ADHESION MEASUREMENTS OF THIN METALLIC FILMS: COMPARISON OF THE DIRECT PULL-OFF AND THE SCRATCH METHODS

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1. Introduction

The adhesion of thin evaporated metallic films to their substrates is one of the important problems in physics as well as in surface coating techniques. Various aspects of adhesion measurements, including experimental techniques, have been reviewed [1 to 8] and proposed to determine the adhesion qualitatively or quantitatively. A quantitative comparison of adhesion strengths using different techniques has been made. For this purpose, two methods of degrading the films were tested.

The so-called "direct pull method" is applied to the measurement of adhesion of vacuum-deposited thin film coatings on glass substrates. Application of this method provides information on the cohesive as well as the adhesive properties of thin films.

This method suits to show whether the adhesive strength of the film is stronger or weaker than the cohesive strength of the film depending upon where the breakage occurs.

Another frequently used method, primarily for metal films, is the "scratch method", suggested by Heavens [9] and extensively used by Benjamin, Weaver [7] and Hill [10]; references to their works as well as a summary of some of their results are given by Campbell [11]. The method has also been analysed by Hamersky [12] and Butler et al. [13]. The scratch test consists of drawing a smoothly rounded tip of known radius across a thin film and repeating this procedure with increased vertical loads on the tip until the film is removed from the substrate.

The amount of load on the tip at film failure is a quantitative measure of the durability of the film–substrate interface. From the width of the scratch for a particular load and the indentation hardness of the substrate, the shear stress required to remove the film can be calculated. So, the usefulness of the scratch test as a valuable tool for a quantitative comparison of the adhesion of different thin films has been demonstrated.

2. Experimental procedure

2.1. *The direct pull-off method*

Scheme of the apparatus is shown in Fig. 1. The films were sandwiched between the ends of two stainless steel rods with a thin layer of epoxy. A uniform thickness of epoxy is important to the technique. The rods with the sandwiched layers were placed in an alignment tray to maintain the rods in proper alignment. The force of adhesion per unit area was obtained by dividing the force required to pull the film off the substrate by the contact area of the rods. This procedure is based on the assumptions that the pulling stress is uniformly distributed across the area and that all the interfaces are smooth. After the films were pulled, three types of breakages were observed as shown in Fig. 2.

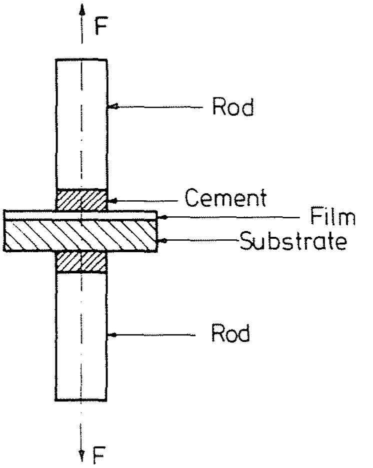

Fig. 1. Components of the apparatus for the "direct pull-off method"

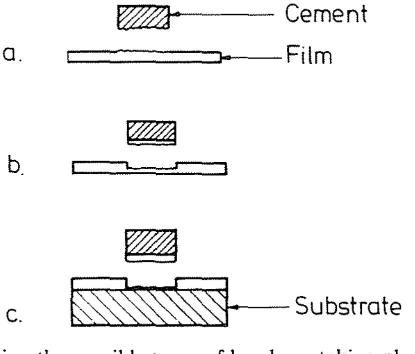

Fig. 2. Diagrams showing the possible types of breakage taking place after the pull test: *a* cement-film breakage; *b* film cohesive breakage; *c* film substrate breakage

2.2. *Scratching apparatus* (Scratch method)

The scratch tester as used in our investigations is shown schematically in Fig. 3. Adjusting of the stylus was made across the film to make the scratch by the vertical movement of the stylus and the $x-y$ table [14] on which the test specimen was attached. A series of parallel scratches in the film is made with a different normal load on the stylus, and the maximum load used depends on the nature of the test specimen and the stylus radius. Scratches were formed by placing the loaded stylus on specimen surface and moving the stage. It is to be noted that the substrate bearing the film under test was mounted under the stylus on the coordinate table which could be moved horizontally in two directions.

