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DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

[illegible], B.A., B.S., M.S.
The Ohio State University
1967

BATTELLE MEMORIAL INSTITUTE
INDUSTRIAL AND SCIENTIFIC RESEARCH
COLUMBUS 1, OHIO

June 20, 1947

Commanding General
Watertown Arsenal
Watertown, Mass.

Attention Laboratory - Dr. P. R. Kosting

Gentlemen:

Enclosed is a copy of a doctoral dissertation covering fundamental work on chromium plating recently completed in the Battelle laboratories. This dissertation work was done while the author, Cloyd A. Snavely, held a Battelle Memorial Institute - Ohio State University Fellowship, and has been accepted by the Graduate School of The Ohio State University.

The program of experimental work on the electrodeposition of chromium, currently being carried out at Battelle under Contract W33-019-ord-6267, is largely based upon the fundamental theory presented in the dissertation. It is hoped that the dissertation will serve as a useful reference in your laboratories.

A copy of the dissertation has also been sent to Dr. [illegible]. Blum, National Bureau of Standards.

Very truly yours,

Charles L Faust
Charles L. Faust

CLF:LBF

Enc.

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THE THEORY FOR THE MECHANISM OF CHROMIUM PLATING: THE THEORY FOR THE PHYSICAL CHARACTERISTICS OF CHROMIUM PLATE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the
Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

BY

CLOYD ARTEN SNAVELY, B.A., B.S., M.S.
The Ohio State University
1947

Approved by:

Adviser

BATTELLE MEMORIAL INSTITUTE

FOREWORD

The work recounted in the following chapters represents the writer's first venture in the field of electroplating. After a sober consideration of the various fields of engineering endeavor open to one with a background training in metallurgy, electroplating was chosen as a field in which much fundamental work is needed, and in which any fundamental work would be directly applicable to practical industrial problems. This project was undertaken as the first step in entering the field with the idea that a lifetime of interesting and profitable work might be found beyond this initial project. Events of the past year have confirmed this idea.

The writer once thought that a considerable opportunity existed in application of the principles and tools of metallurgy to the study of electroplates. After over twelve months intensive work on this fundamental problem, this view is no longer held. It is now believed that the opportunity exists in the application of the principles and tools of science, along with a modicum of logic and a dash of hard work. As the search for facts carries the worker further and further into the fundamentals of any one science, it becomes clear that no dividing line exists between the true sciences, whether metallurgy, physics, chemistry, or other. As regards hard work, this is a matter of mental attitude and need not fatigue the scientist who is working in a field which furnishes exhilarating discoveries at reasonably close intervals to maintain his interest and whet his inquisitiveness. If such discoveries are not forthcoming — well — there are other fields of endeavor.

The present work was undertaken without a concrete plan as to where it would end. The initial aim, to develop a reason for the cracks in chromium plate, proved to be a fortunate choice, as all of the considerations later developed center around this cracking phenomenon. It was recognized at the outset that any contribution to the understanding of the subject would be of value. In fact, from this standpoint, it is believed that the subject has been an ideal one for the purpose. So little has been understood about chromium plate that a serious investigation, using the unsurpassed array of equipment at hand, was bound to turn up a reasonable amount of new information on the subject.

In the opinion of the writer, research at its worst consists of long series of meticulously conducted tests, the results of which are tabulated, plotted, divided, squared, or extrapolated to make them fit into some pattern which can be put forth as the product of the research. Research at its best, on the other hand, consists of the development of theoretical considerations first, then, by use of a limited number of properly directed simple tests, the proof or disproof of the hypothetical tenets. New hypotheses are built upon the results of these tests and, in turn, subjected to experimental scrutiny. It is a matter of personal pride that the present project, while not ideally prosecuted in many respects, has followed the latter course in considerable part. In fact, the chief satisfaction derived from the project is connected with this, rather than with the specific results.

The chapters which follow have been written with the thought that the possible readers might be specially interested in engineering fields other than electroplating. Chapter I is meant to serve as a general introduction to chromium plating. Chapters II and III cover the theoretical and factual developments which are the main product of the project. Chapter IV is an attempt to rationalize the uses of chromium plate in terms of the principles set forth in the preceding chapters. Chapter V is something apart. Here are presented some thoughts which could not be dovetailed into the earlier chapters because they are entirely too speculative, or because they are related to the main subject only by the fancy of the writer. Some of these speculations point to possible researches in which the writer would like to have a hand. Barring this, it is hoped that others will find some of the considerations worthy of thought and possible further development.

The writer wishes to express his gratitude to those responsible for the founding and administration of Battelle Memorial Institute for the sponsorship of this work. They have provided the necessary funds, the necessary equipment, and the necessary "atmosphere" for the prosecution of the project. Special thanks are due certain elements of the "atmosphere": to Dr. J. R. Van Pelt, for administrative supervision, advice, and encouragement of the highest type; to Drs. H. W. Gillett and O. E. Harder for technical criticism of the work as it progressed; to Dr. C. L. Faust, for all of these things, and technical supervision as well; to Dr. C. M. Schwartz, D. A. Vaughan, and J. R. Doig for instruction and help in the use of X-ray equipment, and the interpretation of X-ray results. Apart from the Battelle "atmosphere", Professor D. J. Demorest, the writer's faculty advisor at The Ohio State University, followed the work closely and interjected timely advice when such was needed. In many instances the lack of expressed criticism from these men was of considerable help because this carried with it the implied opinion that the work was proceeding on a theoroticaily sound basis.

In conclusion, the writer would like to express the usual thought of one looking back on a completed research, "I shoulda done it in half the time".

Cloyd A. Snavely

February, 1947
Battelle Memorial Institute
Columbus, Ohio

TABLE OF CONTENTS

Page

CHAPTER I

CHAPTER II

CHAPTER III

TABLE OF CONTENTS (Continued)

Page

CHAPTER IV

CHAPTER V

APPENDIX

AUTOBIOGRAPHY

CHAPTER I

AN INTRODUCTION TO CHROMIUM PLATING

Chromium plating has assumed industrial importance because of the special characteristics of the metal chromium, and of the plated metal chromium. A distinction is made because somewhat different characteristics are observed in chromium plate as compared to chromium produced by pyrometallurgical methods. These differences, in general, are herein ascribed to the fact that chromium may be electrodeposited as an unstable hydride which decomposes to a normal metallic structure with occluded hydrogen.

"Pure" chromium has been described(1) as a soft, fairly ductile metal with a blue-white metallic luster. Chromium plate is ordinarily neither ductile nor soft by the same standards. The chemical properties of "pure" and electroplated chromium are very similar. They are both attacked by the halogen acids, and passivated in the same manner by other, oxidizing, acids. They are alike in their resistance to surface tarnish or discoloration. It is therefore the physical properties of chromium plate, its hardness, ductility, and related properties, which set it aside from "pure" chromium.

As to purity, chromium plate normally contains large quantities of hydrogen, and considerable amounts of chromium oxide. The oxide is probably in a hydrated form. Early searchers for the reasons underlying the special physical properties of chromium plate pounced upon the presence of hydrogen in the plate as indicative of the formation of a hard, brittle hydride. This theory was largely discarded in favor of the view that the hydrogen is occluded within voids in the plate and produces considerable internal stress within the plate. In addition, the fine grain size of bright chromium plate was discovered, and this was related to the hardness of the plate. Other investigators studied the chromium oxide inclusions in the plate. From such studies, they related the physical properties of the plate to the size and distribution of the inclusions.

Though many competent investigators gave attention to the problem, the fact remains that, after three decades of intensive industrial exploitation of the chromium plating process, no coherent theoretical background explanation for the physical properties of chromium has been presented. A similar lack of coherent theory exists as regards the functioning of the various components of the chromium plating bath.

Looking beyond the immediate field of chromium plating, an identical situation exists in the plating field in general. The various electroplating processes are significantly interrelated. Consideration of the chromium plating process has produced factual information which appears equally applicable to other plating processes. Electroplates are very often observed to contain contractile stresses, and, occasionally, seemingly expansile stresses. Electroplates vary greatly in hardness, grain size, and crystal orientation. Certain specific materials added in small amount to plating baths, and described under the general term "brighteners", produce wide variations in the characteristics of plates. The cathodic process is reversible for certain metals while for certain others it is irreversible. Satisfactory explanations for these and many similar phenomena simply have not been advanced. It is often stated that electroplating is currently undergoing the change from an art to a science. Consideration of the type of information available in the field leads to the opinion that a considerable elucidation of background theory is necessary to complete the yet impending metamorphosis.

The considerations presented herein are built around two main principles: 1. The phenomena occurring in the chromium plating bath under different plating conditions appear to be closely related to the hydrogen ion concentration of the diffusion layer, or "cathode film", immediately adjacent to the cathode; 2. The special characteristics of chromium plate may be related to structural changes occurring in the metal during, and after, deposition. A complete chapter is devoted to each of these principles in the later, detailed discussion.

The chromium plating bath in general commercial use consists simply of anhydrous chromic acid dissolved in water with a small amount of added sulfuric acid. The concentration of the solution constituents may be varied over a considerable range with satisfactory results in terms of a bright, relatively smooth, chromium plate. A satisfactory solution might contain 300 g./l. CrO_3 and 3.00 g./l. H_2SO_4. More important than the total concentration of chromic or sulfuric acids in the bath is the weight ratio between these acids. This ratio, termed the "acid ratio" (CrO_3/SO_4), is generally controlled at 80/1, 125/1, or in the general region of these limits. Acid ratios considerably above and below these limits are sometimes used, purposely or inadvertently, but are seldom recommended.

In general, commercial uses for chromium plate have demanded a bright plate above all else. Practically all investigators have been primarily concerned with studying solution phenomena leading to the production of a bright plate. With any given plating solution composition, any number of conditions may be set up which will produce a plate which is not bright. By deliberately selecting solution compositions and plating conditions outside the normal bright ranges, and studying the resulting plates, the effects of the various possible composition and condition changes have been largely determined in the present work.

"Insoluble anodes" composed of antimonial lead are recommended for chromium plating. Pure lead or iron anodes have been used but are less satisfactory because both are less inert than are lead alloy anodes to the chemical environment prevailing in the bath. Iron anodes also seem to lack the desirable properties associated with the lead oxide coatings formed on lead or lead alloy anodes during electrolysis of the chromium plating bath.

The chromium deposited on the cathode is taken directly from the plating bath with no anodic replenishment. Periodic additions of chromic acid to the bath are therefore necessary. The sulphate concentration of the bath is not similarly reduced, the only appreciable losses of this constituent being the amount removed from the bath in the solution film clinging to the plated work. Such losses are referred to as "drag-out" losses. Periodic checks are necessary to keep the acid ratio within desired limits.

Electrolysis of the chromium plating bath produces several results other than the reduction of chromium to the metallic state. Hydrogen is discharged at the cathode and oxygen at the anode. Chromium is also reduced from the hexavalent to the trivalent state at the cathode, and the reverse process occurs at the anode. This partial reduction and reoxidation of chromium appears to have an extremely important function in the plating process. The trivalent chromium has been shown to exist in the plating bath as discrete dispersoid particles of positive charge rather than as simple ions. The bath is thus a colloidal system consisting of a dispersoid in an electrolyte rather than a simple true solution.

The concentration of trivalent chromium in a bath operating under a given set of conditions normally reaches an equilibrium value. At this equilibrium concentration, the partial reduction of chromium at the cathode matches the reoxidation proceeding at the anode. It has been shown$_{(2)}$ that lead or lead alloy anodes establish an equilibrium concentration at a considerably lower value than do iron anodes. This is ascribed to the oxygen overvoltage characteristics of a lead oxide layer which forms on the anodes during electrolysis. The equilibrium concentration of trivalent chromium varies with the relation between the areas of anode and cathode being used. For usual commercial work, the equilibrium concentration is kept as low as possible by making the anode area several times as large as the cathode area.

The trivalent dispersoid particles have been considered undesirable in the bath for several reasons. They reduce the effective ionic concentration of the bath and thus reduce the bath conductivity. In this way the plating tank potential drop is increased with an attendant decrease in electrical efficiency. When the trivalent chromium concentration of a bath exceeds several per cent of the total chromium in the bath, there occurs an appreciable narrowing of the range of current densities producing a bright plate. This is a very undesirable effect, especially if the work being plated is of somewhat complex shape, and therefore does not draw a uniform current density over its surface. In such a case, it is likely that some areas of the work might receive a dull, commercially unsatisfactory plate.

The effect of cathode current density on the character and appearance of the chromium plate is of considerable importance. A current density just sufficiently high to produce a plate gives a light-colored, but milky-appearing plate. A somewhat higher current density produces a bright plate. As the current density is further increased, a value is reached at which dull-white deposits are produced. These high current density, dull deposits are often referred to as "burnt" plates. Above a certain high current density, all plating ceases. The range of current densities producing bright plates is termed the "bright" plating range. The bath temperature has a considerable effect on the bright range. If the temperature is raised, the upper and lower limits of the bright range are both increased and the range is also widened. This relation continues from atmospheric temperatures to a temperature of the order of 60°C. At temperatures near the boiling point of the solution, bright plates cannot be produced regardless of the current density used.

The hardness of chromium plate varies considerably as plating conditions are varied. In general, the conditions producing the brightest plate also produce the hardest plate. Dull plates may be produced with an equivalent Brinell hardness of under 400. Bright plates of equivalent Brinell hardness as high as 700 have been produced.

