on H-13 as do 1 μm thick films of these materials. Elevation to 700° C of certain ion beam sputter deposited coatings did not affect the film-substrate bond strength.

M_o and Cu films deposited by ion plating and rf sources showed decreased adherence after exposure to elevated temperatures.

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5. J. A. Thornton, "Influence of Substrate Temperature and Deposited Rate on Structure of Thick Sputtered-Copper Coatings," J. Vac. Sci. Technol., 12 (4), 830-835 (1975).

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TABLE I. - SPUTTER DEPOSITION RATES FOR VARIOUS TARGET MATERIALS

[Ion energy, 1000 eV, ion current density at the target, 1 mA/cm^2; target to substrate distance, 19 cm, ion source to target, 19 cm.]

Target material	Ag	Au	Si_3N_4	Cr_3C_2	Pt	Ni	Cr	AlN	Co	Mo	W	ZrO_2	Ta_5Si_3
Deposition rate, Å/min	120	97	96	96	48	27	26	25	24	19	16	16	15

TABLE II. - ADHERENCE OF MATERIALS ION BEAM SPUTTER DEPOSITED ON H-13 STEEL

Coating material	Coating adherence for various thicknesses, lb/in^2			
	1 μm	2 μm	4 μm	8 μm
NASA-Lewis coatings				
Au	7930*	7760*	8000*	7120*
Ag	8420*	8320*		8430* (10 μm)
Pt	7770* (1.5 μm)	7210* (2.5 μm)	7690* (3.5 μm)	7430* (5.5 μm)
W	5400	6200		
Mo	8020*	8480*	8460* (3 μm)	8460* (6 μm)
Ni	8340*	8640*	8180* (3.6 μm)	
Cr	7890*	8060*	8230*	
Commonwealth Eng. coatings				
Co	8060* (0.6 μm)	4160* (1.2 μm)	8155* (2.4 μm)	7690 (4.8 μm)
MgO	6340* (0.3 μm)	6650* (0.6 μm)	6560* (1.2 μm)	6250* (2.4 μm)
AlN	8240*	8460*	8435*	4940
Si_3N_4	8206*	8520*	8136*	2815
Cr_3C_2	7116*	8123*	8086*	8033
Mo	7800*	7600*	6700*	5400
Cr_2O_3	7326*	7776*	7116*	6573
Ta_5Si_3	7625*	7918*	7743*	7847*
B_4C	3365	570	303	0
CrB_2	7486*	7838*	8030*	0
SiC	7282*	7968	477	6488

*Bond broke at epoxy-film interface.

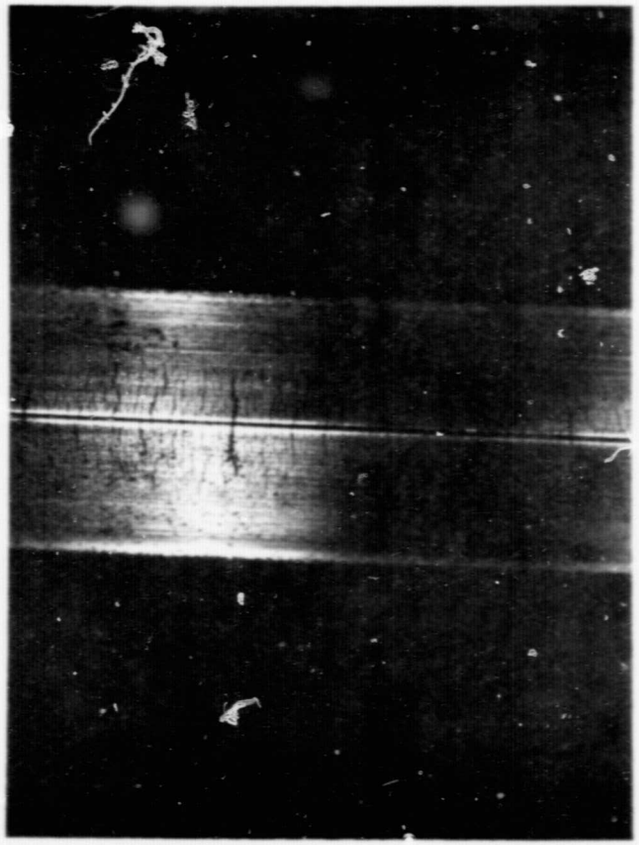


Figure 1. - H13 die surface after numerous castings.

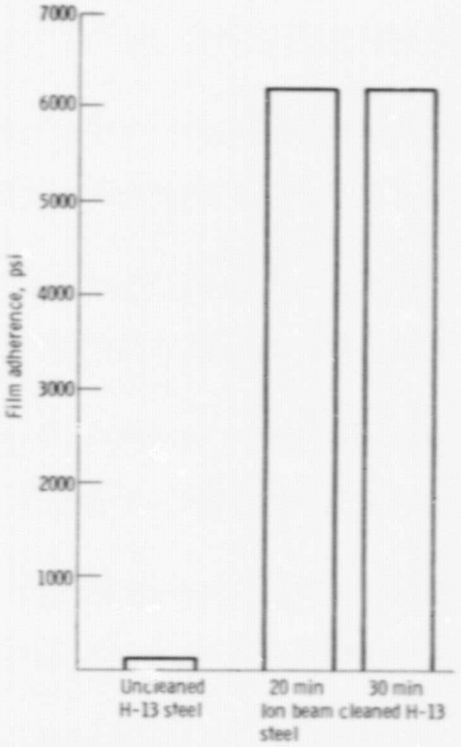


Fig. 2. - Film adherence of 1 µm Cu deposited on H-13 steel.

