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Table I

Metal	%C Wire elongation	
	5%	10%
Ta (50Å)	91.5	89
16Cr, 14Ni, bal. Fe	87	84
304 Stainless	86	77
Fe	81	56
Al (average of 3)	75	50
60Ni, 16Cr, bal. Fe	56	54
Zr	52	38
80Ni, 20Cr	16	18

alloy also. The films appear to be substantially less ductile than those on the Cr, Ni, Fe alloys. This alloy also proved to be inhomogeneous.

For pure iron, Fig. 9, the data again suggest appreciable ductility for the oxide film.

In order to make a semiquantitative comparison of materials we have listed in Table I the value of %C, which is defined by the equation

$$\%C = \frac{i_e - i}{i_e} \times 100 \qquad [1]$$

in which i_e and i are the currents (at the same elongation) for specimens anodized at the straining potential and at a higher potential, respectively. The value of %C gives a rough measure of the fraction of the newly generated specimen area which is covered by the original oxide film; for a completely ductile film %C should be 100, while for a brittle film it should be 0.

Conclusions

The ductility of some of these passive films may be as great as that of Ta_2O_5, which evidently can be stretched as much as 50%. Because of the difficulties of interpretation it is perhaps premature to speculate about the mechanisms of deformation and implications. Perhaps the easy deformation results from ion motion under the applied electric field, as suggested by Bradhurst and Leach (6) and by Leach and Neufeld (7).

The presence of water, which is known to enhance deformation of some nonmetallic materials (10, 11), may also be important. Finally, the difference in ease of deformation of bulk oxides and passive films may be associated with differences in the structures of these two types of materials. One implication of the results may be that the explanation for the better resistance of high nickel alloys to stress corrosion cracking does not lie in the reaction film ductility.

Acknowledgment

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Anodic Dissolution of Zinc in Potassium Nitrate

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ABSTRACT

The apparent valence of pure zinc dissolving anodically in 3% KNO_3 was determined as a function of current density, temperature, and ultrasonic agitation. The apparent valence of zinc dissolving anodically at 24°C diminishes from 2.01 ± 0.01 at low current densities to 1.86 at about 50 ma and remains fairly constant up to about 80 ma cm^{-2}. This valence is affected to some extent by the preparation, e.g., polishing of the electrode, but is independent of its structure (mono- or polycrystal). Ultrasonic vibrations do not influence the apparent valence at high current densities. In all cases a black film (corrosion product) spalls off the anode but to a larger extent with ultrasonics. The apparent valence decreases with increasing temperature (measurements between 25° and 68°C) and again with increasing current density, and appears to vary as a function of metal history. Fine metallic Zn particles are found in the dark corrosion product. The average size of the particles increases with increasing temperature. On the basis of the above, it is concluded that the normal valency of zinc ions, +2, does not change during anodic dissolution in nitrate solutions, but the apparent valence of less than 2 arises as a consequence of increased local corrosion and of surface disintegration of the anode. Both occur outside the electrical circuit thus accounting for the lower coulombic equivalent. A mechanism for the disintegration phenomenon is presented.

When either Zn or Cd (having a normal valence of +2) is dissolved anodically in aqueous neutral salt solutions, containing nitrate, chlorate, or bromate ions, the number of coulombs required to dissolve one gram equivalent of metal is less than the faradaic weight equivalent, especially at high current densities. Other active metals, such as Be, Mg, Al, In, Ga, Tl, Fe, Sn, and Pb also exhibit this phenomenon.

One mechanism which has received wide acceptance is the concept of the "uncommon valence ion" as pro-

posed by Epelboin (1) for zinc undergoing anodic dissolution in perchlorate solution. Later work on Zn, Cd and other metals by Davidson and co-workers (2-6) has supported this mechanism, the results having been attributed to the expulsion of univalent ions.

The purpose of this study was to obtain experimental data for the anodic dissolution of zinc in 3% aqueous KNO_3 as a function of: (*i*) current density, (*ii*) temperature, and (*iii*) ultrasonic vibrations, and to establish a mechanism consistent with the results.

Experimental

Effect of Current Density

Apparatus.—The apparatus consisted of a 400 ml cell, a zinc electrode made of either a polycrystalline bar (99.99% purity) or of a single crystal (exposed surface nearly parallel to the basal plane, 99.95% purity), an external d-c source, a sensitive milliammeter, a decade type resistance box, a knife switch, and a platinum cathode, all connected in series. A microburet of 10 ml capacity with 0.02 ml graduations was used to titrate the zinc content of the electrolyte following electrolysis.