The physical structure of chromium plate has been studied by numerous investigators(3,4,5,6,7). It has been shown that thin bright plates, of the type ordinarily used for decorative applications, (approximately 0.00002" in thickness) contain scattered pores reaching from the plate surface to the basis metal. Somewhat thicker bright plates are not porous but are cracked, the cracks appearing always to extend in a direction normal to the basis metal. While the decorative plates appear to be ductile to a certain degree, thicker plates of 0.0005" or more in thickness are extremely brittle. Metallographic examinations of cross-sectioned and etched thick plates have revealed that the cracks vary considerably in length and dispersion according to the plating conditions used. In addition, it has been found that the cracks are not voids, but are filled with a chromic oxide (probably hydrated). This enclosed chromic hydroxide has been termed "inclusions" in the plate. The form of these inclusions is such that they constitute cell-like walls around sections of plate, the walls always being perpendicular to the basis metal.

The porosity of thin chromium plate, and the lack of ductility in thicker plates, accounts for the application of deposits of more ductile, corrosion resisting plates such as copper and nickel under chromium plates used for decorative purposes.

The normal atomic structure of chromium which is stable at atmospheric temperature is the body-centered cubic arrangement. An unstable hexagonal form of chromium was first produced by electrodeposition two decades ago(8). The hexagonal form has since been studied to some extent. It has been shown that it spontaneously transforms to the body-centered cubic arrangement during a relatively short period of time.(9, 10) The present work has shown the hexagonal form of chromium to be a hydride of general formula Cr_2H to CrH. When a formula range is stated in this manner hereafter, the existence of a continuous range of formulae between the two limits is implied. In the present case, a composition range is defined between 33 atomic per cent hydrogen and 50 atomic per cent hydrogen.

A third form of electrodeposited chromium, in the face-centered cubic arrangement, has been produced during the present work. This form too, is an unstable hydride, decomposing to the body-centered cubic metallic arrangement spontaneously at atmospheric temperatures. This hydride is of the general formula CrH to CrH_2.

An important feature of these decompositions is the amount of volume shrinkage involved. The specific volume of the hexagonal hydride is decreased by 15.6 per cent in decomposing to the body-centered cubic metallic arrangement. A slightly greater shrinkage occurs during a shift from the face-centered cubic hydride to the body-centered cubic form. This information is calculated from X-ray data.

In these decompositions, and in the solution phenomena producing the unstable hydrides, lie the solution to the special characteristics of chromium plate. Here also is provided a clue to the reasons for the special characteristics of other plates such as iron and nickel, an insight into the mechanism of stress raising in any electroplate, and an initial element of factual evidence supporting an established hypothesis for the true cause of "metal overvoltage".

The information presented thus far has been in the nature of background material to prepare the reader for the detailed, argumentative chapters to follow. It is to be emphasized that while the theoretical aspects of chromium plating, or of most other plating processes, are not well developed in the published literature, a wealth of practical and empirical literature exists in the field. Such a background of information is an almost indispensable aid in the development of a comprehensive theory for a process. Indeed, a fitting test for a new theory often consists of trying it to explain all existing empirical data related to it in any way.

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CHAPTER II

THE CHEMISTRY OF THE CHROMIUM PLATING PROCESS

A complex process such as chromium plating is often difficult to discuss logically by reason of the interrelation of the various factors which contribute to the characteristics of the end product of the process. Operating conditions of bath temperature and current density, along with bath concentration in terms of total chromic acid, trivalent chromium, sulphate ion, hydrogen ion, and "foreign" ions (Fe^{+++}, Al^{+++}, etc.,) are the interrelated variables which are to be considered in this chapter. Other related problems involve the character and function of the bath constituents as they exist during the plating process.

It is usual to present a review of previous work, then an account of experiments conducted, and finally a discussion of the experiments which ends in the propounding of a theory. In this case, it is believed that such a presentation would lead to much back thumbing and general confusion. Therefore, a complete review of the theory of the chromium plating process as developed in the present project will be presented first. Following this, experiments in support of the theory will be recounted and discussed. The work of previous investigators will be mentioned and discussed wherever appropriate, rather than in a separate section.

The Theory of the Chromium Plating Process

It is believed that the reduction of chromium ions is actually accomplished by hydrogen atoms rather than by direct electron transfer from cathode to chromium ion. Such reduction requires a cathode film pH within certain pH limits, and a sufficient supply of atomic hydrogen. Fortunately, the factors governing the pH of the cathode film and the supply of atomic hydrogen operate to satisfy both of these conditions for plating at the same time.

The hydrogen gas produced at the cathode during many electrolytic processes originates in the water in the electrolyzed bath. The water is dissociated into hydrogen ions and hydroxyl ions. The positively charged hydrogen ions (or hydronium ions, if such a concept is preferred) are attracted to the cathode (negatively charged electrode) and migrate through the bath to the cathode. Upon reaching the cathode the hydrogen ions receive an electron and become hydrogen atoms. As hydrogen atoms are very active, they do not long remain as such in the bath. Several distinct paths of action are possible. When the cathode material is capable of receiving solute hydrogen, a portion of the atomic hydrogen generated at the cathode surface will enter the cathode by diffusion. This accounts for but a very small portion of the hydrogen generated in chromium plating. A second possibility is that two hydrogen atoms will come in contact near the cathode and form a hydrogen molecule. Such molecules are relatively inert at ordinary temperatures and tend to join together to form gas bubbles which escape near the cathode at the bath surface. This process accounts for a major portion of the hydrogen generated in chromium plating. The third possibility is that hydrogen atoms will meet positive ions or complex forms and reduce them by transferring electrons to them. The result of such electron transfer is that the positive ion is reduced to a lower oxidation state and the hydrogen atoms are "oxidized" to hydrogen ions. Such hydrogen ions may then be in the same state as when first attracted to the cathode, may be combined with negative ions wrested from the reduced material (such as hydroxyl ions) or may become a part of complex particles formed by some of the partially reduced ions. A considerable portion of the atomic hydrogen produced in the chromium plating process follows such paths.

When hydrogen ions are discharged at a cathode, the previously existing equilibrium between hydrogen ions and hydroxyl ions is upset. The hydrogen ion concentration in the vicinity of the cathode is lowered, and the hydroxyl ion concentration therefore increases to reestablish the equilibrium for the dissociation of water. This process may be considered from several viewpoints but all will agree that the net effect is an increase in the pH of the cathode film (diffusion film surrounding the cathode). Thus, the effect of hydrogen discharge at the cathode is, first, to produce a cathode film containing highly reducing atomic hydrogen, and, second, to raise the cathode film pH above that of the solution proper.

The concentration of both atomic hydrogen and hydroxyl ion in the cathode film may be increased by impeding diffusion within the cathode film and the solution proper. Such a role is assumed by the trivalent chromium in the chromium plating bath. Some of the hexavalent chromium in a new chromic acid plating bath is cathodically reduced as soon as electrolysis of the bath begins, providing the cell potential is above a certain minimum. This minimum potential is slightly below the bubble potential of the cathode. The bubble potential of a solution is defined as the lowest potential at which a visible evolution of gas occurs. Such reduction is incomplete as it apparently stops at the trivalent (chromic) stage. It is entirely possible that the divalent (chromous) stage is reached and that this divalent chromium then reacts with hexavalent chromium to form trivalent chromium from both the higher and lower valence forms. At any rate, trivalent chromium is produced in considerable quantities in the vicinity of the cathode. This trivalent chromium forms a complex basic oxide particle which exists in the plating bath as a dispersoid. The bath is thus a colloidal system. The dispersoid is electropositively charged and is attracted to the cathode.

The dispersoid increases the viscosity of the cathode film and thus impedes diffusion with and into that film. In this way, hydrogen atoms may exist for a longer time in the film without contacting other hydrogen atoms with which they may combine. Similarly, the migration speed and/or diffusion rate of hydrogen ions moving into the cathode area from the solution proper is decreased. Further, the effective cross-sectional area through which hydrogen ions may move to the cathode is reduced by the dispersoid particles which may be compared to a semipermeable membrane around the cathode. Identical considerations apply to the migration or diffusion of hydroxyl ions away from the cathode. This phenomenon is considered of lesser importance than the hydrogen ion transfer because of the greater transport number of the hydrogen ion.

The pH of the cathode film may not only be increased by the dispersoid, it may also be controlled within certain limits by the dispersoid. If the rate of removal of hydrogen ions (i.e.,current density), and the other relevant conditions are such that the cathode film pH is increased to a value exceeding the isoelectric point of the dispersoid, then the dispersoid is repulsed by the cathode and moves away from it. This, in effect, destroys the semipermeable membrane about the cathode and allows free access of hydrogen ions to the cathode area. The film pH is soon lowered and the membrane again closes in. Thus, by a sort of dynamic equilibrium mechanism, the pH of the cathode film is controlled near the dispersoid's isoelectric point.

Other factors also exert an influence on the cathode film pH. An increase in chromic acid concentration increases the viscosity of the entire plating bath and therefore favors an increase in cathode film pH by lowering diffusion rates. A decrease of bath temperature has the same effect. An increase in the amount of trivalent dispersoid in the bath also increases the over-all viscosity of the bath. An increase in current density increases the rate of removal of hydrogen ions. This explains the interdependency of temperature and current density in chromium plating. If the temperature of the bath is changed appreciably, a proportionate change in current density is necessary to maintain the cathode film pH within proper limits. The trivalent chromium dispersoid membrane can only control the film pH to a certain extent, and the other factors of bath temperature, current density, total trivalent chromium concentration, and total chromic acid concentration must be maintained within certain related limits in order to obtain chromium plates.

Another important factor in the functioning of the dispersoid membrane remains to be discussed. This is the action of the sulphate ion. The main effect of the sulphate ion in the chromium plating bath is to reduce the isoelectric point of the trivalent chromium dispersoid. This, in turn, causes the dispersoid to control the cathode film pH at a lower value. The dispersoid particles strongly adsorb the sulphate ion. This explains why so small a concentration of sulphate can have such an important effect on the functioning of the bath. It also explains why an increase in sulphate concentration serves to counteract the effect of too great a trivalent chromium concentration in the bath.

Certain "foreign" ions which are sometimes added to the chromium plating bath similarly affect the isoelectric point of the dispersoid. Among these are Fe^{+++} and Al^{+++}. Appreciable additions of these elements to the chromium plating bath cause the dispersoid to control the cathode film pH in the lower portion of the plating range. This produces a milky-appearing, relatively unstressed plate. The physical characteristics of such plates are dealt with in the next chapter. It is believed that the iron or aluminum ions are taken into the trivalent chromium dispersoid and thus change its properties somewhat in the direction of lower isoelectric point.

The reduction of chromium to the purely metallic state (body-centered cubic lattice arrangement) occurs only within a very narrow cathode film pH range which is at the very bottom of the larger pH range within which plates are produced. At an intermediate film pH, the hexagonal close-packed hydride is produced. At high film pH values, the face-centered cubic hydride is produced. Between these ranges of pH values, mixtures of the various plate structures are produced. Figure 1 illustrates this relation of film pH to plate structure schematically. The actual pH values which should be assigned to the various points on the figure are not known. It is estimated that they range between values of 1 to 6.

The reduction of chromic acid is entirely a stepwise process since it is accomplished by single electron transfer. The first steps, from the hexavalent to the trivalent stage, may occur through a chromic/chromous couple as illustrated by the equation:

$$Cr^{+6} + 3Cr^{+2} \longrightarrow 4Cr^{+3}.$$

It is believed that trivalent chromium is reduced to the chromous state

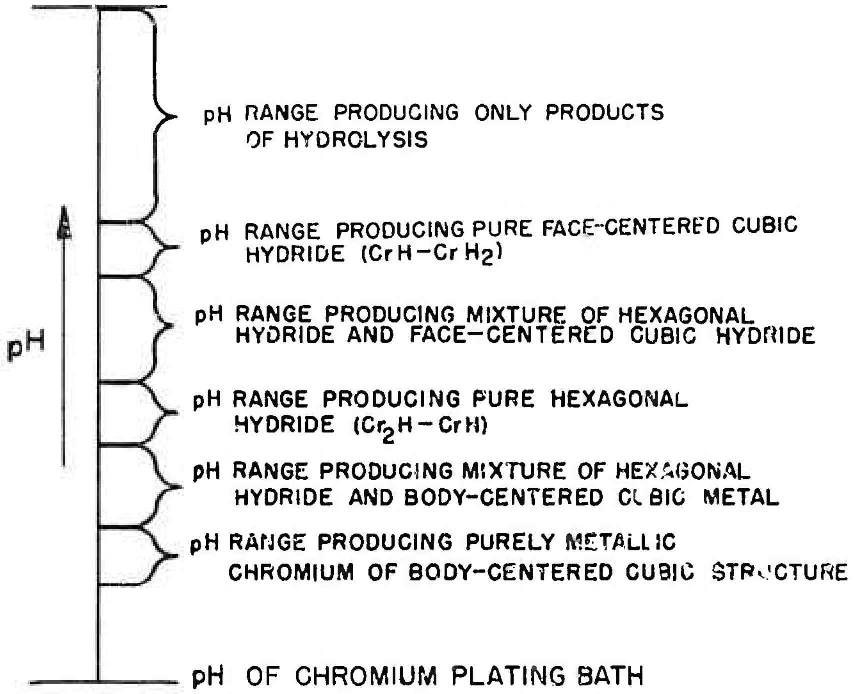

FIG. 1 — SCHEMATIC REPRESENTATION OF RELATION BETWEEN CATHODE-FILM p^H AND THE STRUCTURE OF THE PLATE PRODUCED IN THE CHROMIUM PLATING PROCESS (ACTUAL p^H VALUES OF ALL POINTS EXCEPT BOTTOM OF SCALE ARE UNKNOWN)

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within the cathode film by atomic hydrogen. If any of this chromous chromium (probably existing as a hydroxide at the environmental pH) escapes to the outskirts of the film, it has the opportunity to reduce hexavalent chromium. Since the chromous hydroxide is thought to exist as positively charged particles, such escape would appear unlikely if it were not for the extreme agitation effect of the molecular hydrogen gas escaping from the cathode film in bubble form. Such agitation is believed sufficient to carry a considerable portion of the chromous chromium formed at the cathode to the outside of the cathode film where it may contact hexavalent chromium.