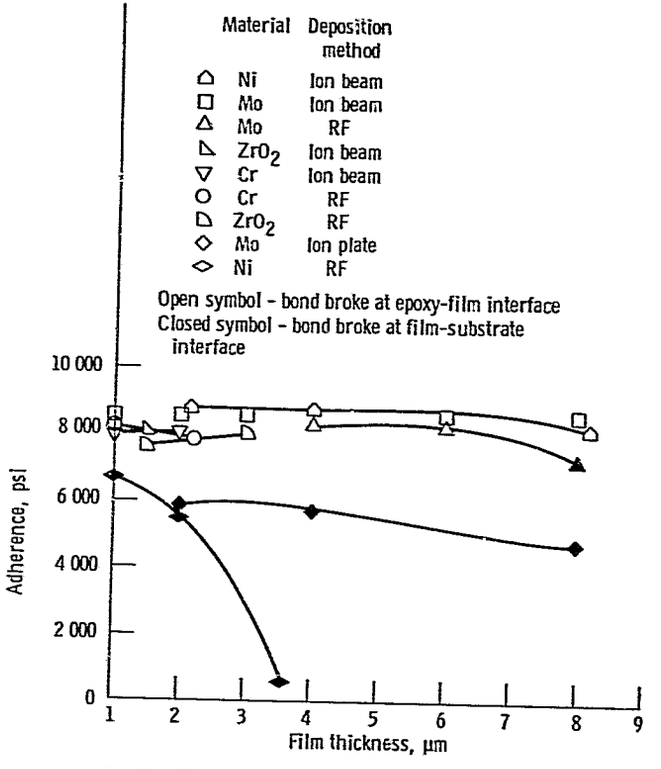
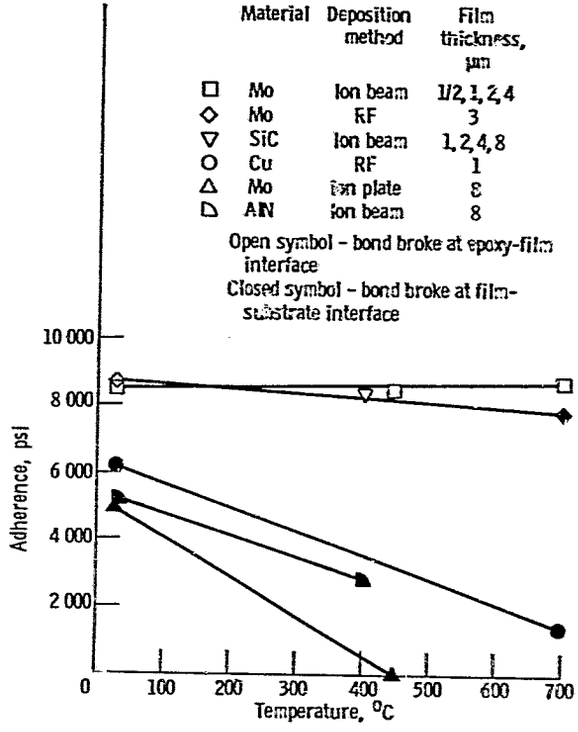


Fig. 3. - Film adherence as a function of thickness for Mo, Cr, Ni, and ZrO_2 using different deposition systems.



(a) Film adherence changed.

Material	Film thickness, μm	Temperature level, °C
Co	0.6, 1, 2, 2.4, 4, 8	400
SiC	1, 2, 4, 8	400
CrO_2	1, 2, 4, 8	400 - 700
CrB_2	1, 2, 4	400
AlN	1, 2, 4	400 - 700
Si_3N_4	1	700
Ta_5Si_3	1, 2, 4, 8	700

(b) No change in film adherence.

Fig. 4. - Material film adherence to H-13 after exposure to elevated temperature.

Figure 5. - Craters formed by a center punch on coated H13.

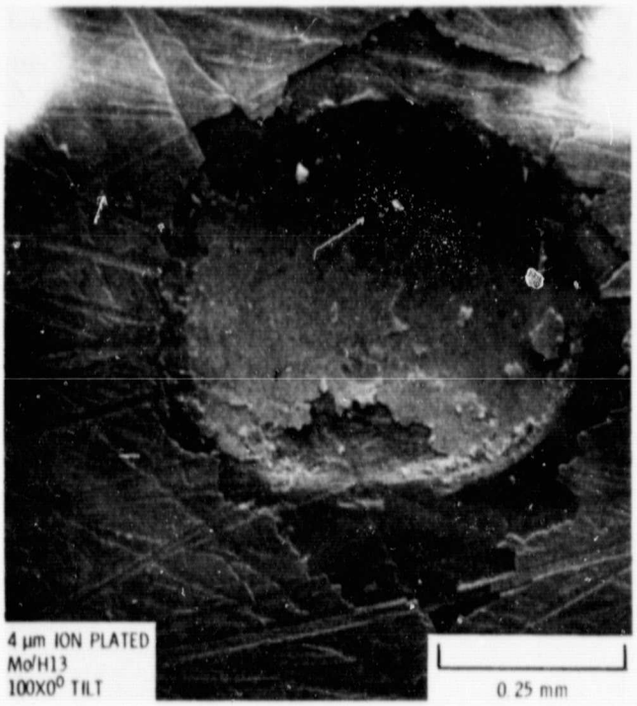


Figure 5. - Concluded.