Procedure.—The zinc electrodes were polished shortly before each run. Two hundred ml of a 3% KNO_3 solution were transferred to the thermostatted cell (24.0° ± 0.5°C). Air was not excluded because experiments in a N_2 atmosphere gave the same results within the limits of error. The Zn anode and the Pt cathode were then inserted and connected in series with the external circuit and the circuit closed. A timer and milliammeter were used to measure the number of coulombs passed (checked by a copper coulometer). After a sufficient time interval the circuit was broken and the electrodes removed from the beaker. Any loosely adhering film on the anode was removed by scrubbing with a rubber policeman in the electrolyte. Two drops of 6M HCl added dissolved the sediment. The clear solution was then diluted to 500 ml with distilled water. Aliquots of 100 ml volume were withdrawn from this solution, heated to about 90°C, buffered to *p*H of 10, and titrated with disodium EDTA standardized against 99.99% pure Zn, using Erichrome Black T as indicator. Thus, the weight loss *w* of the Zn electrode was calculated.

Results

Influence of current density.—The valence *V* was determined from Eq. [1]

$$V = ItA/Fw \qquad [1]$$

where *It* is the quantity of electricity in coulombs, *A* the atomic mass of Zn, *F* is Faraday's constant, and *w* the weight loss of the anode (calculated from titration data). The measurements were performed over a current density range of 0.5 to 85 ma·cm^{-2} with a possible error range of ±1%. Since the behavior of a polycrystalline and of the single crystal anode (0001 plane exposed) was the same (see Table I), the resulting

Table I. Calculated valence of Zn ions going into solution at 24.0° ± 0.1°C from M-monocrystalline or P-polycrystalline Zn anodes

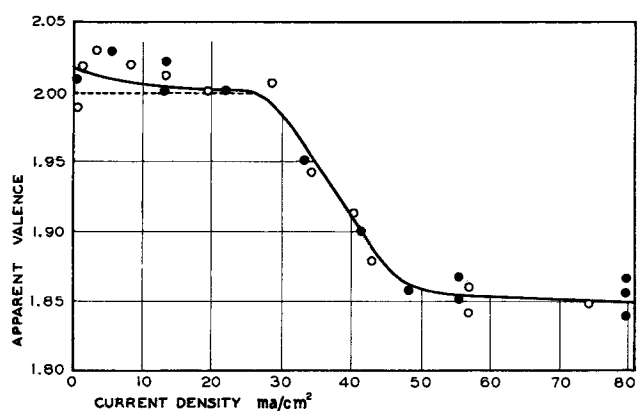| Time, sec	Current density, ma·cm^{-2}	Zn anode	Valence calculated
63,000	0.38	M	2.00
25,900	0.52	P	2.01
32,800	0.75	M	2.03
86,400	0.57	P	1.99
2,500	19.85	M	2.00
2,500	22.41	P	2.00
2,500	33.30	M	1.95
2,500	34.10	P	1.94
2,500	55.10	M	1.85
2,000	57.0	P	1.84
2,500	79.4	M	1.86
2,000	74.1	P	1.85

Fig. 1. Calculated valence as a function of current density for Zn dissolving anodically in 3% KNO_3. Dots, monocrystal; circles, polycrystal.

data were combined and are presented graphically in Fig. 1.

At low current densities (< 30 ma·cm^{-2}) a very thin, usually spotty, black film was observed on the face of the anode. On removal from the electrolyte the film turned grayish white after about 5 min exposure. Tests at higher current densities (> 30 ma·cm^{-2}) resulted in a thicker and continuous black film. Also a white precipitate was observed directly below the vertical electrode. An x-ray analysis of the deposit revealed it to be ZnO.

Since there was no difference between a mono- and polycrystalline anode, no attempt was made to use various crystalline planes for dissolution. Table I and Fig. 1 show that the calculated valence of Zn-ions approaches, with increasing current density, a fairly constant value of 1.86 ± 0.01, which is in agreement with the results of previous investigators (2). However, the constant value of about 2 at small current densities (up to 30 ma·cm^{-2}) is not always observed. Depending on experimental conditions, the drop can start at a much lower current (7). The calculated valence drops lower, even down to 1.65 if the consecutive tests are performed without repolishing the electrode, merely transferring it (after rinsing with distilled water) to a fresh solution to start another run.

A black film was always observed forming on the Zn anode. At low current densities the film was thin and its thickness increased with the current. On removal of the anode from the solution, the black film turned grayish white in a few minutes, as observed for Mg (8). X-ray analysis showed the grayish film to consist of ZnO and/or $Zn(OH)_2$. If the Zn anode was etched slightly with dilute H_2SO_4 before the run, the black film formed at electrolysis spalled from the anode upon application of ultrasonic agitation. A sample of the gray black sediment was collected, quickly rinsed by decantation with water, and then washed with dry acetone. Even then part of the sample turned white after filtering. The darkest flakes were examined under the microscope, using oil immersion objectives, at magnifications of 1430. In the reflected light parts of the sample revealed a multitude of shiny metallic particles embedded in the corrosion product ZnO or $Zn(OH)_2$. The diameter of the smallest particles was of the order of 10^{-5} mm. Larger chunks, as found during electrolysis of Zn in $NaBrO_3$ solutions (9), were also observed floating around in the oil. All the metallic particles were completely opaque to transmitted light. They consisted of Zn, as proved by x-ray diffraction.

It is, therefore, clear that the deviation from Faraday's law or the calculated lower valence of Zn ions (Fig. 1, Table I) is, in part, the result of surface disintegration of the Zn anode during dissolution which occurs outside the faradaic current and, hence, contributes to the calculation of ions of lower valence.
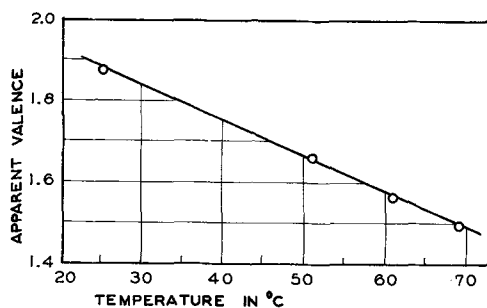
Fig. 2. Apparent valence as a function of temperature for Zn dissolving anodically in 3% KNO₃ solution. 50 to 80 ma.cm⁻² (see Fig. 1.).

Fig. 3. The variation of log (2 minus apparent valence) with reciprocal absolute temperature.

Thus, this valence is only apparent, particularly as the existence of Zn^+ has not been confirmed analytically (2). Furthermore, no lower valence was calculated when the disintegration of the anode was prevented, e.g., by amalgamation (10). Amalgams as anodes produce only normal valence ions, as found for Al(11), Ga(12), In(13), Tl(14), and Sn(15). Unfortunately it is difficult to collect the particles and quantitatively determine the amount of Zn particles present due to the high activity of the fine particles. However, the presence of metallic particles in large amounts, and the absence of Zn^+, together with the absence of disintegration (in case of an amalgamated anode) and the calculated normal charge of the Zn-ions are sufficient evidence for anodic surface disintegration.

Effect of temperature on apparent valence.—The apparatus and procedure were similar to previous studies. The cell was open to the atmosphere and any evaporation which occurred during electrolysis was corrected by addition of water at the same temperature to the electrolyte. The apparent valence as a function of temperature is shown in Fig. 2.

Some current density experiments were also performed at a temperature of 87°C. At this temperature the apparent valence dropped to 1.13 and to 1.10 for a poly- and monocrystal at current densities of 57 and 79 ma·cm⁻², respectively. Under such conditions the apparent valence seemed to be a function of time, current density, and perhaps of crystal structure. A large amount of gray corrosion product was observed on the bottom of the reaction beaker. On treatment with HCl, the material evolved hydrogen, indicating that chunks of Zn were still present in the hydroxide, while the fine metallic particles had rapidly reacted with H_2O (hydrolysis) at the elevated temperature. The larger chunks were also detected microscopically. The electrolyte contained nitrite ions, the amount of which was proportional to the decrease in apparent valence.

The activation energy.—It was speculated that this temperature dependence could be related to the activation energy by assuming that the over-all rate constant k was proportional to the normal valence less the apparent valence. Accordingly, an Arrhenius plot of log(2 minus apparent valence) vs. reciprocal temperature was made as illustrated in Fig. 3. An activation energy of ~4.2 kcal was found from the slope of the straight line.