The mechanism of reduction of chromous to metallic chromium is believed to be through an intermediate hydride stage. If the pH of the cathode film is relatively low, hydrogen atoms reduce the chromous ions and combine with the hydroxyl ions wrested from the chromium. Any hydrides formed are unstable to the extent that they break up when the chromium atom assumes its proper position in the body-centered cubic lattice of the plate. If the pH of the cathode film is of intermediate value, hydrides of general formula M_2H to MH are formed. These hydrides persist during crystallization of the plate and the resultant structure is the hexagonal close-packed hydride of chromium. When the cathode film pH is high (relatively), hydrides of general formula MH to MH_2 are formed and crystallize as the face-centered cubic hydride of chromium.

The theory ends here. No explanation of the basic reasons for the apparent relation between film pH and the type of plate produced, hydride or otherwise, has yet been developed. Factual evidence in support of the theory as given above will now be presented.

Experiments in the Electrolysis of Chromic Acid

Consider an experiment in which a small portion of chromic acid solution (250 g./l. reagent grade CrO_3 in H_2O) is placed in a small beaker and a strip of lead sheet (an anode) is hung in the solution along one side of the beaker. Along the opposite side of the beaker is hung a length of copper wire. After some time the surface of the portion of the wire immersed in the solution will be observed to be brightened. This brightening is ascribed to chemical attack on the wire by the chromic acid. The outer layer of the wire is dissolved, exposing a new, clean metal surface.

If the wire is now made cathodic to the lead anode through an external source of potential, a small amount of electrical current passes through the solution. As the cell potential is raised, the cell current gradually increases. At a cell potential of the order of 1.9 volts, a dark layer is observed to be forming on the cathode surface. This layer, or film, appears to increase in thickness for a short time, then may be seen falling away from the cathode toward the bottom of the beaker as a series of dark, cloud-like, formations. Although these dark formations appear always to be falling to the bottom of the beaker, no appreciable dark layer builds up on the bottom. In some manner the material is dispersed through the solution, as shown by the gradual darkening and loss of transparency in the entire solution. Periodic analysis of the darkened solution shows that the trivalent chromium concentration is steadily increasing. It is concluded that the dark material is the trivalent chromium dispersoid which is produced by cathodic reduction from the hexavalent state.

As the cell potential is further increased, a point is reached at which hydrogen gas bubbles begin to form on the cathode. These bubbles slowly grow in size, finally detach themselves from the cathode, and rise to the solution surface where they burst. In this fashion, a large portion of the atomic hydrogen produced at the cathode escapes from the solution without performing any useful service. A somewhat smaller portion is known to penetrate into the cathode in the atomic form. The evolution of hydrogen continues for a time, then rather abruptly stops. The cell amperage, which had considerably decreased when hydrogen evolution began, goes back to a higher value when hydrogen evolution stops. The cell voltage decreases considerably. After a short period, the evolution of hydrogen begins again, the cell amperage again is reduced in value, and the cell potential is increased accordingly. The non-gassing period is soon repeated, however. This periodic phenomenon goes on for some time. The upper and lower limits of cell voltage gradually approach a common midpoint, and the frequency of the cycles is increased. Finally, equilibrium is reached at an intermediate cell voltage and the evolution of hydrogen proceeds at an intermediate rate, but continuously. This type of periodic performance has been studied by various investigators. The conclusion appears to be that a continuous film of some sort tends to form on the cathode, then breaks. The nature of the film is a matter of considerable speculation. This will be discussed in more detail in a later chapter. The existence of a surface film on the cathode which has reached equilibrium after a number of periodic cycles can be substantiated by a few simple tests. Such a cathode may be removed from the solution, allowed to dry, and exposed to the air for 24 hours. When reintroduced into the solution, it will still exhibit equilibrium characteristics. However, if it is now wiped briskly with a dry towel, and reintroduced into the solution, the periodic performance again may be produced. Thus, the existence of a fairly stable, but easily abraded, film is established. Identical results are obtained when an iron cathode is substituted for the copper cathode in this apparatus.

If the cell potential is raised to just above the potential range producing the periodic phenomenon, either while the periodicity is occurring or with a fresh cathode which has not undergone the periodic performance, the evolution of hydrogen at the cathode is continuous, and the cathode is brightened. This brightening occurs more rapidly than that occurring when no current is flowing. It is believed that the atomic hydrogen released at the wire cathode surface quickly reduces any metal oxides or other compounds present, thus brightening the surface almost instantaneously. No metal deposits are produced at this cell potential or below it. In fact, the metal appears to suffer extremely rapid attack from the plating solution at this potential. Regardless of statements in the literature that deposits should be produced at or below the potential at which gas evolution begins, the fact remains that no deposits are obtained.

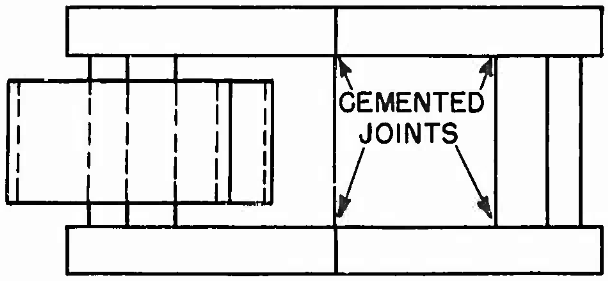
A further increase in cell potential does produce a metal deposit in addition to more rapid gas evolution. The first deposit is thin and gray appearing. Attempts to build it to greater thickness by prolonged electrolysis only serve to cover it with a black coating. This black coating has been described as an oxide or hydroxide. The present work indicated that it is the face-centered cubic hydride. Further increases in cell potential produce plates in which only the black hydride is visible.

Addition of sufficient H_2SO_4 to the solution to bring the acid ratio (CrO_3/SO_4) to 100/1 produces different results. The periodic performance is repeated at approximately the same cell potential as before, and a similar range of potential exists within which hydrogen is evolved and no metal deposition occurs. However, when the potential is raised to the point at which metal deposition does occur, the deposition continues uninterrupted, and thick deposits may be produced. As mentioned in the previous chapter, dull, bright, and again dull deposits are produced as the cell potential is successively raised. The sulfate ion thus has an extremely important effect in the chromium plating solution.

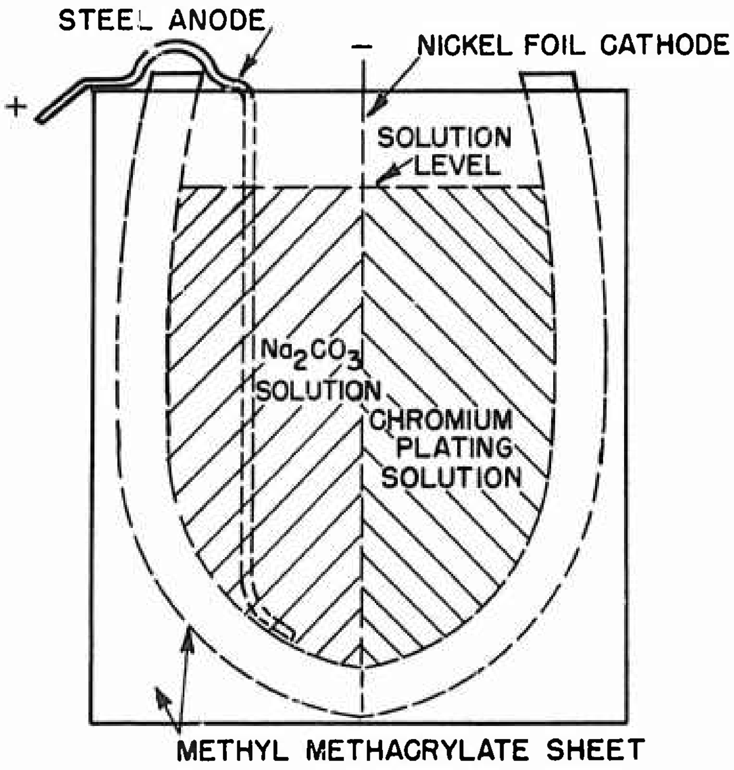
When a new plating solution is prepared, it is reddish-brown colored and reasonably transparent, so that things occurring at anodes and cathodes hung in the solution may be observed. After a short period of use, however, the solution becomes darker and opaque so that objects within the bath cannot be seen. This opacity is caused by the trivalent chromium dispersoid particles produced in the bath. While these particles are sufficiently small to be difficult, or impossible, to detect with the ultramicroscope, they are sufficiently large to interrupt the passage of light through the solution. As previously mentioned, the dispersoid particles are electropositively charged. Their electric charge and the Brownian movement evidently serves to keep them widely dispersed in the bath. The fact that these dispersoid particles appear in the chromium plating bath in appreciable concentration very soon after plating begins, indicates that their concentration near the place of their origin, the cathode surface, must be considerable at the very beginning of metal deposition. Kasper(1) made a detailed study of these dispersoid particles and of their behavior under various conditions. The present knowledge of the character and composition of the dispersoid particles is, for the most part, a result of that study.

The Reduction of Chromic Acid by Atomic Hydrogen

A Lucite cell was constructed, then sawed in two equal parts. The parts were then cemented back together with a nickel foil membrane placed at the cement joint. Thus, the cell was divided into two compartments by the nickel foil. The foil consisted of electrolytic nickel, 0.0012" thick. A steel strip was placed in one compartment near the end of the cell. This compartment was filled to within a half inch of the top with a 30 g./l. Na_2CO_3 solution. The opposite compartment was filled to the same level with unused chromium plating solution (300 g./l. reagent grade CrO_3, 3 g./l. H_2SO_4). The volume of solution in each compartment was then approximately 17 cc. The foil area in contact with the solutions was approximately $1\frac{1}{2}$ sq. in. on each side. Figure 2 illustrates the cell setup. The steel strip in the sodium carbonate solution compartment was made anodic and the nickel foil cathodic. The cell amperage was controlled so that the cathode current density was in the range between 0.75 and 1.0 amps./sq. in. This produced a rapid evolution of gaseous hydrogen at the foil cathode and of oxygen at the steel anode. The current also produced a considerable heating effect in the electrolyzed compartment. After about an hour, the temperature held steady at 60°C. A color change in the chromic acid solution was noted soon after the experiment was begun. The solution gradually darkened and, after an hour, was as coffee colored and opaque as a used plating solution. The electrolysis was continued for eight hours. The chromic acid solution was then pipetted from the cell and analyzed for trivalent chromium.



TOP VIEW



SIDE VIEW

FIG. 2—CELL USED TO SUPPLY ATOMIC HYDROGEN TO CHROMIUM PLATING SOLUTION

47389

Ten and nine-tenths per cent of the total chromium in the bath was in the trivalent state. Only a negligible amount of trivalent chromium existed in the solution initially put into the cell.

This experiment is presented as proof of the fact that chromium can be reduced from the hexavalent to trivalent state by atomic hydrogen. The only reducing agent present in the chromic acid compartment was atomic hydrogen which diffused through the nickel foil to reduce the chromic acid at the foil-chromic acid solution interface. Whether or not the chromium was reduced to the divalent state, then reoxidized to the trivalent state by the chromic/chromous couple mechanism is an unanswered question. The pH at the foil solution interface must be even lower than that of the solution proper because of the hydrogen atoms diffusing through the foil and being changed to hydrogen ions when they relinquish electrons to chromium ions. Under such acid conditions, it is doubtful that chromous ions could exist for any appreciable length of time.

The Production of the Hexagonal Hydride of Chromium

Several authors$_{(2,3)}$ defined conditions under which a hexagonal (sic) form of chromium was produced. They did not realize that the hexagonal form was other than a pure metal. In both cases, the chromium bath was reduced by an addition of sugar or other reducing agents so that the trivalent chromium concentration of the bath was much higher than ever used in commercial operations. In the one case$_{(2)}$, a bath formula was given involving the addition of 10 g./l. of cane sugar to a 600 g./l. chromic acid solution with an acid ratio (CrO_3/SO_4) of 163/1. By following these instructions for bath preparation, it has been found that approximately 12 per cent of the chromium in the bath is reduced to the trivalent state. Electrolysis of this bath at a temperature of 18°C. and at a current density of 1.3 amps./sq. in. was recommended to produce the hexagonal structure. In the other case(3), the condition established for the production of hexagonal (?) chromium was the presence of over 18 per cent of the bath chromium in the trivalent state. In this case, the acid ratio (CrO_3/SO_4) was 47/1. The current density used was 0.7 amp./sq. in. and the bath temperature was 16°C. It is noteworthy that in both cases the bath temperature was kept low. The difference in total chromic acid, sulphate additions and per cent of reduced chromium in the baths is also significant.