The x movement in the plane of the page drives the stylus from right to left to make the scratch, and the y movement perpendicular to the plane of the page indexes the stylus for the next scratch. Following the scratching movement, the lever is unloaded by raising the stylus off the sample. The scratch is then inspected by reflected light using any suitable microscope lamp advantageously positioned to detect film failure.

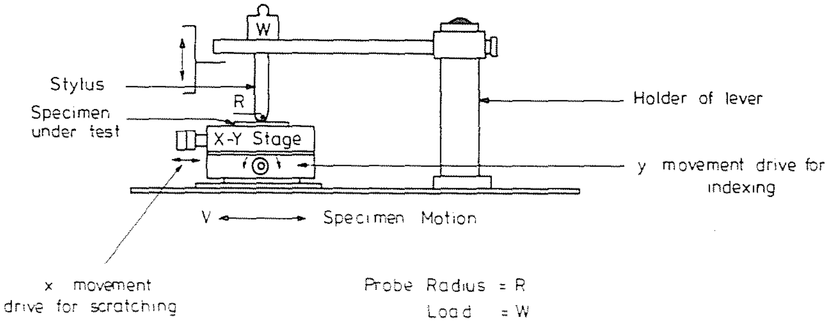

Fig. 3. Scheme of scratch adhesion tester

2.2.1. *Scratch procedure*

The samples were placed and clamped on the stage of the scratch tester, and the stylus was allowed to exert the desired load on the film side of the specimen. The applied loads were limited to 100 g since at or above this value, the substrate was often found table damaged. While the load was applied, the specimen was moved at a specified speed by a constant velocity motor.

The actual determination of film adhesion consists in preparing a series of scratches at successively higher loads until a clear channel is observed in either the film or the substrate.

2.3. *Sample preparation*

The glass substrates were thoroughly cleaned by immersion in a boiling hydrogen peroxide and then rinsed several times in distilled water. In addition, the substrates were repeatedly rinsed in distilled analytical alcohol.

Vacuum deposition from directly heated sources was used for copper, aluminium, chromium and nickel.

In some cases glow-discharge cleaning was applied before film deposition.

3. Results and Discussion

For the sake of comparison two types of test have been investigated; the stylus or scratch test where the film is "scratched" off the substrate, and a test where the film is "pulled" off the substrate.

It has to be noted that for the scratch test, a new model has been developed [15], based on the model of Weaver [16] but introducing friction as one of the principal parameters. So, the maximum shear according to the above mentioned new model was calculated and compared with the values of the normal pulling force at failure obtained by the so-called "direct pull-off method". Table 1 shows the quantitative results of adhesion tests for the various deposition parameters. The data have been presented in tabular rather than in graphic form like in the case of a methodical investigation of specific deposition parameters.

The results obtained for the adhesion values of different layers prepared under different conditions were compared.

The pull test [17, 18] shows whether the adhesive strength of the film is stronger or weaker than the cohesive strength of the film depending upon where the failure occurs.

However, the method is difficult to adapt to quantitative measurements, particularly with strongly adherent layers. Chromium and some aluminium layers which were aged for a long time are extremely adherent to glass and can not be pulled off. "On the other hand, the standard deviation of the values obtained by the pulling method is also influenced by the true random fluctuations of the force of adhesion, errors in alignment of the experimental set-up and by the non-uniformities of the epoxy layers used to pull the coatings off the substrate. Some factors contribute to the uncertainty in the adhesion measurements by the direct pull method such as: the difficulty in determining the exact area of contact; premature yielding of the epoxy due to the irreproducibility of preparation and curing; the fracture of substrates before the separation of the layers from the substrates." [17].

The limited number of data, hints that the pull off test only provides a test of cohesive rather than adhesive strength. Results for both techniques show that substrate heating affects the adhesion strength between the substrate and the film.

Good adhesion results from the formation of a transition layer between the substrate material and the film material. This interfacial region arises by diffusion; the activation energy for diffusion may come from any source such as heating of the substrate.

It is interesting to note that films formed on substrates which had been subjected to glow discharge had a higher scratch resistance which still increased with the time of exposure in air, while the pull-off test indicated a decrease in adhesion. The increase in scratch resistance may be due to oxidation of the layer reducing the friction between stylus and film.

The results showed that the higher rate of deposition gave poorer adhesion, and if the practical adhesion of a film is very poor, then it is easier discerned by the scratch technique than by the pull technique. According to the above mentioned both techniques, in either case the measurement is a qualitative indication of film adherence rather than an unequivocal measurement of adhesive forces.

The pull method provides a test of cohesive strength and a valuable comparative tool for determining the degree and nature of adhesion.

The scratch test has been shown to be very sensitive, since applied loads just less than the critical value sometimes produced detachment in short strips, leaving other regions intact. Loads much less than critical tended to produce small furrows in the film but did not cause detachment.

It has been observed that both tests used for measuring practical adhesion are destructive in nature and can not be compared quantitatively but they are in good agreement qualitatively.

Furthermore, no consistent use was made of units for expressing adhesion values, i.e. making comparison of the two methods is uneasy. Also, the experimental data of the scratch and pull-off methods were not comparable. The differences in adhesion values much exceeded the systematic errors of these methods. The difference between these values may result from the experimental techniques and the informativeness of these methods.

Table 1

Adhesion Strengths *vs.* Deposition Parameters

Deposit	Film thickness, (nm)	Substrate heating	Rate of deposition, (nm/s)	Vacuum, (Pa)	Time of glow dischange	Critical load, (N)	Shear stress, ($\times 10^7$ Pa)	Normal pulling force at failure, ($\times 10^7$ Pa)	Failure state
Cu	135	None	·45	8×10^{-4}	None	·04	3.77	2.06	Adhesive failure at film-substrate interface
Cu	135	250 °C, 1h	·75	8×10^{-4}	None	·03	3.02	2.10	Adhesive failure at film-substrate interface
Cu	85	None	·70	8×10^{-4}	30 min	·04	4.035	.90	Adhesive failure at film-substrate interface
Cu	140	250 °C, 1h	·46	5×10^{-4}	20 min	·04	3.587	1.95	Adhesive failure at film-substrate interface
Cu	140	None	·77	3×10^{-3}	20 min	·05	4.48	1.95	Adhesive failure at film-substrate interface
Cu	95	250 °C, 1h	·52	1×10^{-2}	30 min	·05	4.63	.67	Adhesive failure at film-substrate interface
Cu	214	250 °C, 1h	·50	1×10^{-2}	30 min	·07	5.82	1.10	Adhesive failure at film-substrate interface
Cu	60	None	·50	2×10^{-1}	15 min	·06	5.22	1.34	Adhesive failure at film-substrate interface
Cu	160	250 °C, 1h	·59	2×10^{-1}	None	·10	6.5	.83	Adhesive failure at film-substrate interface
Cu	220	None	·91	2.5×10^{-3}	15 min	·065	5.48	.78	Adhesive failure at film-substrate interface
Cu	240	None	1.5	2.5×10^{-3}	30 min	·07	5.73	1.80	Adhesive failure at film-substrate interface
Cu	120	250 °C, 1h	·33	1.5×10^{-3}	None	·06	5.381	2.20	Adhesive failure at film-substrate interface
Cu	130	None	·36	1.5×10^{-3}	None	·10	6.727	1.90	Adhesive failure at film-substrate interface
Al	280	None	·66	2.5×10^{-4}	20 min	·10	6.807	2.40	Adhesive failure at film-substrate interface
Al	150	None	·83	2.5×10^{-4}	None	·10	6.421	–	Cohesive failure in the cement
Al	280	250 °C, 1h	·58	2.5×10^{-4}	20 min	·08	5.95	2.50	Adhesive failure at film-substrate interface
Al	120	250 °C	·66	2.5×10^{-4}	15 min	·075	6.05	1.60	Adhesive failure at film-substrate interface
Al	120	None	·33	1.5×10^{-3}	15 min	·12	7.06	1.80	Adhesive failure at film-substrate interface
Al	175	250 °C, 1h	·97	2×10^{-1}	15 min	·12	7.369	–	Cohesive failure in substrate
Al	300	250 °C, 1h	·83	2×10^{-1}	30 min	·15	8.07	–	Cohesive failure in substrate
Al	145	None	·34	1.5×10^{-2}	20 min	·15	8.229	2.30	Adhesive failure at film-substrate interface
Al	200	250 °C, 1h	·47	2.5×10^{-4}	20 min	·10	6.807	2.75	Adhesive failure at film-substrate interface
Cr	150	None	·50	2×10^{-3}	None	·45	11.4	–	Cohesive failure in cement

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Cr	150	250 °C, 1h	·62	2×10^{-3}	None	·40	9.11	–	Cohesive failure in substrate
Cr	200	None	·66	2×10^{-3}	15 min	·40	9.577	–	Cohesive failure in cement
Cr	120	250 °C, 1h	·80	8×10^{-4}	15 min	·30	8.31	–	Cohesive failure in cement
Cr	120	None	·40	2×10^{-3}	None	·45	11.71	–	Cohesive failure in cement
Cr	250	250 °C, 1h	1.4	2.5×10^{-1}	15 min	·45	11.50	–	Cohesive failure in substrate
Cr	300	250 °C, 1h	1.0	2.5×10^{-1}	30 min	·45	11.30	–	Cohesive failure in substrate
Cr	350	None	·97	2×10^{-2}	20 min	·40	9.417	–	Cohesive failure in substrate
Ni	130	None	·54	8×10^{-4}	None	·10	6.727	.74	Adhesive failure at film-substrate interface
Ni	130	250 °C, 1h	·62	8×10^{-4}	None	·10	6.5	.74	Adhesive failure at film-substrate interface
Ni	100	None	·55	8×10^{-4}	30 min	·12	7.136	.86	Adhesive failure at film-substrate interface
Ni	160	250 °C, 1h	·44	2.5×10^{-3}	20 min	·15	8.392	1.20	Adhesive failure at film-substrate interface
Ni	160	None	·38	3×10^{-2}	20 min	·17	8.73	1.10	Adhesive failure at film-substrate interface
Ni	200	250 °C, 1h	·48	3×10^{-2}	15 min	·17	8.977	.97	Adhesive failure at film-substrate interface
Ni	250	250 °C, 1h	·59	3×10^{-2}	30 min	·16	8.37	2.00	Adhesive failure at film-substrate interface
Ni	300	None	·83	2×10^{-3}	20 min	·16	8.693	1.30	Adhesive failure at film-substrate interface

Note that the radius of stylus used in scratchs = 62 μm

Summary

The direct pull-off and the scratch method were used to compare the adhesion values of thin metallic films of copper, aluminium, chromium and nickel prepared under different deposition conditions.

The direct pull-off method has the inherent restriction that the adhesion to be measured must be lower than the adhesion of epoxy cement to the film and the rod, or the cohesion of epoxy cement itself. This method provides information on the nature and degree of adhesion. The scratch test was also used with caution for qualitative comparisons of the above mentioned layers under certain restricted conditions. The scratch test proved to be very sensitive, since applied loads just less than the critical value sometimes produced de-adhesion in short strips, leaving other regions intact. Both of these methods were used quantitatively to compare the adhesion values.

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