Application of ultrasonic vibrations.—The beaker used in the previous experiments was replaced by an ultrasonic cell of equivalent diameter and connected to an ultrasonic generator. Vibrations of a frequency of 32,500 cycles sec⁻¹ and of maximum possible amplitude were passed through the reaction cell during the electrolysis. The results were both of quantitative as well as of qualitative nature. The average value for the apparent valence of a poly- and monocrystalline anode at current densities between 50 and 80 ma·cm⁻² was about 1.84 ± 0.01, while without ultrasonics a valence of 1.86 ± 0.01 was obtained. Thus, the
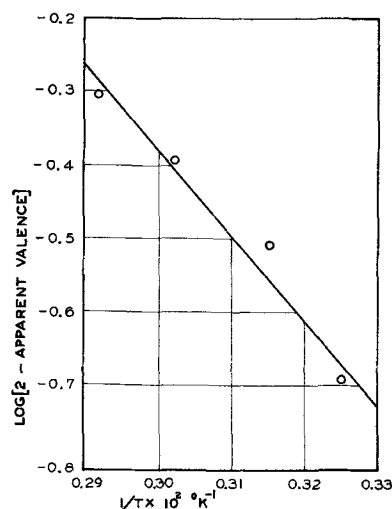
difference was very small and within the limits of error. With ultrasonic stirring the solution turned gray black in a few minutes and the electrodes became barely visible. When the circuit was opened and ultrasonic stirring stopped, the dark flakes settled to the bottom. As previously mentioned, the sediment contained metallic Zn in the form of very fine particles or larger chunks. A few drops of concentrated HCl were added to the electrolyte to determine quantitatively the Zn which spalled from the anode. The sediment dissolved easily. Etched Zn electrodes gave the same apparent valence as nonetched ones. The gelatinous $Zn(OH)_2$ film generally formed during electrolysis was not present to any appreciable degree.

Discussion and Conclusions

At current densities of 50 to 80 ma·cm⁻², the apparent valence of zinc was found to be 1.86 ± 0.01. This value is in agreement with the results of previous works cited (2, 10). However, when the current density dropped below 50 ma·cm⁻² the valence started increasing, and below 30 ma·cm⁻² values close to the normal oxidation state of two were obtained.

These results are more in accord with the concept of anodic disintegration rather than with that of formation of lower valence ions, since the rate of mass loss due to breakout of particles from the anode must be a function of the instantaneous current density (16). On this basis one would expect a decrease in the apparent valence with increasing current density possibly to some limiting value (Fig. 1). This expectation was clearly verified for Mg and Cd anodes (17). It is noteworthy that at low current densities, <10 ma·cm⁻², the metal surface was in most cases completely free of the black surface film, suggesting that no disintegration of the anodic surface occurred.

Furthermore, it is difficult, on the basis of lower valence ion formation, to explain the appearance of the very small and larger metallic particles, usually embedded in the surface oxide layer, which impart the dark color to the latter. According to the older theory Zn particles should appear as a consequence of a reduction-oxidation reaction

$$2Zn^+ \rightarrow Zn^{++} + Zn \qquad [2]$$
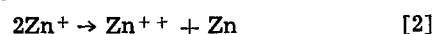
However, the improbability of such reactions, especially as regards very active metals, has been discussed previously (8, 11, 18).

All these results can be satisfactorily explained by assuming that the only faradaic process is

$$Zn \rightarrow Zn^{++} + 2e \qquad [2a]$$
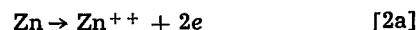
In addition to [2a] there is surface disintegration, oxidation (reactions [3] and [4]) and self dissolution,

thus resulting in more Zn dissolved than expected according to [2a].

The exact mechanism of surface disintegration is presently not known in detail, but the observations made with Zn anodes suggest a mechanism as follows: The Zn anode adsorbs onto its surface NO_3^-, similarly as is proposed for BrO_3^- (9)

$$Zn + NO_3^- \rightarrow ZnO + NO_2^- \qquad [3]$$
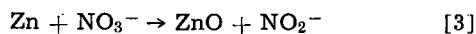
This action increases with increasing nitrate concentration resulting in a decreased apparent valence (7). Simultaneously, hydrolysis may also occur

$$ZnO \text{ (on the Zn surface)} + H_2O \rightarrow Zn(OH)_2 \quad [4]$$
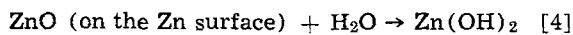
These generally thin oxide layers will vary in adherence and thickness, depending on the surface structure of the Zn anode. There will be places where the oxide layer adheres very well and where it will be thicker, causing partial passivation of the anode. On application of an anodic current the weakest spots will be attacked first and there the Zn^{++} will go into solution, partially undermining the passive spots, but no noticeable separation of these weakened metallic places from the anode will occur. With an increase of the current density, the flow of the electrons from the anode will be increased. Since the positive ions in the solid will be in excess, ions (Zn^{++}) will be driven into solution by a repulsion force corresponding to the Nernst solution tension P. It is, possibly, not always realized how large this force is. It can be calculated from Nernst's original equation

$$P = p \cdot \exp\left(-\epsilon n F/RT\right) \qquad [5]$$

where p is the osmotic pressure of the Zn^{++} in the electrolyte, ϵ the potential of Zn ($=-0.76$v, hydrogen scale), n the valence of Zn-ions, F Faraday's constant, R the gas constant, and T the absolute temperature. For a standard Zn electrode a value of P of about 10^{26} atm is obtained which represents the free energy expressed in pressure units. If only a part of this pressure (due to the limited current) is in action, even then the pressure which drives the ions into solution is enormous. Therefore, the moving ions may hit the oxide layer on the electrode surface with such force that this layer breaks away from the surface. However, if the layer adheres well to the metal, it can carry small particles of the electrode metal with it (19). And this is what is observed: metallic particles in an oxide network. The oxide may react further with H_2O, Eq. [4], and then the particles will appear embedded in a white oxide or hydroxide layer (11). The particles break away at places where their contact with the bulk of the electrode is somehow weakened, e.g., by undermining. The clean metallic surface is now able to react again with the electrolyte or with the NO_3^- according to Eq. [3] and after some time the process of disintegration can start again at the same site. However, at high current densities there will be less time for the oxidation reaction [3]. Hence, the degree of disintegration and the apparent valence will approach a constant value with increasing current (Fig. 1). Under such conditions the apparent valence may even increase because there will be less opportunity for the ions, going into solution, to take with them parts of the oxide layer containing fragments of the anodic metal (14).

Thus, the degree of disintegration and, hence, the apparent valence will depend on the quality of the oxide layer on the Zn anode, the formation of which depends on the nature of the electrolyte: there may be electrolytes producing porous or weakly adhering layers, or both, and as a result the apparent valence will be close to normal.

This concept explains why the apparent valence is the same for both poly- and monocrystalline anodic surfaces. Evidently oxide layers of the same quality are produced on Zn of various surface structures (in the same solutions). The grain boundaries are of little influence since disintegration occurs within these borders (the grains themselves are not falling out). However, if the anode surface is not repolished between the runs, the surface becomes rough and there will be an increased possibility for breakout of larger metallic particles together with the oxide layer: a lower apparent valence is observed (down to 1.65). Forces introduced by ultrasonic vibration are small as compared with those represented by Eq. [5]. Therefore, these vibrations will not markedly influence the degree of disintegration and the apparent valence. However, ultrasonic agitation is sufficient to disperse the oxide flakes loosely adhering to the Zn electrode, especially the white gelatinous hydroxide which is formed on the Zn particles (Eq. [4]). All this is consistent with the experimental results, and the white hydroxide is not found on the Zn anode if ultrasonic waves are applied.

It is more difficult to understand the influence of temperature on the degree of disintegration. Although the temperature coefficient of potential change $\partial\epsilon/\partial T$ for Zn is known (20), there are still some difficulties in the application of the original Nernst equation, as the osmotic pressure p (Eq. [5]) changes (increases) with temperature. However, considering the derivation of the equation, the solution pressure P will increase with temperature and, hence, the degree of disintegration. The apparent valence will decrease (Fig. 2). The increased P may not be the only reason for the increased disintegration rate, because compressional stresses between the anodic film and the bulk of the anode may increase with temperature and force the film to crumple or dilate. In addition hydrogen developed due to the very slow reaction

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + 2H \qquad [6]$$
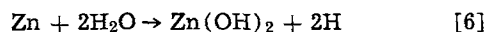
may increase the spalling of the oxide layer containing larger metallic particles. The activation energy of about 4.2 kcal (Fig. 3) suggests other possible rate determining steps such as adsorption or some other physical process.

The Zn particles which spall from the electrode are very small and completely clean toward the side of the anode. They, therefore, will be vary active and react with water according to [6] and still faster with an oxidizer, if such is present in the electrolyte. In nitrate solution reaction [3] occurs. Indeed, NO_2^- ions can be proved to be in solution and their amount is proportional to the amount of departure from the apparent valency (2-6). If disintegration of the Zn anode is prevented, NO_2^- ions are not present in the electrolyte (10, 17).

In conclusion, the assumption of formation of lower valence ions, the presence of which cannot be proved, is not necessary and does not account for the experimental data. It is very improbable that the number of lower valence Zn ions formed will depend on current density, the nature of the electrolyte, the temperature, and the surface treatment of the anode. Surface disintegration of the dissolving anode can account for the observed facts, including the reducing ability of the anolyte.

Acknowledgment

Any discussion of this paper will appear in a Discussion Section to be published in the June 1968 JOURNAL.

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Adherence and Porosity in Ion Plated Gold

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ABSTRACT

The accelerated ion deposition process is shown to provide gold films and coatings which are strongly adherent even when deposited on oxidized beryllium-copper substrates. The porosity of these coatings when deposited under conditions which provide high substrate surface temperature is undetectable at thicknesses of approximately 2μ and is the result of the formation of a gold-copper solid solution.

The ion plating process developed by Mattox (1) has been demonstrated to provide excellent adherence across a film-substrate boundary, and the observed adherence is apparently less dependent on meticulous precleaning treatment than in conventional deposition processes. Further, qualitative observation of the films deposited by the process has indicated that nonporous deposits could be obtained in thicknesses in the micron range and that the porosity resulting from substrate surface contamination can be eliminated or controlled. It is the purpose of this paper to discuss the adherence and porosity of ion plated gold films and to project a mechanism for the formation of the adherent, nonporous deposits formed.

Experimental Procedure

The apparatus used to deposit the ion plated gold is shown in Fig. 1 and is essentially that described by
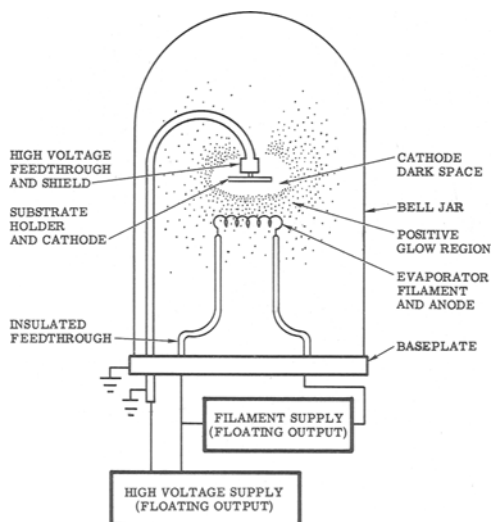
Mattox (1). Specimens were prepared in the configuration shown in Fig. 2a, in order that subsequent adherence tests could be performed.

The specimens used for adherence determination were firmly clamped to the substrate holder to maximize heat transfer and are indicated as the low-temperature group. In contrast, the specimens on which porosity and alloying observations were made were supported along approximately 0.8 cm² at the sample ends to minimize heat transfer to the substrate holder and are called the high-temperature group. Porosity data for the low-temperature group are also reported.

Sample Preparation

High-temperature group.—Specimens were 0.8 cm thick annealed beryllium copper alloy, not heat-treated. Surfaces were lightly abraded with steel wool and rinsed in acetone prior to plating.

All ion bombardment and ion plating was at 5 kv, 0.5 ma/cm². Specimens in the low-temperature group were ion plated for 2 min. Specimens in the high temperature were argon ion bombarded for 10 min and ion plated for times as shown in Table I.
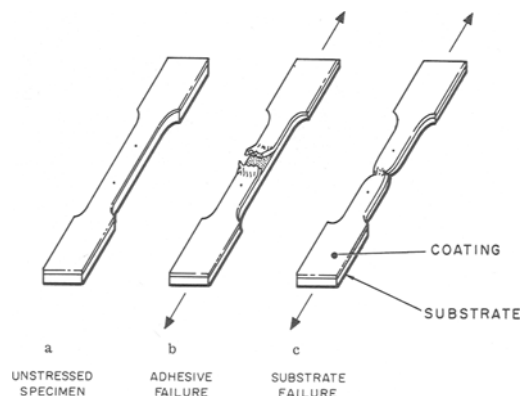

Fig. 1. Ion plating apparatus

Fig. 2. Tensile adhesion test