A bath was prepared containing 251 g./l. CrO_3 with an acid ratio of approximately 100/1. Sugar was added until 24.6 per cent of the bath chromium was reduced to the trivalent state. The bath was cooled to various temperatures below 10°C. and plates were produced at various current densities. The samples so produced were X-rayed soon after plating. The data obtained are given in Chart I, (Bath No. 2). The hexagonal hydride of chromium was produced from this bath, but extreme difficulty was experienced in trying to obtain thick plates considered suitable for metallographic studies. In most cases, the plates obtained on continued electrolysis were dark and covered with a black layer. Bright plates were obtainable in thin layers only, as produced by a few minutes electrolysis.

Metallographic examination of some hexagonal plates prepared from this bath revealed discrete crystal forms oriented with respect to the basis metal. Apparently the C-axis of each of the crystals was perpendicular to the basis metal. The basal planes at the plate surface were bounded at the corners by many 60° and 120° angles, as shown in a photomicrograph of a typical sample (Figure 3). This sample was heated to

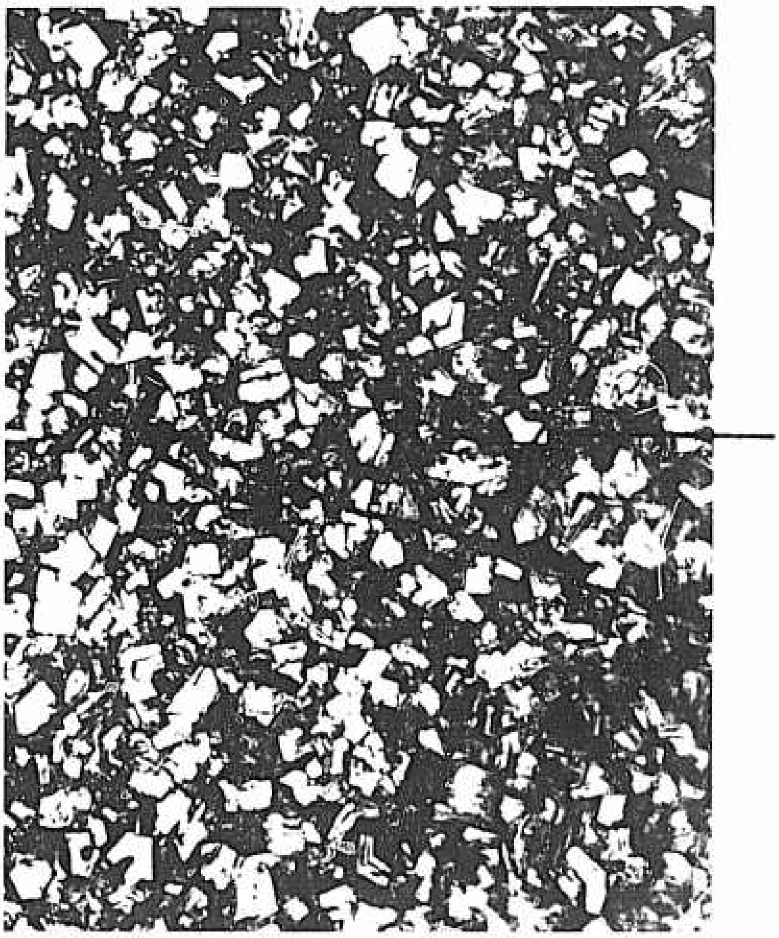
CHART I

Bath No.	Total Cr as CrO_3	Total Cr as Cr	Cr^{+6}	Cr^{+3}	% Cr^{+3}	SO_4	Acid Ratio $\left(\frac{CrO_3}{SO_4}\right)$	Comments
1	359	-	-	-	-	3.6	$\frac{100}{1}$	Conventional chromium plating bath. A definite increase in hardness of plate with increase in thickness of plate was noted. Bath temperature 50°C.
2	251	130	98	32	24.8	$\cong 2.5$	$\cong \frac{100}{1}$	Narrow bright range at approximately 0.12 amps./sq. in. for short plating cycles. Longer plating times at this C.D. produced grayish hexagonal plate. T = 0°C. to 10°C.
3	289	151	108	43	25.9	2.34	$\frac{123}{1}$	Narrow bright current density range at approximately 0.1 amp./sq. in. No hexagonal deposits obtained. T = 20°C. ± 2°
4	276	144	107	37	25.8	5.05	$\frac{50}{1}$	Narrow bright range between 0.2 and 0.25 amps./sq. in. No hexagonal deposits obtained. T = 20°C. ± 2°
5	256	134	92	42	31.2	4.02	$\frac{64}{1}$	Bright range from 0.15 to 0.25 amps./sq. in. No hexagonal deposits obtained. T = 20°C. ± 2°
6	256	133	111	22	16.5	4.81	$\frac{53}{1}$	No bright range found. Gray plates with scattered bright areas produced. No hexagonal deposits. T = 20°C. ± 2°

CHART I (Continued)

Bath No.	Total Cr as CrO_3	Total Cr as Cr	Cr^{+6}	Cr^{+3}	% Cr^{+3}	SO_4	Acid Ratio $\left(\frac{CrO_3}{SO_4}\right)$	Comments
7	570	296	272	24	8.1	5.90	$\frac{97}{1}$	Clear white plates in current density range from 0.1 to 0.4 amps./sq. in. No hexagonal plates obtained. T = 0°C. to 20°C.
8	575	300	256	44	14.5	5.86	$\frac{98}{1}$	Gray-white deposits obtained at high current densities of 1.5 to 7 amps./sq. in. Bright deposit obtained at 0.5 amps./sq. in. Gray plates peeled leaving bright, thin layer of plate on the basis metal. T = 5°C. to 10°C.
9	631	318	239	79	24.7	6.00	$\frac{105}{1}$	Bright range between 0.1 and 0.6 amps./sq. in. for plating times 10 minutes. Long time plate at 0.2 amp./sq. in. gave gray-white plate. Higher current densities produced brown film on gray plate. T = 5°C. to 10°C.
10	587	305	281	24	7.9	3.00	$\frac{196}{1}$	Very white plates at current densities from 0.3 to 0.6 amps./sq. in. All plates produced at temperatures below 12°C. were completely hexagonal. T = 0°C. to 34°C.

Note: T given for each bath indicates temperature or temperature range investigated.



Unetched Surface 49457 1000X

Figure 3. Surface of chromium plate produced as hexagonal hydride of large crystal size. Photographed after heating in oven at 150°C. for 45 minutes. This decomposed the hydride and caused formation of the cracks visible in the photograph. Note crack through crystal indicated by arrow. Note also 60° and 120° angles in boundaries of many of the crystals. The structure was body-centered cubic as photographed and the observed crystals represent pseudomorphs of the prior hexagonal structure.

150°C. for 45 minutes in an air oven to complete the transformation to the body-centered cubic form. Cracks visible in the crystal faces are the result of the shrinkage attendant to the decomposition of the hydride. The hexagonal forms remain as pseudomorphs regardless of body-centered cubic structure existing when photographed.

Other samples produced from this bath were more finely crystalline. Electrolysis for twelve or more hours under carefully controlled conditions was necessary to produce large crystals of perfect orientation.

A number of variations of total chromic acid, trivalent chromium, and sulfate ion in the bath were then used in an attempt to obtain more satisfactory hexagonal chromium deposits. The data obtained are summarized in Chart I (Bath Nos. 3 to 10, inclusive). As annotated, a number of the baths were operated at temperatures near 20°C. It was hoped to obtain hexagonal plates at such temperatures and relieve experimental difficulties experienced in maintaining baths at lower temperatures for long plating periods.

A bath (No. 10 of Chart I) was prepared containing 587 g./l. CrO_3 (600 g./l. intended) and sulphate to give an acid ratio 196/1 (200/1 intended). Sugar was added in the amount of 10 g./l. This reduced about 12 per cent of the bath chromium to the trivalent state. This bath was similar to Bath No. 2 in that cooling to 12°C. or below was necessary to be sure of producing a hexagonal structure. Higher temperatures produced mixtures of hexagonal and body-centered cubic structures as before. The type of structures produced at a given temperature below 12°C. was found to be somewhat dependent on the current density. Low current density produced some body-centered cubic chromium in an otherwise hexagonal plate, even when all other conditions favored the hexagonal structure. When the current density was increased, a purely hexagonal plate was produced. These plates were white, could be built to any desired thickness at good plating speed, and were satisfactory in every way for study. After a number of samples had been plated from this bath, the Cr^{+3} content had been reduced to 7.9 per cent of the total Cr content as noted in the chart.

In all of these cases, the surfaces of the plates, which were from one to several thousandths of an inch in thickness, were X-rayed on an X-ray spectrometer to determine the structure present. The X-raying was done within an hour after plating in each case, as the hexagonal hydride is liable to decompose spontaneously to the body-centered cubic metal form within a relatively short time after plating. The first layer of plate to be deposited was studied in several samples by dissolving off the brass basis metal slug with nitric acid and X-raying the surface of the plate formerly in contact with the basis metal. In all cases, this rear surface of the plate was found to be body-centered cubic even though the front surface was hexagonal. Samples were then produced under the identical conditions of bath composition, temperature, and current density, producing a hexagonal plate on continued plating. The plating was interrupted after three minutes and the samples X-rayed as soon as possible. This involved a period of approximately 30 minutes till the X-ray work was completed. The plate so produced was entirely body-centered cubic. This led to the conclusion that the plates produced at low pH, before the cathode film has reached an equilibrium at a higher pH value, are always body-centered cubic in structure.

At this point, it would seem that hexagonal plates are favored by an increase in chromic acid concentration, an increase in trivalent chromium concentration within limits, a decrease in bath temperature, an increase in current density, and a decrease in sulphate concentration. Of these, the changes in chromic acid concentration, trivalent chromium concentration, and temperature, may be interpreted as favoring a high cathode film pH by increasing the viscosity of the plating bath and impeding diffusion. An increase in current density may be interpreted as favoring an increased cathode film pH by removing hydrogen ions from the film at an increased rate. The effect of the sulphate is not so easily interpreted in physical terms. It is only possible to say that a decrease in sulphate ion concentration has the same effect as factors tending to increase the bath viscosity. It is not at once apparent that the presence or absence of a small addition of sulphate ion in the bath could have any appreciable effect on the bath viscosity. Therefore this possibility is laid aside.

Some viscosity measurements were conducted on chromic acid solutions to supply definite information on this score. These data were used to plot the curve shown in Figure 4. Although three points are considered insufficient to use for plotting a curve with any degree of accuracy, a curve has been drawn with the limitations of the data in mind. The most concentrated of the solutions was partially reduced by an addition of cane sugar. After several days, 8.8 per cent of the chromium in the solution was reduced to the trivalent state. Some evaporation had occurred. The solution was carefully diluted back to the original total chromium concentration. The viscosity of the reduced solution was then measured and found to be considerably increased over the viscosity of the same solution before the reduction occurred. The results of these measurements are also indicated in Figure 4.

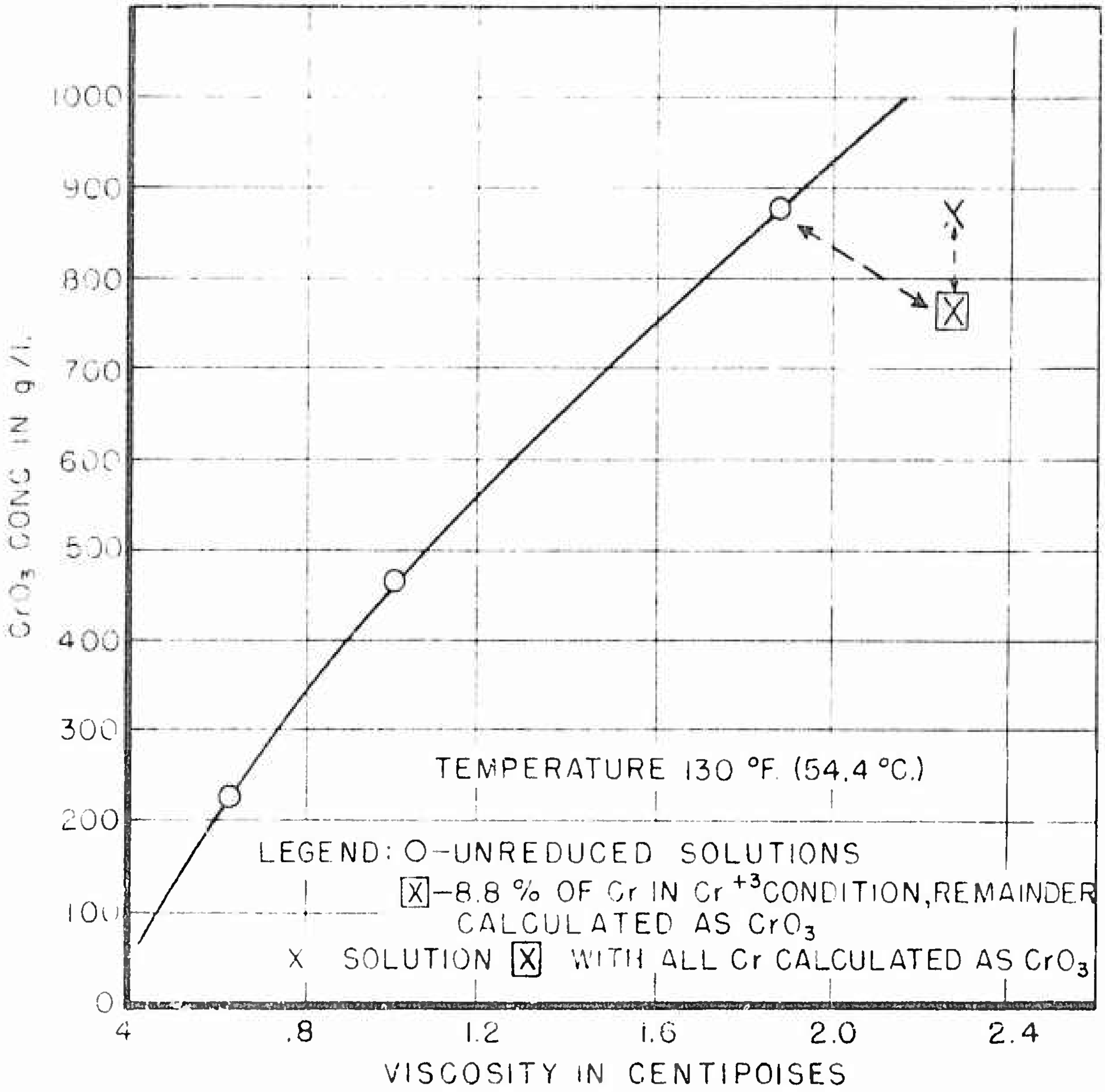


FIG. 4 – VISCOSITY OF AQUEOUS CHROMIC ACID SOLUTIONS

0-4540

Another experiment was conducted in which a 250 g./l. solution of commercial chromic acid was electrolyzed at temperatures between 4° and 8°C. Since the sulphate present in the commercial acid as impurity was just under 0.1 per cent, the acid ratio in this bath was approximately 1000/1. The current density was held between 0.4 and 0.6 amp./sq. in. The plate produced was dark and rough. X-rayed nine hours after removal from the bath, it was found to be composed of a mixture of hexagonal- and body-centered cubic structures with the hexagonal probably predominating (as deduced from the relative strengths of the lines on the X-ray pattern).

This experiment confirmed the opinion that trivalent chromium and sulphate ion in the bath have opposite effects. A bath containing a normal (for bright commercial plating) sulphate ion concentration will produce a hexagonal plate only when the trivalent chromium content is high. If the sulphate content is lowered, the trivalent chromium content may also be lowered and the hexagonal plate still obtained.

The Production of the Face-Centered Cubic Hydride of Chromium

A solution containing 911 g./l. CrO_3 with a 300/1 acid ratio was prepared. Ten g./l. of sugar was added to this bath. Approximately five per cent of the chromium was thus reduced to the trivalent state. Samples plated from this bath at temperatures below 5°C. and at current densities of approximately 0.8 amp./sq. in. produced an X-ray spectrometer pattern different than either the hexagonal- or body-centered cubic forms. After a 17-hour interval, an X-ray pattern was obtained containing the lines of body-centered cubic chromium in addition to the unidentified lines. It became evident that the plate was changing to the body-centered cubic form. The previously unidentified lines were found to be those of a face-centered cubic structure with a lattice parameter (a_o) of 3.84 A. It was concluded that a second unstable structure of chromium had been produced in addition to the hexagonal form. The information leading to the conclusion that this and the hexagonal structure are both hydrides will be discussed in the next chapter.

Reinspection of the X-ray patterns for all the hexagonal samples X-rayed previously revealed that many of these contained the first strong line of the face-centered cubic pattern. Failure of additional lines of this pattern to appear, and the proximity of the line obtained to a possible line of the hexagonal pattern, had caused a failure to interpret these X-ray patterns properly in the first analysis. Indications of face-centered cubic structure in addition to the hexagonal structure were thus identified in some plates from Bath No. 2 of Chart I, and in the plate from the 250 g./1. solution of commercial chromic acid with no sulphate addition (1000/1 acid ratio bath). The plates from the latter bath contained body-centered cubic chromium as well as the two hydride forms. Consideration of these facts leads to the conclusion that the conditions producing the face-centered cubic plate are simply more extreme cases of the conditions producing the hexagonal plate. In other words, a cathode film of elevated pH produces a hexagonal plate and a cathode film of more elevated pH produces a face-centered cubic plate.

A bath prepared with 1021 g./1. CrO_3, and with an acid ratio of approximately 300/1 was reduced with sugar in the amount of 20 g./1. Seven and four-tenths per cent of the bath chromium was thus reduced to the trivalent state. Samples plated from this bath were entirely face-centered cubic and had a smoother, more lustrous, surface than previous face-centered cubic plates. The color was still black, however. These plate surfaces were extremely scratch resistant. These plates were comparatively stable structurally and were held for approximately a week at laboratory temperature before any evidence of decomposition of the hydride was detectable by X-ray tests. The performance of this bath further bears out the idea that a high cathode film pH favors a face-centered cubic structure — and the higher the pH the more stable the structure.

Factual information which led to the construction of Figure 1 has now been presented.

Experiments Concerning the Effect of Sulphate

Kasper(1) proposed a theory for the action of sulphate in the chromium plating bath which involved a reduction of the electrophoretic velocity of the trivalent dispersoid and a coagulating effect on the dispersoid collected at the cathode. He made extensive studies of the character of the dispersoid and much of the present knowledge concerning this material is based on his work. He showed experimentally that the isoelectric point of the dispersoid is about 6(pH of 6) when no sulphate exists in its environment. He also showed that the electrophoretic velocity of the dispersoid is considerably reduced by small amounts of sulphate ion. A perusal of the literature on colloidal systems indicates that when the electrophoretic velocity of a positively charged dispersoid is reduced, the isoelectric point of the dispersoid is reduced at the same time(4). If such reasoning is applied to the sulphate-trivalent chromium dispersoid relation, the concept of cathode film pH control by the dispersoid operating at its isoelectric point is the logical result.

In the experiments thus far described, the acid ratio was fixed at or between the limits of 49/1 and 1000/1. An acid ratio of 20/1 was selected as a proper extreme in the direction of high sulphate concentration. A 250 g./l. CrO_3 bath was prepared and the sulphate concentration adjusted to 12.5 g./l. Plates produced from this bath at atmospheric temperature and below were found to peel. The peeling was not from the basis metal, however. A thin chromium plate always remained on the basis metal. The overlying plate peeled from this initial layer. The plates were always entirely body-centered cubic, bright to dull-white, and extremely hard. Plates produced at temperatures above atmospheric showed less tendency to peel.

It appears that the effect of sulphate concentration of the bath on the type of deposits is just as specific as the effect of current density, of trivalent chromium concentration, or of total chromic acid concentration. Baths low in sulphate ion concentration produced comparatively stable hydrides when electrolyzed under proper conditions. Baths high in sulphate concentration produced extremely unstable hydrides when electrolyzed under similar conditions.

Cross-sectioned, polished, and etched samples of plate produced from the baths of various sulphate ion concentration revealed that the inclusions in the plate grow shorter and more numerous as the sulphate concentration increases. The length of the inclusions is taken as a direct indication of the amount and relative stability of the hydride originally deposited. These structural considerations are more fully discussed in the next chapter.

The theory for the action of sulphate in the bath is now supported by factual evidence. First, a higher than normal sulphate concentration in the plating bath causes plates similar to those produced from cathode films of relatively low pH. Second, the sulphate ion is strongly adsorbed by the trivalent chromium dispersoid. Third, the dispersoid is electropositively charged in strong acid media. Fourth, adsorbed sulphate ion reduces the electrophoretic velocity of the dispersoid and from this may be considered to reduce the isoelectric point of the dispersoid.

No tests of the effect of "foreign" ions such as Fe^{+++} and Al^{+++} in the chromium plating bath were made during the present work. However, from the descriptions of such plates in the literature$_{(5,6)}$ and by application of the principles of colloid chemistry, a satisfactory explanation of the role of these foreign ions in the bath may be developed.

In high-temperature plating (85°C. or above) the presence of considerable concentrations of Fe^{+++} or Al^{+++} in the bath is said$_{(5)}$ to favor soft plates. This is interpreted as favoring a low cathode film pH so that the proportion of body-centered cubic chromium in the plate is increased and the grain size is increased. In plating at more normal temperatures$_{(6)}$, appreciable concentrations of these "foreign" ions are said to produce "milky", soft, and relatively ductile plates. Such plates are producible from an ordinary bath at the very lowest limit of current density at which any plate at all is obtained. Therefore, a low cathode film pH is again indicated. It is commonly believed that colloidal particles are often intermediate between the properties of either of the components. Such is definitely known to be the case for certain iron and chromium combinations. The view here taken is that both iron and aluminum ions tend to combine with the trivalent chromium dispersoid and reduce the isoelectric point of the dispersoid. In this way the pH of the cathode film is controlled at a lower value when the "foreign" ions are present in the bath.

The Trivalent Salt Chromium Plating Baths

While a very limited amount of experimental work was done with trivalent salt chromium plating baths during the present investigation, some obvious shortcomings of this type of bath may be pointed out. The low cathode efficiency and the reduction from the hexavalent state inherent in the chromic acid bath are incentives to the search for a more efficient process. If chromium could be reduced from a trivalent salt bath, the necessary valence change would require only half the electrical energy required to reduce hexavalent chromium. With other conditions properly held within reasonable limits, an increase in cathode efficiency might also be possible and a considerable increase in electrical efficiency would be assured. Attempts to formulate a satisfactory trivalent salt bath have thus far been unsuccessful.

Apparently, here, as in the chromic acid bath, the cathode film pH is the important factor. Trivalent salts, and the various mineral and organic acids used in bath formulae to date, do not control the cathode film pH at a sufficiently low value to allow continued plating. The true test of a plating bath is its stability on continued electrolysis. Trivalent salt chromium baths do not appear to "wear" well under this test. Glowing first reports of results with trivalent salt baths have been given on the basis of plates produced during electrolysis periods of a few minutes. However, a half-hour plate is usually found to be a black or greenish mess. Often the bright plate deposited during the first minutes of plating dissolves or falls off on continued electrolysis. A green or black hydroxide layer or precipitate on or around the cathode shows that the cathode film has become so alkaline that hydrolysis of the chromium salts has taken place.

The importance of the strong acidity of the chromic acid bath is thus emphasized. The dynamic equilibrium between the hydrogen ion content of the cathode film and of the solution proper is the key to the success of this bath. It would appear that a similar equilibrium must be established in any successful trivalent salt bath.

Discussion of the Theory

The theory for chromium plating elucidated at the beginning of the chapter is partially new and partially a further development of previously presented theories. Kasper(1,7,8), Liebrich(9), and Rogers(10) are each responsible for portions of the theory. Kasper's work was of use mainly in that a detailed study was made of the nature and properties of the trivalent dispersoid in the bath. He also suggested the importance of the cathode film pH in the production of bright plates or of any plates at all. Liebrich's contribution is less tangible. While his paper is in the nature of a general discussion of cathodic phenomena and gives few definite suggestions concerning any strong points of the present theory, general support of the concept of the reduction by hydrogen and the isoelectric performance of the dispersoid is there found. Rogers further emphasized the importance of the cathode film pH. Rogers' outstanding contribution was the view that atomic hydrogen is responsible for the reduction of chromium. He also made passing mention of a belief that high-current density plating produced chromium hydrides. However, the only evidence presented to support this belief was the fact that chromium plate contains large quantities of hydrogen. It is believed that all of Rogers' plates, as he saw them, were body-centered cubic in structure and contained hydrogen in entrapped rather than combined form.

Aside from the helpful portion of Kasper's work, much was said in his papers, and in Kasper and Blum's(11) criticism of Rogers' paper, which unfortunately discredited Rogers' work. Kasper flatly stated that the reduction of hexavalent chromium to the trivalent state by atomic hydrogen is thermodynamically impossible. The present work confirms Rogers' opinion to the contrary. Kasper's third paper(8) was devoted to a supposed proof that chromium is cathodically reduced directly from the hexavalent to the metallic states. This conclusion was based on the experimentally determined fact that iron, copper, cadmium, zinc, and nickel can exist in the chromium plating bath in the ionic form and not be deposited in preference to chromium. The false reasoning from this point arose from a failure to recognize the possibility that such simple ions might exist in the bath proper but not in the cathode film.

The concept that the plate structure varies with cathode film pH is probably a logical outgrowth of the previous work, once the fact that the structures can vary is presented. However, this outgrowth is a product of the present work and therefore is new material. The concept of the function of the sulphate ion and the so-called "foreign" ions in the bath is entirely new, although it is supported as much by Kasper's work as by the present investigation. This concept may represent the weakest part of the theory and will most certainly be attacked. The weakness lies in the indirect nature of the proof material rather than in a lack of agreement with any observed or theoretical facts.

The strongest attacks are expected on the concept of reduction by atomic hydrogen. This is true, not because of any weakness in the theory but rather because the theory is so far departed from the now accepted ideas. It is fortunate that the experimental evidence very strongly supports this portion of the theory.

The theory herein developed should prove useful in future attempts to improve the chromium plating process, and also should be amenable to limited extension to other plating processes. The present work has brought the theory of chromium plating to the point where it explains this empirically developed process as used commercially. Future improvements in the process may be hoped for by following paths of investigation indicated by the basic theory now available. The possibility of extension of the theory to other plating processes is discussed in a later chapter.

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CHAPTER III

THE METALLURGICAL ASPECTS OF CHROMIUM PLATE

The Hydrides of Chromium

As previously stated, chromium plate may be deposited as a body-centered cubic metallic structure, as a hexagonal hydride, and as a face-centered cubic hydride. Both hydrides contain the hydrogen as interstitial atoms in a metal atom lattice. Data based on X-ray and chemical analysis are now offered as proof of the existence of these hydrides.

Table I gives data obtained by calculation and experiment. X-ray equipment used in obtaining the experimental data was an X-ray spectrometer as described by Friedman(1). Approximately 250 samples of plate were produced during this investigation and most of these were X-rayed from 1 to 10 times to identify their initial structures and any structural changes occurring after the initial determination. Sample A of Table I was plated in the hexagonal hydride structure. After an X-ray examination, the sample was treated for an hour in an oven at 150°C. Upon re-examination by X-ray, it was found that the plate was entirely body-centered cubic. Sample B was plated in the face-centered cubic hydride structure as shown by X-ray examination immediately after plating. After an oven treatment at 150°C. for an hour, this plate too had changed to the body-centered cubic atomic arrangement. In other experiments, the rate of decomposition of a given sample of chromium hydride was found to depend on its relative stability, as influenced by plating conditions, and on the ambient temperature after the sample was removed from the plating bath. The decomposition at atmospheric temperature was observed to continue for from three to eight weeks in specific cases studied.

TABLE I

	Cu Radiation				2θ (In Degrees)						
Sample	38.2	40.7	40.8	43.5	44.4	47.25	57.1	64.6	68.8	83.1	87.2
B.C.C. * CHROMIUM					X			X			
F.C.C. * CHROMIUM HYDRIDE		X				X			X	X	X
H.C.P. * CHROMIUM HYDRIDE	X			X			X				
SAMPLE A AS PLATED	X			X			X				
SAMPLE A ** AFTER HEATING					X			X			
SAMPLE B AS PLATED		X				X			X	X	X
SAMPLE B ** AFTER HEATING					X			X			

* Values of 2θ for B.C.C. and H.C.P. structures calculated from established lattice constants. 2θ values for F.C.C. structure are experimental values obtained in the present work.

** "Heating" consisted of placing samples in an oven held at 150°C. for an hour to decompose the hydride structure.

The lattice dimensions of hexagonal (now known to be the hexagonal hydride) chromium are given in the literature(2) as $a = 2.71(7)A$ and $c = 4.41(8)A$. The face-centered cubic structure has a lattice parameter $a_o = 3.85A$.* The distances between centers of adjacent chromium atoms in both of these structures is approximately 2.712A.** The lattice parameter of body-centered cubic chromium is given in the literature as $a_o = 2.87(6)A$. The distance between centers of adjacent atoms in this structure is 2.492(9)A. The coordination number of a given atomic arrangement is defined as the number of equidistant atom neighbors each atom possesses. For the body-centered cubic arrangement, the coordination number is 8. For the face-centered cubic and hexagonal close-packed arrangements, the coordination number is 12.

Considering the atoms of chromium to be of sufficient size to just make contact with each of their neighbors in each of the three structures, the atomic radius of the body-centered cubic chromium is then 1.24+A and the atomic radius of chromium in the face-centered cubic or hexagonal structures would be approximately 1.35+A. It is well established that the atomic radius of a given element is dependent on the type of structure in which the element appears. Goldschmidt(3) developed the principle that the atomic radius decreases as the number of close neighbors which the atom possesses is decreased. This decrease is given as 3 per cent for a change of coordination number from 12 to 8. If this is correct, then one or the other of the atomic radii values given above as calculated from lattice constants must be incorrect. 1.35 dimished by

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*Note: Refer to Appendix for calculations leading to this figure.

**Note: The hexagonal structure has 6 atoms at a distance of 2.709A from any given atom, and 6 more atoms at 2.717A. This difference is so small that the structure is here discussed as an ideal close-packed one.

3 per cent (X 0.97) is 1.31A which would be expected for the atomic radius of chromium of coordination number 8. On the other hand 1.24A x 1.03 is 1.28A which might be expected to be the atomic radius of chromium with a coordination number of 12. Clearly there is a discrepancy in the theory or in the lattice constants.

Westgren$_{(4)}$ reviewed the literature concerning the structures of alloys containing chromium and the other transition elements. The collected data presented show that, within certain atomic size restrictions, the transition elements combine with the metalloids, hydrogen, boron, carbon, or nitrogen, to form interstitial alloys of simple structure. The size restriction requires that the ratio of the atomic radii, R metalloid:R metal, be less than 0.59. If this ratio is over 0.59, the structures assumed are complex. The interstitial positions of the metalloid atoms in the metal atom lattice are determined by the size of the interstitial openings in the lattice and the size of the metalloid atoms. In general, hydrogen atoms are believed to occupy the second largest openings in the lattice. Metal-hydrogen combinations of the general formula MH to MH_2 crystallize in the face-centered cubic atomic arrangement with metal atoms at the normal corner and face-centered positions of the unit cell. The hydrogen atoms then occupy half of the second largest interstitial openings to form a zincblende type structure (Figure 5) for the formula MH, and all of the second largest interstitial openings to form a fluorite type structure (Figure 6) for the formula MH_2.

Metal-hydrogen combinations of the formula M_2H to MH tend to crystallize in the hexagonal close-packed arrangement. Here too, the hydrogen atoms occupy the second largest interstices in the lattice,

Figure 5. Zincblende type structure (taken from Westgren, Jnl. Franklin Inst., 212, (1931), 577). The face-centered cubic hydride of chromium may assume this structure, the circles representing the chromium atoms, and the black dots representing the hydrogen atoms. This structure corresponds to the formula CrH.

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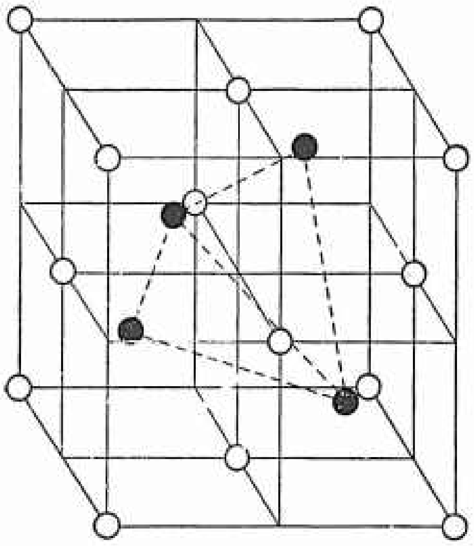

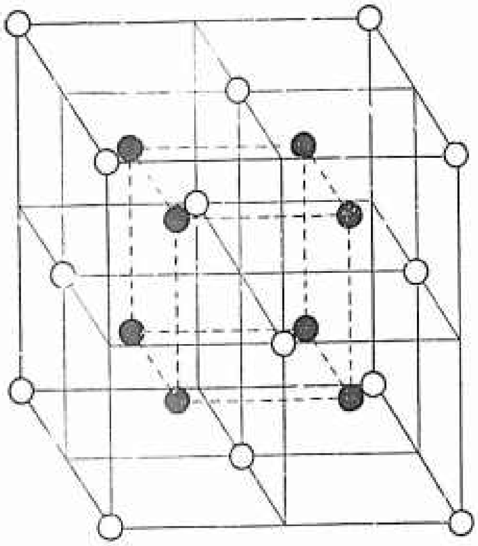

Figure 6. (Fluorite type structure (taken from Westgren, Jnl. Franklin Inst., 212, (1931), 577). The face-centered cubic hydride of chromium may assume this structure, the circles representing the chromium atoms, and the black dots representing the hydrogen atoms. This structure corresponds to the Formula CrH_2.

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producing an incomplete or complete wurtzite type structure (Figure 7) depending on the proportion of the interstitial positions filled. The positions given for the hydrogen atoms are logical deductions from the experimental data rather than experimentally proven facts. The metalloid atoms are too small to produce X-ray diffraction effects and therefore do not produce lines on X-ray patterns. It should also be mentioned that there are several exceptions to the general rules given above. For instance Pd-H crystallizes in the body-centered cubic system and the hydrogen atoms occupy the largest interstitial openings in the lattice.

It is now not surprising that the hexagonal and face-centered cubic structures may be treated as hydrides. As mentioned above, the atomic radius of chromium in the body-centered cubic arrangement is 1.24+A, and the Goldschmidt correction applied to this would require a radius of 1.28+A for atomic arrangements of coordination number 12. If atoms of radius 1.28+A are considered to be the metal atoms in a face-centered cubic lattice of parameter 3.85A, the largest opening in the structure is at the center of the unit cube. This opening is 1.29A in smallest diameter. The second largest openings are 0.78A in smallest diameter and are centered on positions in the unit cube of $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$, and the seven corresponding positions in the lattice (Figure 6). The diameter of interstitial hydrogen atoms in face-centered cubic structures is given by Westgren as being between 0.80A and 1.00A. It is evident that a hydrogen atom of this approximate size can account for the larger than expected lattice parameter of the face-centered cubic chromium plate. On the basis of this information, it may be concluded that the face-centered cubic plate is in reality a hydride of the zincblende type of structure. Since the fluorite type structure is only a more filled up version of

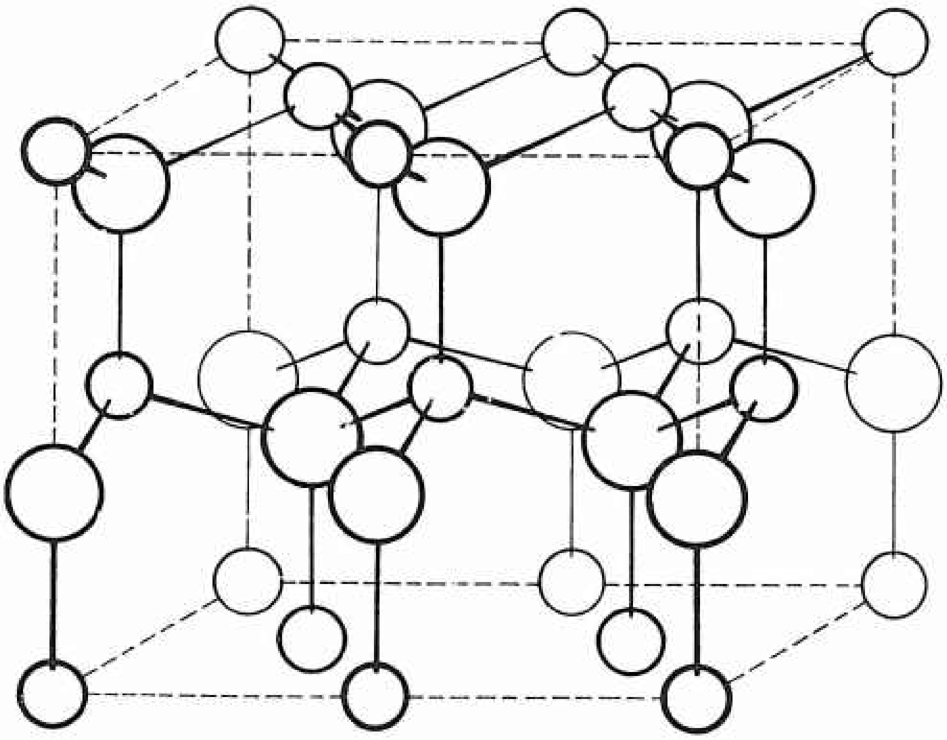

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Figure 7. Wurtzite type structure (taken from Pauling, "The Nature of the Chemical Bond", Cornell University Press). The hexagonal hydride of chromium assumes this general type of structure. The large circles represent chromium atoms and the smaller circles represent hydrogen atoms. The structure shown is represented by the formula CrH. As many as half of the hydrogen atoms may be missing from this structure. In such a case the structure is represented by the formula Cr_2H.

the zincblende structure, it is likely that any combination of chromium-hydrogen atoms from 50 atomic per cent Cr—50 atomic per cent H (zincblende type) to 33 atomic per cent Cr—67 atomic per cent H (fluorite type) should be possible.

A similar calculation in the case of the hexagonal plate serves to illustrate that a chromium atom of radius 1.28A and a hydrogen atom of diameter 0.76A will account for the lattice spacing, if the hydrogen atoms are again assigned to the second largest interstices in the lattice. This produces a wurtzite type structure as might be expected from Westgren's data. It is therefore logical to conclude that the hexagonal plate is also a hydride. It is significant that half of the interstitial atoms may be removed from the wurtzite structure without destroying the stability of the structure. Thus, a hydride composition of from 33 atomic per cent hydrogen (with half of the interstitial atoms of the wurtzite structure present) to 50 atomic per cent hydrogen (completed wurtzite structure) is possible.

The coordination number of the interstitial atoms in both the wurtzite and zincblende type structures is 4. It is perhaps significant that this is so, but the significance is not at once evident. Possibly some further studies of bonding in crystals will illuminate the situation. No further discussion of bonding will be given here, but some speculations on the matter will be presented in a latter chapter.

To provide further proof that the hexagonal and face-centered chromium plates are hydrides, some hydrogen extraction tests were undertaken. A sample of face-centered cubic plate was produced from a bath containing 1021 g./l. CrO_3, 300/1 acid ratio, and with 7.4 per cent of the total bath chromium in the trivalent state. The bath temperature was 0° to 4°C., the current density 0.8 amp./sq.in. and the plating time $7\frac{1}{2}$ hours. The backing for this plate was copper foil, 0.002 inch thick. Upon removal from the plating bath, the sample was quickly rinsed, sponged dry with a towel, and placed under mercury in an inverted test tube. This operation required approximately two minutes. Gas was evolved from the specimen for less than twenty-four hours at an appreciable rate, no further cold evolution being noted in three days. The sample was then transferred to a gas extraction apparatus where it was heated to 650°C. and held at this temperature for 30 minutes while under vacuum. The gas extracted by this treatment was analyzed and found to be pure hydrogen as was the gas obtained by cold evolution. Calculated at S.T.P., the cold evolution gas was 1.41 ml. and the warm extraction gas was 10.80 ml. in volume, giving a total gas content of 12.21 ml. for the sample. This amount of hydrogen was considered to be evolved entirely from the chromium plate as previous experience has shown that a negligible amount of hydrogen may be held in a copper disc measuring only $\frac{1}{2}$ inch in diameter and 0.002 inch in thickness. The apparatus used to extract the hydrogen was similar to that described by Newell$_{(16)}$.

The copper backing was stripped off the sample in nitric acid and the residue was weighed. It was then treated with hydrochloric acid. Some of the chromium was thus dissolved, but much was not. The undissolved residue was a green powder and it was concluded that it was chromic oxide (Cr_2O_3). This was fused with potassium bisulfate but some residue remained after this treatment. A sodium peroxide fusion treatment served to dissolve this residue. The entire lot of dissolved chromium was then oxidized with sodium peroxide and titrated by the iodine — thiosulphate method. The amount of chromium in the sample was thus found to be 0.0329 gram. Since the weight of the sample was 0.0511 gram, it is evident that roughly half of the sample was in the form of Cr_2O_3 after the high-temperature extraction treatment.

The chromium atom to hydrogen atom ratio calculated from the above data is 1:1.7*. This result entirely agrees with the expectations as a chromium:hydrogen ratio anywhere within the limits of 1:1 and 1:2 would satisfy the requirements previously established for the face-centered cubic structure.

No similar tests were undertaken for the hexagonal hydride as it was doubted that a sufficiently pure sample could be obtained. The first layer of plate deposited is invariably predominantly body-centered cubic under plating conditions producing the hexagonal hydride after equilibrium is reached in the cathode film.

It is natural to inquire into the possibility that the body-centered cubic form of chromium plate may be a hydride. The only interstices in the body-centered cubic atomic arrangement are those at the face-centered positions. In the chromium lattice, these openings are 1:58A in least diameter. Since no cases of hydrogen atoms assuming so great a size are known, it is concluded that these face-centered interstices could not be occupied by hydrogen atoms. All indications are that an interstitial atom must be sufficiently large to contact all surrounding atoms if a stable or even metastable interstitial solid solution type of structure is to be established. It is therefore concluded that the hydrogen present in body-centered cubic chromium plate is occluded as molecular hydrogen in voids somewhat larger than the crystal lattice interstices. This is in agreement with the conclusions of previous

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*See Appendix for calculations.

investigators(5,6). Apparently much of the hydrogen of the hydride forms does not escape when the hydrides decompose but is occluded in the body-centered cubic decomposition product.

The Cause of Inclusion-Filled Cracks in Chromium Plate

Having established the fact that chromium may be plated as an unstable hydride form, the properties and structure of chromium plate may now be examined in a new light. Calculations* indicate that the volume shrinkage attending the decomposition of the hydrides is over 15 per cent if a completely unstrained body-centered cubic lattice is assumed. When the hydrides decompose, a considerable number of cracks may be observed to form, presumably caused by this shrinkage. Examination of the cross section of the plate shows that these cracks are perpendicular to the basis metal and reach from the surface of the plate to the basis metal.

Consider the possibility that a similar decomposition and cracking occurs during the plating of the common commercial variety of bright, hard, chromium. As shown by Cymboliste(7) the length of the inclusions in chromium plate is influenced by the plating solution composition and the plating conditions. Cymboliste's observations have been corroborated in the present work. In addition it has been noted that, within the limits of the bright plating range, those constituents and conditions favoring a higher cathode film pH produce a plate with more and smaller cracks than those favoring a somewhat lower film pH.

It was indicated in the previous chapter that the proportion of the hexagonal hydride in the plate increases as the cathode film pH

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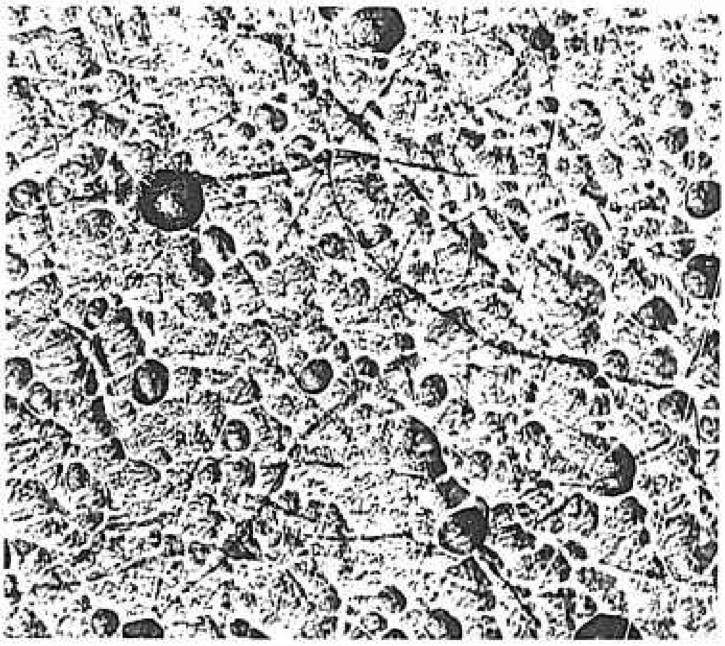
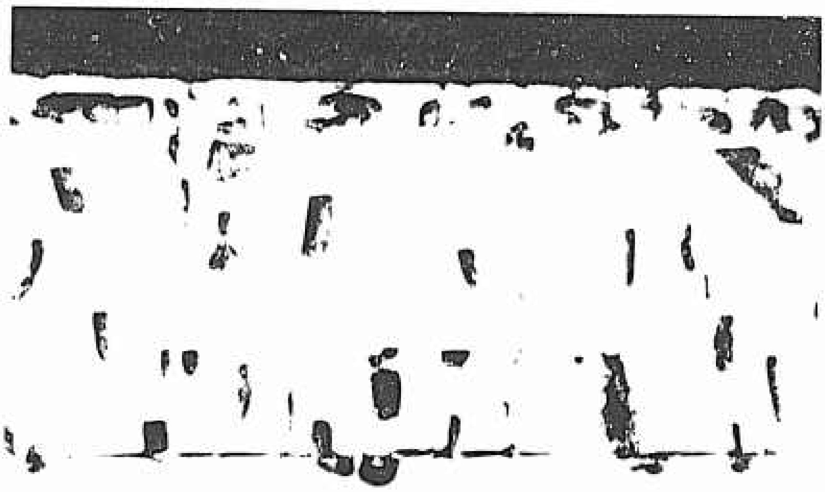
*See Appendix for calculations.

increases. This may be brought forward to explain the change in the crack pattern as the pH of the film increases. If a plate consisting of a mixture of body-centered cubic and hexagonal crystals is predominately body-centered cubic, but a small amount of over-all shrinkage will occur when the hexagonal crystals decompose to make the plate wholly body-centered cubic. The strain produced by this shrinkage may lie within the elastic and plastic deformation limits of the plate and no cracking need occur. Another plate, also a mixture of the body-centered cubic and hexagonal crystal forms, but predominately hexagonal, will shrink so greatly during the decomposition of the hexagonal crystals that the elastic and plastic deformation limits of the plate will be exceeded and cracking will occur on a large scale. When such decomposition and cracking occurs during the plating operation, and the cracks extend to the plate surface, then a partial vacuum will be created within the crack voids and a sample of the solution at the cathode surface will rush into the cracks. Thus, the cracks will not be empty voids but will be filled with cathode film material. As plating continues, these cracks will be bridged over and the cathode film material will be sealed inside the plate as inclusions. The presence of such inclusions was shown by Cymboliste(7). Cohen(8) conducted experiments which showed that, after heating, the inclusion material was chromic oxide (Cr_2O_3). In the same work, the cell-like structure of the inclusion-crack network was established. The walls of the cells were presented as being perpendicular to the surface of the plate. The structure of the inclusion cells is illustrated by Figures 8 and 9, which show the inclusion-filled crack pattern of a typical bright chromium plate from plate surface and cross-sectional views. Figure 10 represents the same surface at a greater magnification.



Unetched Surface 49458 200X

Figure 8. Surface of hard chromium plate showing crack system and nodular appearance. Bath composition, 250 g./l. CrO_3, 2.5 g./l. SO_4. Bath temperature 60°C. (140°F.). Current density 1.8 amps./sq.in. Plating time 7 hours. Nodular appearance is emphasized by limited depth of focus of microscope at this magnification.



Etched Surface 49459 200X

Figure 9. Cross section of chromium plate shown in Figure 8. A five-second electrolytic etch has been applied at 6V. in 10 per cent chromic acid solution at atmospheric temperature. Note form of inclusions. Chromium has been etched away, allowing inclusions to fall sidewise on etched surface of plate in many cases. Some inclusions have broken off during the etching process leaving the cracks they formerly filled visible as thin lines. Inclusions at an acute angle with the etched surface appear as large dark areas.

Unetched Surface 49460 350X

Figure 10. Same surface of chromium plate as is shown in Figure 8. Note the various steps in the formation and covering over of cracks as they are illustrated in this photograph. Freshly formed cracks are very prominently evident. Old cracks are more obscure. Very faint indications of many cracks which are nearly obliterated by covering metal deposit are yet visible on close inspection.

The presence of the inclusion-filled voids in bright chromium plate is taken as proof that the plate is deposited largely as the hydride which decomposes to form a cracked plate while the plating process is in progress. The length of the cracks (i.e. inclusions) is determined by the proportion of hydride in the deposit, and by the stability of the hydride under the plating conditions in use. A large proportion of very unstable hydride in the plate decomposes rapidly and crack-producing strains are established in relatively thin layers of plate. This limits the length of the cracks to the thickness of the plate layer. As plating continues, the old cracks are sealed over and new cracks develop. The new cracks always extend from the surface of the plate to a depth in the plate at which decomposition shrinkage stresses have been considerably relieved by previous cracking. Thus, the length of the cracks is indicative of, but not an absolute measure of, the thickness of plate in which hydride decomposition is proceeding at any given time during the plating process. Other considerations may considerably influence the length of the cracks. In a plate containing only a small amount of the hexagonal hydride, crack-producing stresses may not be built up until practically all of the hydride has decomposed. This may require so much time that when cracking does occur, the plate is thick and the cracks are comparatively long. This view is substantiated by the distribution of cracks in plates which have been cross sectioned. When cracks are short, they are also very numerous and closely spaced. When cracks are longer, they are considerably less numerous, are widely spaced, and appear to be considerably less in aggregate volume than the short cracks.

The Grain Size of Chromium Plate

Wood(9) made studies of the grain size of bright chromium plate by measuring the broadening of the lines of X-ray diffraction patterns. It was shown that the grain size of bright chromium plate is of the order of 14×10^{-7} cm. whereas the smallest grains producible in metals by cold working are of the order of 10^{-4} cm. in average diameter. This led to the conclusion that the grain size of chromium plate is an inherent property of the plate and that the grain size measurements were not confused by strained crystal lattices. No reason was offered for the fine-grained character of the plate. However, the effect of the grain size upon the properties of the plate was discussed.

In the plating process, the first atoms to be deposited are considered to form crystal nuclei about which subsequently deposited atoms arrange themselves in a regular fashion to build up the crystals which compose the finished plate. The grain size of the initial plate layer depends simply on the number of crystal nuclei formed, as each nucleus tends to grow in directions parallel to the basis metal until further growth in these directions is interrupted by contact with adjoining crystals. At the same time, growth away from the basis metal occurs. This latter type of growth also continues until interrupted. Interruption may occur by encroachment of a neighboring crystal, by formation of a new nucleus at the plate surface which receives depositing atoms in preference to the established crystal, or by various other mechanisms which have been advanced to explain the phenomenon as observed in many instances. In the case of chromium plating, a new reason for the formation of new nuclei at the plate surface may be introduced. This new view involves the decomposition of the crystal nuclei after they have experienced only limited growth. This removal of the nuclei forces depositing atoms to form new nuclei which in turn decompose. Thus, a fine-grained structure is produced.

It has been indicated herein that bright chromium plate is deposited largely as a chromium hydride which decomposes spontaneously to form a body-centered cubic metal structure. Such a decomposition must occur within each individual hydride grain. When a normal allotropic transformation occurs in a metallic structure, the nucleation of the new phase is considered to begin at the grain boundaries. Transformation then proceeds from the grain surface to the interior. At some time in the process, a shell of the new phase surrounds a core of the old phase. It is not at once evident if a similar situation exists in the decomposition of chromium hydride. It appears logical to assume that hydrogen is lost first from the outside atom layers of each hydride crystal and that nucleation of the body-centered cubic structure therefore begins in these layers. If such layers then extend completely around a crystal, that crystal is effectively removed from the action as a nucleus for further hydride deposition, even though it may yet be composed mainly of the encircled hydride. Depositing hydride must then form new nuclei overlying such encircled ones. Deposition on these new nuclei may continue only until they are similarly encircled. By such a mechanism, formation of an aggregate of fine grains may be pictured.

However, this need not be the ultimate step in the production of the grains of the final plate. When the outer shell of a hydride crystal decomposes to the body-centered cubic arrangement, it can no longer completely reach around the hydride core by reason of the shrinkage involved in the decomposition. Rupture of the shell is inevitable. As the decomposition zone moves to the center of the crystal, these surface ruptures must be propagated to the center also, so that the parent hydride crystal is divided into a number of smaller metal crystals. The paths followed by the ruptures then become grain boundaries in the final aggregate. During the decomposition of the hydride, the interstitial hydrogen is released. This hydrogen is soluble in the body-centered cubic metal decomposition product without any lattice distortion (refer to page 51), so long as it remains in the atomic form. It may be occluded as molecular hydrogen in any ruptures or irregularities in the crystal structure which are of sufficient size to accommodate the hydrogen molecule. It is considered likely that such occlusion may occur in the ruptures pictured above as occurring within the grains during the hydride decomposition.

Each individual hydride grain has been pictured as breaking into a number of smaller grains or crystallites. These grains may be separated by small distances and should lie in very similar orientation as regards crystal planes. Since the intergranular voids do not communicate with the atmosphere, there is no possibility that oxidation of the void surfaces will occur.

Hidnert(10) showed that chromium plate may undergo a volume shrinkage of approximately 2.3 per cent when heated to a temperature of 500°C. for the first time. The position is here taken that this shrinkage may be partly due to relief of internal stress but is mainly caused by the closing up of the voids between crystallites. It is probable that this closing up cannot occur until the hydrogen is removed from the voids, and the mobility of the atoms comprising the crystal lattice is increased. Both of these effects occur when the plate is heated.

Two different shrinkage effects occurring during the plating process have now been discussed and it is desired to emphasize the difference between the two. The large-scale effect is the opening of cracks in the plate which are filled with inclusion material drawn from the cathode film. These cracks are oriented perpendicular to the plate surface. It is believed that they contain occluded hydrogen in addition to the so-called inclusions. The other, small-scale effect is rupture between sections of the hydride crystals during decomposition. This divides the already fine-grained structure into even smaller grains, produces a multitude of extremely small voids, and provides for the occlusion of a considerable volume of molecular hydrogen.

In connection with the discussion of the grain size of chromium plate, Figure 3 of Chapter II is of interest. The plate pictured was entirely hexagonal in structure when first X-rayed. It was then treated at 150°C. for 45 minutes in an air oven. As shown by a subsequent X-ray test, this treatment completely decomposed the hydride. A number of cracks were observed to appear as shown in the photomicrograph. Note the 30°, 60°, and 120° angles at the corners of many of the crystals, and also the perpendicularity of the crystals to the basis metal. Evidently the 001 crystallographic planes of the hexagonal structure were parallel to the basis metal. After the decomposition of the hydride, the crystal outlines remained as pseudomorphs of the previous structure. This case illustrates the point that coarse crystals result if the hydride is produced in a relatively stable form.

Stress in Chromium Plate

A study of the stress in chromium plate was made by Hume-Rothery and Wyllie(11) with somewhat anomalous results. A conventional chromium plating bath was used and plates were produced under conditions of constant temperature with current density as a variable. The plates were based on thin strips of steel and the curvature of the plated strip was measured. Precise mathematical calculations were made of the residual stress necessary to produce the measured curvatures in the strips. These calculations revealed the presence of extremely high contractile stresses in the plates. Presumably the authors recognized the fact that they were measuring an over-all stress in a cracked coating rather than in a sound, elastically contracting, metal layer. It must be assumed that the plates were cracked, since the plating conditions used invariably produce cracked plates. Therefore, the measured curvatures of the composite strips were only a partial measure of the total contraction occurring in the plates.

Further experiments were conducted in which the steel backing strips were dissolved and the deflection of the unrestrained metal was observed. Plates produced at values of temperature and current density favoring a high cathode film pH exhibited no tendency to curl, indicating that any contractile stress was uniformly distributed through the plate. This might be expected, as such plates contain a relatively large proportion of fairly stable hydride distributed through the plate. Decomposition of the hydride then produces a relatively uniform contraction. Cracks, if formed, are likely to extend through the entire thickness of such a plate. No cracks were reported by the authors, but careful examination of the specimens at high magnification would have been necessary to detect them.

Plates deposited at a temperature and current density producing a somewhat brighter, mat surface, were found to curl, the convex side being that formerly facing the steel basis strip. This is explainable on the basis that the first layer of plate produced was predominately body-centered cubic, and hence contracted little and slowly. The top layers were predominately the hexagonal hydride in a relatively stable condition. These layers therefore decomposed and contracted to a much greater extent than the first layers, and the result was a curvature of the type noted.

A plate produced under the optimum conditions for brightness curled with the concave side being that side formerly facing the steel basis strip. This, too, can be explained on the basis of hydride decomposition. The first plate was predominately body-centered cubic and shrank little. The restraining effect of the basis metal was sufficient to maintain this layer in tension and the shrinkage stresses were insufficient to crack it. The top layers of the plate consisted largely of very unstable hydrides. These bright layers of the plate shrank so much, and cracked so freely, that they no longer acted as a solid coherent body, but rather as so many disconnected islands, or chunks, of metal. The decomposition was rapid and complete. The elastic stresses remaining in these top layers of metal were, therefore, within each chunk of metal. They could not affect the plate as a whole. Sufficient unrelieved shrinkage stresses remained in the initial layers of plate that, when they were released by removal of the backing strip, the entire plate was curved. Thus, the phenomena considered anomalous without the concept of hydride formation are completely and satisfactorily explained when this concept is introduced.

The stress produced in bright chromium plate by the decomposition of the hydride is relieved, for the most part, by cracking. However, some residual stresses must remain in the plate, simply because they are insufficient to produce further cracking. These stresses are contractile. Stresses tending to expand the plate must arise from the occluded hydrogen within all the voids in the plate. It is possible that such stresses contributed to the bending performance of the bright plate described in the preceding paragraph.

Wilson(12) measured the lattice parameter of bright chromium plate before and after a heat treatment to remove the entrapped hydrogen. No change in the parameter during this treatment was noted. It appears that any internal stress sufficient to produce lattice expansion must be sufficient to cause lattice rupture.

Hardness of Chromium Plate

Several papers have been published(4,5,6,8,10,11) in which measurements of the hardness of chromium plate were reported and discussed. Some of the more recent authors recognized the fact that the hardness of chromium plate is dependent on bath composition and plating conditions and is not a constant for the material. No hardness measurements have been made in the present work other than a few simple scratch tests. It is now well known that chromium plated under certain optimum conditions is very hard. It is also established that chromium plated under other conditions is considerably softer. The present investigation has been more concerned with the "why" of this extreme hardness and hardness difference than in the actual numerical value of the hardness. The conclusion has been drawn that the grain size of chromium plate is largely responsible for the plate hardness.

Fully annealed pure chromium is relatively soft, having a hardness of the order of 130 Brinnell number or below(13). The hardness of pure metals may be increased in several ways. Stressing a metal, either internally or externally, increases its hardness. Decreasing the grain size increases the hardness of a metal. Cold work increases the hardness of metals. However, the effect of cold work can be divided into the two above-mentioned categories. It decreases the effective grain size of the metal and also produces residual internal stress. Alloying, another way of hardening a metal, is not here considered because it was shown earlier (page 52) that hydrogen atoms cannot be considered a part of the body-centered cubic chromium plate. Further proof of this is found in the work of Guichard, Clausmann, Billon and Lanthony(6). It was shown that 95 per cent of the hydrogen is driven out of the plate by simultaneous heating and vacuum treatment before any appreciable softening occurs. The remaining 5 per cent of hydrogen is believed to be that chemically combined with the crack-filling inclusion material. This small amount of gas may also be driven off by heating, but the temperature required is above that at which recrystallization probably begins.

Makareva and Biryukov(5) reported that heating chromium plate to 585 °C. drives off 98 per cent of the hydrogen with no hardness loss. No possible alloying elements, other than hydrogen, are present in chromium plate.

The increase of hardness of a metal with decrease in grain size has been illustrated to the lower limits of grain size as produced by cold working and recrystallization(17, 18). It is significant that the curve for increase in hardness vs. decrease in grain size shows an increased increment of hardness for a given decrease of grain size near the lower limits of grain size attained (refer to Figure 11, taken from Wood(17)). A slight additional decrease in grain size would undoubtedly produce a considerable increase in hardness. It is plainly evident that the grain size of chromium plate must be considered a strong factor in the hardening of the plate.

Undoubtedly considerable internal stress exists in chromium plate, as discussed in a previous section. The work of Hidnert and of Makareva and Biryukov may now be combined to indicate that the contribution of this stress to the hardness of chromium plate is of but minor importance. As mentioned before, Hidnert noted a considerable shrinkage occurring in chromium plate heated to 500°C. Makareva and Biryukov found that the hardness of chromium plate did not decrease appreciably when heated to 585°C. Treatment at this temperature would be expected to relieve any internal stress present. Therefore, it may be deduced that a major portion of the internal stress was relieved without a corresponding decrease in hardness.

From these arguments, it appears that the hardness of chromium plate is due mainly to the fine-grained character of the plate. Internal stress arising from occluded hydrogen and residual stress from shrinkage accompanying hydride decomposition are necessarily considered but minor contributing factors. This seems a satisfactory situation from all standpoints, agreeing with the general theory of metals and with the available experimental data.

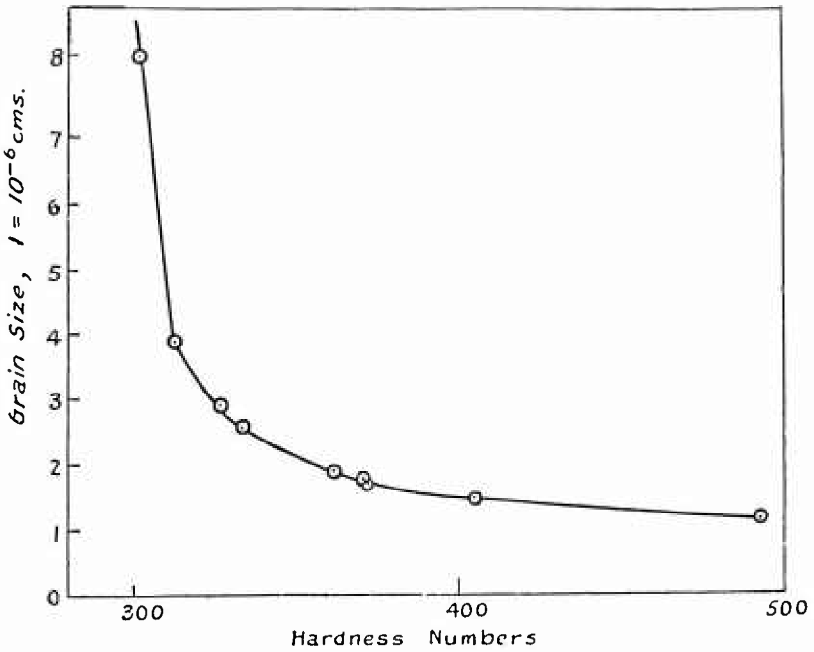


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Figure 11. (Taken from Wood, Phil. Mag., 10, (1930), 1073). This graph illustrates the general type of curve for the hardness increase of metals with decrease in grain size. Chromium plate has been shown to be normally less than 2 x 10^{-6} cm. in average grain diameter.

The Brightness of Chromium Plate

It is considered significant that the same plating conditions which produce the hardest chromium plate also produce the brightest plate. This leads to the deduction that the same cause, the fine-grained character of the plate, underlies both hardness and brightness.

In order to be bright, a plate must be extremely fine grained or be composed of perfectly oriented crystals with a thickly populated plane parallel to the plate surface (or nearly so). Dull plates consist of coarse, randomly oriented grains, or of powdery aggregates which function in the same manner as coarse crystals, in reflecting light. It has been pointed out that chromium plate is extremely fine grained. Hume-Rothery and Wyllie(11) studied the orientation of the grains in chromium plate by X-ray methods. They concluded that the degree of preferred orientation was greater for bright chromium plates than for dull plates. However, they did not make a concurrent study of the grain size of the plates. In general, the (111) plane of the body-centered cubic crystal was found parallel to the plate surface. It must be remembered that the plates studied were, and all bright chromium plates are, the decomposition products of hydrides. Presumably the hydride crystals were oriented as deposited and thus gave rise to other oriented crystals when they decomposed.

Conditions producing large crystals in the plate always produced dull or mat-surfaced plates. These were produced by plating either above or below the bright range. The dullness of such plates is explained as a result of the amount and stability of the hydride in the plate.

At low plating speeds (below the bright range of temperature and current density), the plate is predominately body-centered cubic. This is a result of the low cathode film pH. