The Influence of Internal Stress on the Structure of ElectroDeposits

M. R. J. Wyllie

Articles you may be interested in

Scaling behavior of internal stress in electrodeposited nickel thin films
J. Appl. Phys. 104, 093518 (2008); 10.1063/1.3009336

Internal and effective stresses in nanocrystalline electrodeposited Ni
Appl. Phys. Lett. 89, 073102 (2006); 10.1063/1.2336726

Erratum: "Influence of deposition temperature on the structure and internal stress of TiN films deposited by filtered cathodic vacuum arc" [J. Vac. Sci. Technol. A 20, 1270 (2002)]
J. Vac. Sci. Technol. A 21, 518 (2003); 10.1116/1.1539081

Influence of deposition temperature on the structure and internal stress of TiN films deposited by filtered cathodic vacuum arc
J. Vac. Sci. Technol. A 20, 1270 (2002); 10.1116/1.1481043

INFLUENCE OF TEMPERATURE ON THE CRYSTAL STRUCTURE OF ELECTRODEPOSITED ANTIMONY
J. Appl. Phys. 2, 276 (1932); 10.1063/1.1745054

The Influence of Internal Stress on the Structure of Electro-Deposits

M. R. J. WYLLIE

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

(Received July 22, 1947)

The author's data on the properties of chromium electro-deposited from a standard chromic acid electrolyte are examined in the light of a theory first proposed by Bozorth. It is shown that the data fit well the assumption that the preferred orientation found in these chromium electro-deposits is the result of a slipping process, analogous to cold-working, which occurs during deposition when internal contractile stress reaches a certain critical value. It is further shown that the type of orientation found in chromium deposits is in accord with the theory and it is stated that (111) orientation is to be expected generally for body-centered cubic metals electro-deposited in a state of contractile stress, while (110) or (100) is to be anticipated for face-centered cubic metals deposited with the same type of stress. The orientations of a number of electro-deposited metals are shown to be in agreement with this expectation. Certain anomalies in the stress and orientation results for silver, nickel, and aluminum deposits have also been studied experimentally, and the results explained on the basis of the above theory. In conclusion, the possible mechanism of internal stress formation in electro-deposits is examined.

I. INTRODUCTION

IT was first shown in 1924 by Glocker and Kaupp,[1] as the result of x-ray diffraction analysis, that metals formed by electro-deposition could under certain conditions possess an orientated structure. The orientations observed were of a type known as fiber textures, the metal crystals of the deposits being aligned with a particular crystallographic axis perpendicular to the surface of the cathode but possessing freedom of rotation through 360° about this axis. Subsequent investigations by other workers have extended the range of electro-deposited metals examined by x-ray diffraction and have shown that the majority of the commonly deposited metals may possess a fiber texture of the type first noted by Glocker and Kaupp. These investigations have also proved that the extent of the preferred orientation and to some extent the nature of the orientation are both dependent upon such variables as composition of electrolyte, temperature and current density at which the electro-deposition took place, and nature of the cathode material. The effect of the cathode metal, however, and its influence on the orientation of deposits can frequently be ignored. While under certain favorable conditions a deposit is able to reproduce the structure and lattice spacing of the basis metal on which it is produced for some distance, this effect is generally very limited, particularly if the deposit itself has a strong orientating tendency. Finch and Sun[2] have shown that where the deposition conditions themselves give rise to orientations the effect of the substrate does not extend to a distance of more than 1000A. Orientation results considered in this discussion are limited to those found at thicknesses much greater than 1000A, results which are dependent solely on the deposition conditions and do not result from any substrate influence. The orientation results for chromium, given below, were found to be entirely independent of the nature of the substrate, whether the substrate was itself orientated or unorientated or whether it was a face-centered or body-centered cubic crystal structure being quite immaterial.

Fiber textures have been generally ascribed to a crystal growth process occurring during electrolysis, and the general conception of the mechanism was admirably summed up by Blum, Beckman, and Meyer[3] when they stated "One might expect that preferred orientation would tend to occur generally in electro-deposits because of the highly anisotropic nature of the process—the direction of current flow and diffusion restrictions."

The existence in electro-deposited metals of residual stresses, often of very considerable magnitude, was first reported in 1877 by Mills[4]

[1] R. Glocker and E. Kaupp, Zeits. f. Physik 24, 121 (1924).

[2] G. E. Finch and C. H. Sun, Trans. Faraday Soc. 32, 852 (1936).

[3] W. Blum, A. O. Beckman, and W. R. Meyer, Trans. Electrochem. Soc. 80, 409 (1941).

[4] E. J. Mills, Proc. Roy. Soc. 26, 504 (1877).

who showed, by preparing deposits on the bulb of a thermometer and noting the movement of the mercury thread caused by the distortion of the bulb, that deposits of iron, copper, nickel, and silver were formed in a state of contractile stress, i.e., were apparently endeavoring to shrink and thereby causing the mercury thread to rise, while the exact reverse was the case with deposits of cadmium and zinc, an expansive stress being shown and the mercury thread tending to sink. Mills showed that the forces involved were considerable, the contractile effect of copper on the bulb being as great as a uniformly applied hydrostatic pressure of over one hundred atmospheres. Stoney[5] investigated quantitatively the contractile stresses in certain nickel deposits and showed them to be as much as 19.2 tons per square inch parallel to the plane of the cathode. More recently, Hume-Rothery and Wyllie[6,7] reported that the contractile stresses in chromium deposits may reach values of nearly 30 tons per square inch. Much other valuable work on the effect of electro-deposition conditions on stress has been carried out.[8-11]

Relatively little attention has been paid to the possible effects of these internal stresses on the properties of electro-deposits. It was found by Hume-Rothery and Wyllie, however, that in the case of chromium deposits there appeared to be a clear connection between the internal stress and the extent of preferred orientation, and between stress and such physical properties as hardness and ductility. This paper will seek to explain the preferred orientation and properties of chromium electro-deposits in terms of a plastic deformation process caused by internal stress and will endeavor to show that the theory may be extended to other electro-deposited metals. An attempt will also be made to explain the mechanism of the formation of both contractile and expansive stresses in electro-deposits.

[5] G. G. Stoney, Proc. Roy. Soc. **A82**, 172 (1909).

[6] W. Hume-Rothery and M. R. J. Wyllie, Proc. Roy. Soc. **A181**, 331 (1943).

[7] W. Hume-Rothery and M. R. J. Wyllie, Proc. Roy. Soc. **A182**, 415 (1943).

[8] V. Kohlschutter and E. A. Vuilleumier, Zeits. f. Elektrochemie **24**, 300 (1918).

[9] V. Kohlschutter and F. Jakober, Zeits. f. Elektrochemie **33**, 290 (1927).

[10] E. A. Vuilleumier, Trans. Am. Electrochem. Soc. **42**, 99 (1922).

[11] C. Marie and N. Thon, Comptes rendus **193**, 31 (1931).

II. THE DATA FOR ELECTRO-DEPOSITED CHROMIUM

Hume-Rothery and Wyllie[6] showed that the hardness of chromium electro-deposits produced from an electrolyte comprising 250 grams per liter chromic acid and with a CrO_3 to sulphate ion ratio of 100:1 was a property solely dependent on the structures of the deposits as revealed by x-rays and was independent of the exact conditions under which the structure of a given type was produced. Further work has shown that the principle holds good for the two other physical properties of ductility and internal stress. Thus with increasing temperature of deposition a sequence of structures is found at constant current density, each structure being characterized by its own value for hardness, ductility, and internal stress. With increasing current density the temperature at which a given structure occurs increases, and it appears that the relationship between the temperature and current density producing a structure of a particular type is an exponential one. This relationship, in the case of the most highly preferred type of chromium deposit, has already been pointed out.[6]
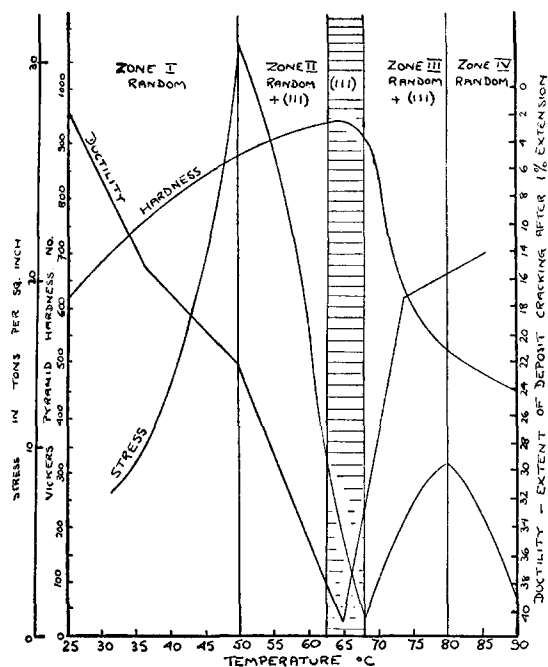

FIG. 1. Properties of chromium electro-deposits; electrolyte 250 g per liter CrO_3: 2.5 g per liter [SO_4'']; current density: 1000 amp. per square foot.

The structure and properties of chromium deposits produced over a wide range of temperature at a constant current density may thus be taken as representative of all deposits obtainable from the particular chromic acid electrolyte used in the experiments. Figure 1, which has been adapted from the papers of Hume-Rothery and Wyllie, and Wyllie,[12] shows on the same diagram curves for the hardness, ductility, and internal stress of electro-deposits produced on a basis metal of carbon steel with increasing temperature of deposition at the constant current density of 1000 amp. per square foot. The diagram has also been divided into four zones to represent the changes in the orientation of deposits 10 microns thick which, as revealed by x-rays, occur with increasing temperature. In Zone I the deposits have a random orientation, but at the border of Zone I and Zone II a trace of orientation of the (111) type is first noticed. With increasing temperature in Zone II two effects are apparent: (a) the number of particles with purely random orientation decreases and (b) the perfection of the alignment of crystals with the (111) orientation increases. In the shaded zone lying between $62\frac{1}{2}°C$ and $67\frac{1}{2}°C$ there are no crystals with random orientation. In this region the appearance of the crystals is very bright and they all have a very strong (111) orientation, the deviation from a perfect (111) orientation not exceeding $\mp 7\frac{1}{2}°$.

In Zone III effects precisely opposite from those operating in Zone II are evident. Here increase of temperature brings about a progressive decrease in the exactness of alignment of the (111) orientation and an increase in the number of particles with a purely random orientation. At the border Zone III/Zone IV all orientation effects finally disappear, and the high temperature Zone IV deposits have a random structure.

The changes of structure revealed by x-rays are followed, particularly noticeably, by the curve giving the values for the residual contractile internal stress in deposits of the same 10-microns thickness. In Zone I stress goes up rapidly to a peak of nearly 30 tons per square inch at about the Zone I/Zone II border. In

Zone II it decreases to a minimum and almost zero value for the deposits of maximum (111) orientation. In Zone III the stress increases again to a smaller maximum of about one-third the previous value at the Zone III/Zone IV border, and then decreases again rapidly in Zone IV.

Ductility values are also at a minimum in the case of the most orientated deposits, but ductility increases rapidly in the case of deposits prepared on both the high and low temperature sides of the region of maximum orientation. Hardness, too, has a maximum value coincident with the region of maximum orientation and falls off in value at both higher and lower temperatures— the more rapidly, however, to the high temperature side.

These data appear to indicate that there is some definite correlation between the physical properties of chromium electro-deposits and their preferred orientation and particularly between the internal stress and orientation. The correlation appeared to the writer to exceed any effects which might be attributable merely to an inherent tendency for the deposit to grow preferentially under certain deposition conditions in a (111) direction, and an attempt is therefore made to explain the correlation on the basis of internal stress.

III. THE RELATIONSHIP BETWEEN STRESS AND TYPE OF ORIENTATION IN ELECTRO-DEPOSITS

A theory attributing the formation of preferred orientation in electro-deposits to internal stress was first put forward by Bozorth.[13] A similar idea had earlier been incorporated in a paper by Greaves,[14] but Greaves had claimed that preferred orientations would be expected only in deposits produced at low current densities while the fine-grained hard deposits resulting from high current density deposition would be entirely random in structure. Greaves attributed internal stress to the effect of the electric field operating during deposition and claimed that only at low current densities, when the atoms had had time to arrange themselves, would orientation effects ensue. The data for chromium are entirely out

[12] M. R. J. Wyllie, Trans Electrochem. Soc. Preprint 92–5 (1947).

[13] R. M. Bozorth, Phys. Rev. 26, 390 (1925).
[14] R. H. Greaves, Metallurgist 1, 141 (1925).

of accord with the views of Greaves, since in the case of chromium it is the hardest deposits of minimum grain size which exhibit the maximum preferred orientation. Bozorth considered that since deformation produced in metals by cold-working gave rise to special orientations, it was natural to suppose that the tension known to be present in many electro-deposited metals produced orientations in them in a manner similar to that in which orientations were produced in hard-drawn wires or rolled sheets. Bozorth considered that the stress was produced by co-deposited hydrogen which diffused out of the metal as the deposit thickened, thus leaving the metal in a state of tension. He supposed that as the process of deposition went on the stress difference between the innermost and outermost layers of the deposit increased and that ultimately the compressive stress in the layers next to the cathode became so great that the crystals were crushed, thus forming new crystals of very small dimensions. In the outer layers, however, where the crystals were formed under greatest tension, the orientations would be most marked. Bozorth's idea thus also accounts for the experimental observation that preferred orientation tends to increase with increasing deposit thickness. Experimentally, Bozorth examined some deposits of iron, nickel, copper, zinc, and cadmium and found marked orientation effects only in iron and nickel. These two metals were found to be much harder than the deposits of random orientation, and this fact Bozorth interpreted as lending support to his view that the orientations observed in the iron and nickel were produced by some sort of cold-working mechanism.

The theory of Bozorth, although clear in its general implications, i.e., that stress in electro-deposits is produced by co-deposited hydrogen and that this stress is responsible for the production of preferred orientation in the deposits by a mechanism analogous to the cold-working of metals, was put forward in a somewhat qualitative manner and was based on rather scanty experimental data. The more comprehensive results available for chromium deposition enable the writer to carry Bozorth's theory a step further.

The deposition of chromium is an extremely inefficient process, and in no case were efficiencies greater than 35 percent noted, the most orientated deposits being characterized by an efficiency of about 9 percent.[6] The bulk of the current is thus consumed in the liberation of hydrogen, and for every atom of chromium laid down at the cathode numerous atoms of hydrogen are simultaneously liberated. It may be assumed that some of these hydrogen atoms are initially entangled in the growing crystal lattice of chromium, causing the lattice to be abnormally expanded. As deposition proceeds the major portion of the hydrogen in the lattice diffuses out, thus leaving the lattice in an expanded and unstable condition. The chromium atoms, therefore, attempt to contract together to their normal interatomic positions. This contraction, however, is opposed by the adhesion of the deposited atoms to the layers below, and a state of strain is thereby set up. It is not suggested that all the hydrogen initially contained in the lattice is lost since a residual expansion of the lattice of electro-deposited chromium has been reported[15] and Hume-Rothery and Wyllie, although unable to determine the lattice parameter of chromium in the "as-deposited" condition because of the extreme diffuseness of the lines on a Debye-Scherrer film, nevertheless found a parameter of 2.8861A at 23°C, as against the normal value of 2.8786A, in the case of a highly orientated deposit annealed in vacuum for 4 hours at 750°C. The suggestion is put forward, however, that immediately after deposition, when the bulk of the hydrogen escapes, the lattice is considerably strained and that this strain is relieved, when it reaches a certain critical value, by an actual slipping or yielding of the metal crystals which are thus left in a condition somewhat analogous to that of a cold-worked metal. On this assumption it may be understood why the temperature and current densities leading to deposits with the most highly preferred orientations are those which lead also to the lowest residual stress, and why such deposits are hard and brittle, since it is known that cold-work increases the hardness and decreases the ductility of a metal. It has been shown that the stresses involved in chromium deposition are very high, and at the moment of

---

[15] W. A. Wood, Phil. Mag. **23**, 984 (1937).

deposition these may well be sufficient to produce plastic deformation. While the stresses involved are thus of sufficient magnitude to justify the concept of plastic distortion occurring, the amount of actual strain involved in the process is more difficult to assess. The distortion necessary to account for stresses of the magnitude actually observed experimentally in deposits would result from an enforced straining of the deposit amounting to perhaps 0.7 percent in directions parallel to the plane of the cathode. This order of magnitude of straining would not normally account for very appreciable internal slip in the crystals of the deposits, and certainly would not be expected to yield the slip into preferred orientations which is postulated below. Reduction in volume of the order of 60 percent is necessary if a block of massive metal is to be so distorted by slip as to show evidence of a preferred orientation. While it is realized that this fact constitutes a potent argument against the slip theory of Bozorth and the writer, it may be argued that the exact mechanism of slip is still obscure and that in the case of a massive block of polycrystalline metal considerable reduction in volume may be essential before the influence of the strain on small crystals becomes sufficiently appreciable and directed so as to produce orientation effects. It is possible that the separating action of co-deposited hydrogen produces during deposition a very much greater strain throughout very small crystals than can ever be detected in a deposit completed and removed from the electrolyte. If this be so, it is suggested that during the contraction of these expanded crystals to approximately normal interatomic distances after loss of hydrogen slip occurs over shorter ranges and very much more freely than in a massive metal, this slip resulting both in a harder and more orientated state of the material than can be achieved by any ordinary cold-working process. On this theory slip-bands would not normally be visible in an electro-deposited metal, and the so-called slip bands observed by Hughes[16] and Tamman[17] in iron and copper deposits, as well as the rhythmic

banding observed in nickel,[18] would be susceptible to explanations other than as confirmation of the internal slip theory suggested.

On the theory outlined above, the data shown in Fig. 1 are readily explicable. Across Zone I the residual stress resulting from the lattice strain caused during deposition is increasing, and the general distortion of the crystal lattice causes both an increase in deposit hardness and a diminution in ductility, but not until the Zone I/Zone II boundary is reached does the lattice strain during deposition attain the critical value for sufficient slip to occur to manifest itself in preferred orientation. In Zone II it may be presumed that the strain set up during deposition steadily increases to reach a maximum value in the shaded region. In this zone, therefore, orientation increases and the residual stress, indicative of strain unrelieved by slip, decreases. Hardness correspondingly increases and ductility further decreases. In Zone III it would appear that the strain resulting immediately after deposition begins to decrease, possibly because of the effects of increased thermal vibration enabling the co-deposited hydrogen to escape more readily. As the strain decreases in magnitude less slip, and therefore preferred orientation, results and more unrelieved strain is left in the lattice to show itself as residual stress. In Zone IV the strain never reaches a value sufficient to cause any orientation and appears to fall off rapidly with increasing temperature. In Zones III and IV hardness also decreases and ductility increases as would be anticipated on the basis of the strain effects postulated.

It remains to be seen what effect the slipping process suggested would have on the crystal orientation, and here an apparent correlation has been found between the textures of electro-deposited metals and of the same metals in the drawn state.

It is well known that when a metal is drawn the resulting texture is such that one or more crystallographic directions lie in the direction of drawing. It has been found that if for a particular metal the drawn texture is such that one or more crystallographic directions lie in the direction of drawing, then the texture of the electro-

[16] W. E. Hughes, J. Iron and Steel Inst. 103(1), 356 (1921).

[17] G. Tamman, *Lehrbuch der Metallkunde* (Leopold Voss, Leipzig, 1932).

[18] See, for example, W. A. Wesley and E. J. Roehl, Trans. Am. Electrochem. Soc. 82, 37 (1942).

deposit, if the latter involves formation with contractile stress, is such that the maximum number of the same directions lie in the plane of the deposit. If, however, the electro-deposit involves expansive stress, the texture is related to the compression texture of the metal.

In the case of body-centered cubic metals it is known that the drawing texture is such that a [110] direction lines in the drawing direction, and the above principles therefore require the maximum number of [110] directions to lie in the plane of the deposit. This condition is satisfied by a (111) orientation since the (111) planes contain three [110] directions and this is the maximum possible. The preferred orientations of body-centered cubic chromium and of iron agree with this principle. That the orientation in iron is (111) has been shown,[13,19] and that the stress is contractile has also been demonstrated.[4,9]

With face-centered cubic metals, drawing produces one of two different textures, or both, with the [100] or [111] directions parallel to the direction of drawing.* The above principle leads to the expectation that electro-deposited face-centered cubic metals will possess preferred orientations with the greatest number of [100] and [111] directions in the plane of the cathode if the deposits are formed with contractile stress. Taking the different planes in order it is found:

Plane parallel to cathode surface	No. of [100] directions in cathode surface	No. of [111] directions in cathode surface
(100)	2	0
(110)	1	2
(111)	0	0
(210)	1	0
(211)	0	1

The planes of the higher indices are all less favorable as regards the number of [100] and [111] directions they contain.

It should be expected that the preferred orientations of electro-deposited face-centered cubic metals will be (100) or (110) if the deposits

involve contractile stress. In agreement with this principle electro-deposits of cobalt formed under conditions likely to give rise to contractile stress[9] have been found with a (110) orientation.[19] Similarly deposits of copper have a (110) or (100) orientation[1,20] when formed under conditions giving rise to contractile stresses.[4,10] Deposits of nickel exhibit very strong contractile stress,[4,5] and the orientations generally reported are (110) or (100), although (211) has been noted.[13] It has been stated[21] that a (100) orientation is always obtained if the electrolyte is stirred by rotating the cathode. The orientation of gold electro-deposits has been shown to be (110),[19] but no reference to the nature of the internal stress appears to exist. The data for silver are more complicated. Glocker and Kaupp stated[1] that both [100] and [111] orientations were observed. On the theory above a [111] orientation would not be expected from a silver deposit possessing contractile stress. However, it has been demonstrated[9] that, depending on the current density of deposition, silver deposits formed from the same solution may have either contractile or expansive stress. Since the compression texture of silver is such that the [110] direction is the direction of compression, a silver deposit formed under conditions of expansive stress might be expected to possess a (111) orientation since the (111) plane, as previously observed, contains three [110] directions.

Experiments, described below, were therefore undertaken to investigate the connection between the direction of stress and orientation in silver deposits. Some experiments involving the deposition of nickel from a nickel chloride solution under various conditions, as well as aluminum from an organic electrolyte, are also noted.

IV. STRESS AND ORIENTATION IN SOME SILVER, NICKEL, AND ALUMINUM DEPOSITS

Silver

Kohlschutter and Jakober[9] showed that silver deposits produced on a platinum cathode from a

[19] G. I. Finch, A. G. Quarrell, and H. Wilman, Trans. Faraday Soc. **31**, 1051 (1935).
* With aluminum the texture is almost entirely [111] whilst copper gives a mixed texture 40 percent [100] and 60 percent [111] and silver a mixed texture 75 percent [100] and only 25 percent [111]. Nickel resembles copper.

[20] H. Hirata and Y. Tanaka, Mem. Coll. Sci. Kyoto Imp. Univ. **A15**, 9 (1932).
[21] W. G. Burgers and H. E. Quanjel, Rec. trav. chim. **61**, 353 (1942).

<div style="text-align:center">(a)   (b)</div>
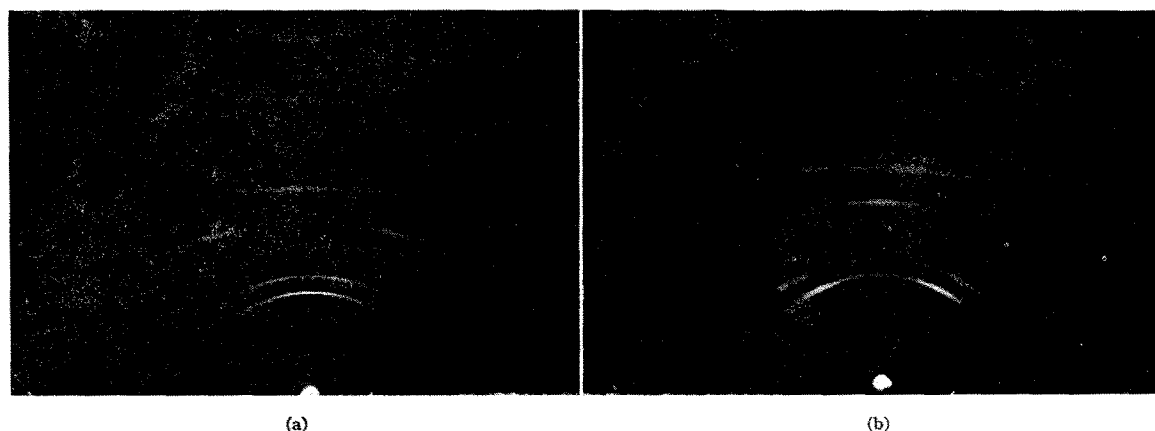
FIG. 2. (a) Silver deposit showing (111) orientation; expansive stress; current density 5 M.A./cm²; temperature 18°C electrolyte: 0.2 M AgCN, 0.4 M KCN. (b) Silver deposit showing (110) orientation; contractile stress; current density 5 M.A./cm²; temperature 18°C; electrolyte: 0.2 M AgCN, 0.2 M KNO₃, 0.4 M KCN.

solution comprising 0.2 M AgCN and 0.4 M KCN possessed strong expansive stress at a current density of 5 milliamp. per square centimeter and considerable contractile stress at a current density of 15 milliamp. per square centimeter. It was decided to reproduce their results and to examine the deposits by the glancing beam x-ray method.[22] One liter of electrolyte was made up 0.2 M AgCN and 0.4 M KCN from British Drug Houses "Analar" silver cyanide and potassium cyanide. The container used was a liter glass beaker. The anode, which closely fitted the whole interior wall of the beaker, was silver foil of 99.99 percent purity. The cathode was silver foil of the same quality as the anode and was 0.05 mm thick and 5 cm wide. This foil had been delivered by its manufacturers in the form of a tight roll and was naturally smooth and springy. When a length of 11 cm was cut from the roll, it curled into a circular segment of about 3 cm diameter, there being a gap of just over 1 cm between the edges of the split cylinder thus formed. Advantage was taken of this phenomenon to measure conveniently the type of stress in deposits. A copper lead was soldered to the inside of the cylinder at a point diametrically opposite the split, and the entire inside of the silver foil as well as the copper wire was stopped off with cellulose varnish. The cylinder was then suspended in the electrolyte by means of the wire so that it was roughly concentric with the silver anode around

²² M. R. J. Wyllie, Rev. Sci. Insts. 18, 425 (1947).

the wall of the beaker. With this arrangement, since deposition can take place only on the outside of the split cylinder, it is clear that any expansive or contractile stresses in silver deposits formed will manifest themselves in a closing or opening of the gap in the cylinder.

At a current density of 5 milliamp. per square centimeter and at 18°C a definite closing of the gap was noted. The effect was not very large, amounting to about 1-cm movement for a deposit thickness of 10 microns. At 10 milliamp. per square centimeter no stress was perceptible, and this was also the case of 15 milliamp. per square centimeter. The latter deposit was a dirty yellow in color, nodular, and rather nonadherent. No evidence of the contractile stress claimed by Kohlschutter and Jakober for a deposit formed at this current density could be detected. X-ray evidence revealed that the deposit produced at 5 milliamp. per square centimeter had a marked (111) orientation (Fig. 2a) but those formed at 10 and 15 milliamp. per square centimeter were random in orientation.

Further investigation showed that contractile stress in silver deposits on a silver cathode could be formed from a solution containing 0.2 M AgCN, 0.2 M KNO₃, and 0.4 M KCN. This solution was made from the previous one by addition of "Analar" brand potassium nitrate. Using the same arrangement of anode and cathode as described previously the following results were obtained at a current density of 5

milliamp. per square centimeter and an electrolyte temperature of 18°C:

Time (minutes)	Distance between the sides of the gap in the split cylinder (millimeters)	Expansion (millimeters)
0	16.21	——
6	18.54	2.32
12	23.70	5.16
18	29.38	5.68
31	38.27	8.89

Total expansion 22.06

X-ray investigation of this deposit (Fig. 2b) showed that it possessed a marked (110) orientation. These data for silver thus tend to substantiate the theory outlined above, insomuch as deposits with contractile stress show a (110) orientation and those with expansive stress a (111) orientation.

Further experiments in silver deposition were conducted to ascertain whether or not the lattice parameter and crystal form of deposits were the same during deposition, i.e., while the current was flowing, as they were after deposition was complete. A possible cause of internal stress may be the deposition of one allotropic form of a metal, this form reverting to a more stable modification of different volume either during deposition or after removal of the specimen from the electrolyte. Such changes would normally escape detection as deposits are examined some considerable time after deposition has ceased. The allotropic modification theory for stress will be further discussed below.

The apparatus used is shown diagramatically in Fig. 3. The electrolyte was 0.2 M AgCN and 0.4 M KCN contained in a rectangular glass vessel 10 cm$\times$6 cm$\times$8 cm. The anode was of 99.99 percent silver sheet 10 cm$\times$8 cm in area arranged against the side of the vessel as shown in the figure. The cathode was a 99.99 percent silver disk 0.2 cm thick and 6 cm in diameter and was screwed to the shaft of an electric motor. The disk was rotated at 1 r.p.m. The bottom of the disk was 2 cm below the surface of the electrolyte. With this arrangement, deposition of silver at 18°C was carried on at a constant current density of 5 milliamp. per square centimeter on the area of the cathode immersed. The portion of disk plated, of course, changed all the time as the disk revolved, but since the portion of the disk not in the electrolyte

remained covered with a film of electrolyte as it revolved, it is possible that some slight deposition always occurred on this portion as well as on the immersed portion. It was, in fact, hoped that this was the case. Normal back reflection photographs, using a revolving circular cassette holder with 120° masks and unscreened cobalt radiation, were taken of (a) the pure silver cathode, (b) the deposit while depositing, and (c) the deposit after deposition ceased. The disk was not touched during this sequence of photographs nor was the electrolyte removed. The beam was arranged to impinge 0.5 cm from the edge of the disk and 1 cm above the electrolyte surface, and the direction of disk rotation was such that the portion of deposit diffracting was that which had just emerged from the electrolyte. Disk to film distance was approximately 3 cm.

Figure 4 shows the result obtained. It is evident that under these conditions there is no difference between the lines given by the deposit during deposition or after deposition has ceased. The lines from the deposit are, however, more diffuse than those from the basis metal, and
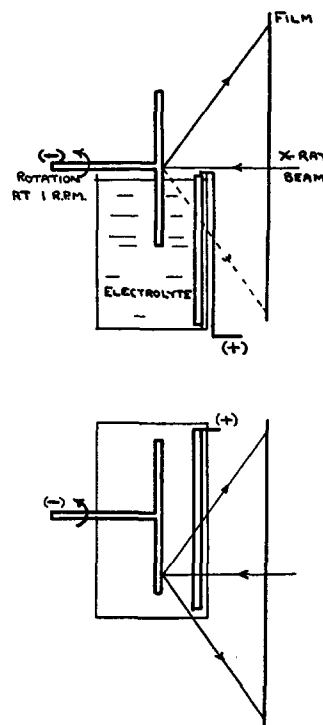

FIG. 3. Schematic drawing of apparatus for taking back reflection x-ray photographs of silver electro-deposits immediately after deposition.

there is possibly a very slight general increase in the lattice parameter of the deposited silver. The effect is not large. It is suggested that the method outlined above deserves wider application to the study of electro-deposition processes generally.

Nickel

The solution chosen was one which has been stated[18] to show particularly large values of contractile stress. It comprised 205 g per liter of $NiCl_2 \cdot 6H_2O$, 8 g per liter of KCl and 17 g per liter of NH_4Cl. The salts used were "Baker's Analysed" reagents, the cobalt content being 0.10 percent, the copper 0.003 percent, and the iron 0.003 percent. Measurement of stress was carried out by depositing nickel on one side of a flexible high carbon steel strip and measuring the direction and magnitude of the curvature of the strip after the deposition was complete. The steel used was of Swedish manufacture and remarkably uniform in its properties. It was 0.25 in. wide and 0.002 in. thick. Bending was measured by determining the distance between the free end of a 14 cm long strip (12 cm being immersed in the electrolyte) relative to a fixed glass pointer when the other end of the strip was clamped in a brass holder. Before deposition the strip was cleaned by cathodic etching in a

FIG. 4. Back reflection x-ray photograph of silver while depositing; current density 5 M.A./cm² temp. 18°C; electrolyte: 0.2 M AgCN, 0.4 M KCN; segment 1: deposition proceeding, current on; segment 2: deposition concluded, current off; segment 3: pure silver basis metal.

solution of sodium carbonate followed by an anodic etch of 30-seconds duration at a current density of 200 amp. per square foot in a 30 percent sulfuric acid solution. The reverse side of the strip was insulated with cellulose varnish. Deposits were prepared in all cases at a thickness of 10 microns, this figure being checked by weighing. A pH of 5.0, measured with a commercial glass electrode, was standardized.

The electrolyte was contained in a glass vessel 10 cm×5 cm×15 cm, the temperature being controlled to 0.1°C by a constant temperature bath. The nickel anodes used were 14 cm×5 cm in area and were of high purity, the material being donated by the International Nickel Company.

Initial experiments were carried out at a current density of 5 amp. per square decimeter and were made to ascertain the effect of temperature on stress. Figure 5 shows the results obtained. It is obvious that, while the stress tends to fall off steadily with increasing temperature of deposition about 25°C, there is a very rapid and immediate decrease below 25°C. Figures of stress are given in millimeters of deflection of the tip of the strip, but it may be pointed out that a deflection of 1 mm represents a contractile stress of about 6 tons per square inch parallel to the plane of the cathode. X-ray investigations showed that in all cases the orientation of these nickel deposits was random.

In terms of the theory outlined above the sudden change of stress below 25°C would be attributable to an internal relief of strain by slip into a preferred orientation. No orientation was found. However, under the microscope the deposits below 25°C all showed numerous cracks, and it was evident that stress was being relieved in these deposits by rupturing of the metal film and not by any possible internal mechanism. The cracking of deposits, with consequent relief of stress, has been pointed out[23] to be a source of error in the measurement of stress in nickel deposits. It was a complication not noticed in the case of chromium.

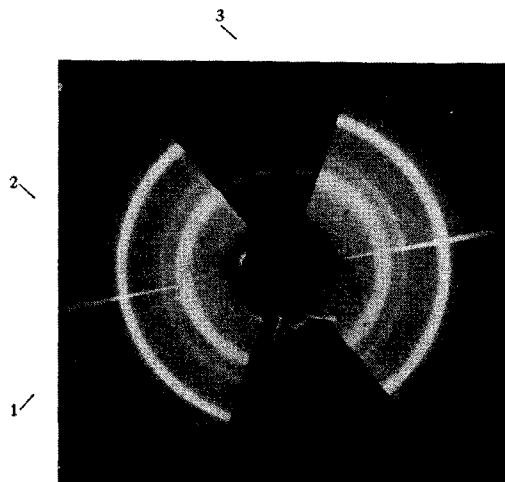The hardness of nickel deposits has been attributed largely to co-deposited basic nickel

[23] D. J. MacNaughtan and A. W. Hothersall, Trans. Faraday Soc. 31, 1168 (1935).

salts,[24,25] and considerable evidence to justify this belief has been presented. At an operating *p*H of 5.0 the *p*H of the cathode film is undoubtedly much higher, as has been experimentally observed,[26] and co-deposition of nickel hydroxide, formed as a sol adjacent to the cathode surface, is almost inevitable. It was considered that the effect of co-deposited basic material highly dispersed in the deposit might be to weaken, to some extent, intergranular cohesion and therefore to promote cracking as well as to inhibit plastic deformation. It is known that the effect of a finely divided second phase in a matrix is to make plastic deformation, and therefore the occurrence of orientation, more difficult.

The only logical method of cutting down the deposition of basic material appeared to be by decreasing the thickness of the cathode film, and this was achieved by affixing anode and cathode, facing each other, at the end of an arm 5 cm in length and rotating this arm about its center in the electrolyte at 25 r.p.m. Under these conditions at 5 amp. per square decimeter, crack-free deposits of low stress values could be fairly reproducibly obtained below 25°C, and these uncracked, fine-grained deposits showed evidence of a (110) orientation. Deposits obtained by the rotating anode and cathode method at temperatures above 25°C did not differ appreciably either in appearance, internal stress, or orientation from those prepared under the same conditions of current density and electrolyte in the absence of rotation.

A point of interest noted when determining stress was the fact that in many cases when the deposit was being soaked in an alcohol/acetone mixture to remove stop-off varnish prior to the bending of the strip being measured, a visible evolution of gas from the deposit occurred, while at the same time further bending of the strip, i.e., contraction of the deposit, took place. It was often necessary to wait several hours before the strip bending reached a final equilibrium value.

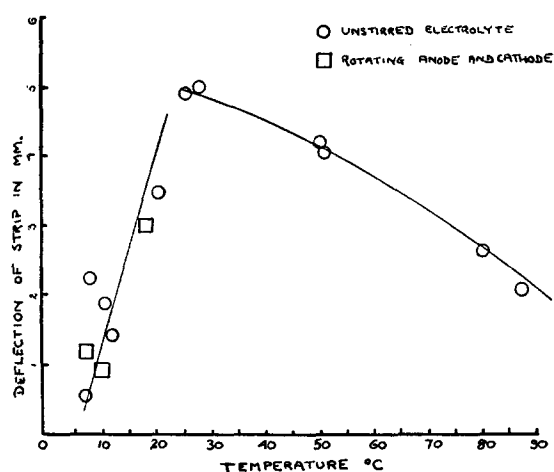The results for nickel deposited from a nickel

FIG. 5. Stress in nickel deposits from nickel chloride electrolyte; current density 5 amp. per square decimeter *p*H 5.0.

chloride electrolyte under these conditions indicate that very high values of contractile stress can occur and that a peak stress is reached at about 25°C whether the electrolyte is stationary or flowing past the cathode. Stress relief below 25°C is generally caused by cracking of the deposit, but if rotation is used the stress is still low and an orientation is observed. This result tends to confirm the statement[21] that nickel deposits from a nickel acetate electrolyte cannot be produced with a definite (100) orientation on a circular cathode of 6-mm diameter unless the cathode is rotated at 100 r.p.m. or more. It was found impossible to obtain satisfactory x-ray photographs of nickel deposits while deposition was being carried on.

Aluminum

Aluminum was deposited on steel strips cleaned in precisely the same way as that used previously for nickel deposition. The non-aqueous electrolyte, essentially aluminum bromide and ethylene bromide, was made up in the manner suggested by Blue and Mathers.[27] Pure aluminum was used as anode and the electrolyte, anode, and steel cathode were enclosed in an airtight cell 4 cm in diameter and 16 cm high. Using a current density of 1 amp. per square decimeter at room temperature, good adherent

[24] D. J. MacNaughtan and R. A. F. Hammond, Trans. Faraday Soc. **27**, 633 (1931).

[25] D. J. MacNaughtan, G. E. Gardam, and R. A. F. Hammond, Trans. Faraday Soc. **29**, 729 (1933).

[26] A. Brenner, Proc. Am. Electroplaters Soc. **28** (1941).

[27] R. D. Blue and F. C. Mathers, Trans. Am. Electrochem. Soc. **65**, 339 (1934).

and bright aluminum deposits were obtained after the electrolyte had been worked for some time. No perceptible stress, either expansive or contractile, was recorded, and x-ray diffraction showed that the deposits were of a grain size of 10^{-2} to 10^{-3} cm and were random in orientation. This appears to be the first occasion on which a determination of the stress and orientation of deposits from non-aqueous solvents has been attempted.

V. THE ORIGIN OF STRESS IN ELECTRO-DEPOSITS

A theory which attributes the orientation of many electro-deposits to stress has already been given, and a mechanism for the possible formation of the contractile stress in chromium electro-deposits has been outlined. The deposition of chromium from an aqueous chromic acid electrolyte is, however, unique among the commonly deposited metals insomuch as the deposition efficiency is extraordinarily low and in all cases liberation of chromium is accompanied by the evolution of very considerable quantities of hydrogen. It remains to be considered whether the co-deposited hydrogen theory is capable of explaining contractile stresses generally, and whether any analogous theory can account for the formation of expansive stresses in certain electro-deposited metals.

Although a number of papers have been published on the experimental determination of stress in deposits, stress data are still scanty. Certain generalizations on the basis of existing results may, however, be made.

(1) Only contractile stresses are exhibited by metals of the transitional groups unless very considerable quantities of organic addition agents are added. E.g., the addition of sufficient sodium napthalene trisulfonate to a nickel bath may eventually produce a slight expansive stress.

(2) Metals such as copper and silver, which are closely related to transitional metals, may exhibit either contractile or expansive stresses depending on the deposition conditions.

(3) Non-transitional metals such as lead, zinc, and cadmium, if stressed at all, show only expansive stresses.

It would also appear that contractile stresses tend to be of considerably greater magnitude than expansive stresses.

The fact that hydrogen is associated with the formation of contractile stresses appears to

derive support from a number of considerations. It is well known that transitional metals, and under certain conditions semitransitional metals such as copper and silver, tend most readily to form stable or metastable alloys with hydrogen. Expansion of the lattices of such metals during deposition and their subsequent contraction is therefore quite feasible. Residual expansions in electro-deposited chromium have been found in this work, and the same is certainly true for palladium.[28,29] Depolarizers and alternating current superimposed on the direct plating current both serve markedly to reduce contractile stress,[9] and their action is almost certainly the oxidation of hydrogen shortly after it is liberated cathodically and before it can exert any considerable effect on the growing metal lattice. The work of Marie and Thon[11] shows that copper deposited from a neutral solution of copper sulphate exhibits expansive stress on bright platinum, silver, and gold substrates but a contraction on a dull platinum base. When the addition of 1 percent sulphuric acid is made contractions occur on both dull and bright platinum, and in the presence of 2 percent H_2SO_4 contractions are observed on all the substrates. These data point both to an over-voltage effect and the relative ease of liberation of hydrogen and metal. Contractile effects increase with time after removal of the deposit from the electrolyte and are accompanied by the liberation of a gas which is almost certainly hydrogen. The annealing of highly stressed deposits at low temperatures frequently increases contractile stress,[23] and gas is evolved. There is, nevertheless, no direct connection between magnitude of stress and amount of co-deposited hydrogen. Thus in Fig. 1 the efficiency of deposition at 1000 amp. per square foot is about 30 percent at 30°C falling to only 5 percent at 85°C, while the values for stress vary as shown. A similar lack of obvious relationship exists in the case of nickel.[30] It has recently been shown[31] that the stress in nickel deposits increases with increase in the pH, and on these data it was claimed that co-deposited

[28] L. McKeehan, Phys. Rev. (2) 21, 334 (1923).
[29] G. Chaudron, J. Bérnard, and A. Michel, Comptes rendus 218, 913 (1944).
[30] D. J. MacNaughtan and A. W. Hothersall, Trans. Faraday Soc. 24, 387 (1928).
[31] B. Martin, Proc. Am. Electroplaters Soc. 207 (1944).

basic material is the cause of stress. Nevertheless, it would appear that some hydrogen is always evolved if contractile stress is to result, and nickel deposits prepared at a pH of as much as 5.7 have been found by direct analysis to contain hydrogen.[32] A tentative conclusion appears to be that hydrogen must be evolved before contractile stress manifests itself, but that there is an optimum amount of hydrogen necessary to produce maximum stress, the amount varying with temperature, the rate of deposition, and other factors not readily capable of quantitative evaluation.

The formation of expansive stresses in silver, copper, zinc, cadmium, and lead deposits under appropriate conditions is more difficult to explain. It may be that both contractile and expansive stresses result from the deposition of one allotropic modification of a metal, this modification reverting to a more stable form, with a consequent volume change, while deposition proceeds. No direct experimental evidence has yet been found to justify this theory, but it is perhaps noteworthy that metals such as nickel, chromium, iron, and cobalt, which all show heavy contractile stresses, can all exist in another crystalline form. The beta-modification of chromium, for example, can be formed from a chromic acid electrolyte if more than 18 percent trivalent chromium exists in the solution,[33] and this modification reverts readily to the normal alpha-form. It is possible that the concentration of trivalent chromium may reach 18 percent in the cathode film by reduction of the hexavalent ion by liberated hydrogen. The beta-form is, however, more close packed than the alpha-modification, and a transformation should cause an expansive rather than a contractile stress. However, the same is true for nickel where the normal beta-nickel is a face-centered cube and the alpha-form a close-packed hexagonal structure. Nevertheless the density of the close-packed nickel when formed by sputtering in hydrogen was estimated as 7.04 against the normal value of 8.9.[34] Here

a change from alpha- to beta-form would cause a contraction of a metal film.

The data of Marie and Thon, given above for copper deposition, show that the stress in the deposits changes from expansive to contractile as the over-voltage of the cathode is lowered or the acidity of the electrolyte is increased. The change from expansive to contractile stress found in silver deposits on platinum[9] formed from the same solution of potassium argento-cyanide takes place with increase of current density. It would appear that in these cases there are two processes at work, one endeavoring to give expansive stress and one contractile. Under conditions giving rise to the liberation of a large quantity of hydrogen the second effect prevails over the first, and contractile stresses result.

It is now suggested that in almost all deposited metals there is a tendency to form expansive stress, but in the case of transitional metals this tendency is always overcome, and in the case of borderline transitional metals it may be overcome by the formation of contractile stress resulting from interference by hydrogen in the growing lattice. Only in the case of non-transitional metals such as lead, zinc, and cadmium is the expansive tendency always greater than the contractile. The proposed mechanism for the formation of the expansive stress is based on the observation that in every stressed deposit investigated the $\Delta F°$ value for the reduction to metal of the metal ion in solution by monatomic hydrogen is favorable to the reaction taking place. Thus the $\Delta F°$ values are -61524 calories for zinc, -90820 for lead, and -112610 for copper for reduction from their divalent ions, and -42120 calories for the reduction of silver from the $Ag(CN)_2{}^-$ complex.[35] Iron, nickel, cobalt, and palladium theoretically may also be reduced. These $\Delta F°$ values, of course, only indicate that the reduction is possible, since the precise concentration of ions and hydrogen in the cathode film cannot be calculated. Assuming, however, that reduction of the metal ion by monatomic hydrogen takes place, metal atoms will be produced at the cathode by two separate and distinct electron-transfer mechanisms. It is suggested that the metal formed by the hydrogen

[32] A. Brenner, J. Research Nat. Bur. Stand. 18, 565 (1937).

[33] L. Wright, H. Hirst, and J. Riley, Trans. Faraday Soc. 31, 1253 (1935).

[34] G. Bredig and R. Allolio, Zeits. f. physik. Chemie 126, 41 (1927).

[35] Values calculated from W. M. Latimer, *Oxidation Potentials* (Prentice-Hall, Inc., New York, 1938).

reduction has little tendency to continue the lattice structure of the nuclei resulting from the deposition of metal by electron gain from the cathode, and that it tends to grow between these nuclei. What may be envisaged crudely as a shouldering apart of the growing deposit occurs, and expansive stress ensues. Under conditions where more monatomic hydrogen than can reduce the metallic ions is being formed, contractile stresses will occur if the metal being deposited is capable of absorbing hydrogen. Thus with silver at 5 milliamp. per square centimeter the stress is expansive; at 15 milliamp. per square centimeter it is contractile. With copper contractile stress occurs only when hydrogen is more readily evolved. The inability of non-transitional metals to form systems with hydrogen causes the stress in electro-deposits of these metals always to be expansive.

VI. LIMITATIONS OF THE STRESS-ORIENTATION THEORY

The theory proposed satisfactorily fits the data for chromium. Experimental findings are limited in the case of other metals, and insufficient data exist to permit a detailed correlation of stress, orientation, and physical properties. For nickel deposits, however, this lack of data is not entirely true. Many papers on nickel deposits have been published, but because of the wide number of electrolyte compositions used and the complicating variable of pH in addition to current density and temperature, it is not easy to generalize the results. It would appear, however, that the internal cold-working mechanism suggested to account largely for the hardness of chromium (supplemented by extremely small grain size and possibly by the effects of a residual interstitial solid solution of hydrogen), can account only for part of the hardness of many deposits of nickel. It is possible that the major portion of the hardness of these deposits results from very finely dispersed basic material contained in the lattice. The hardness of all very hard electro-deposits is greater than that which could be engendered by cold-working the same massive metal or by the known effects of precipitation hardening, alloy formation, or diminution in particle size. It is possible that internal cold-working taking place within small grains immediately after their deposition might produce greater effects than those resulting from ordinary cold-working processes, but on the whole it is felt that the anomalous hardness figures for electro-deposits result from a combination of all the hardening factors outlined above. The degree to which each contributes may vary from metal to metal, i.e., primarily cold-work in chromium and precipitation hardening by co-deposited basic material in nickel deposits.

It is not suggested that growth mechanisms can never be responsible for orientations in electro-deposits since some experiments[36,37] clearly show that, particularly at low current densities, preferential growth of distinct crystal planes may take place. It is, however, suggested that orientations in hard, fine-grained electro-deposits are the result of an internal cold-working mechanism occurring during deposition.

[36] T. Erdey-Gruz, Zeits. f. physik. Chemie A172, 157 (1935).
[37] T. Erdey-Gruz and E. Frankl, Zeits. f. physik. Chemie A178, 266 (1937).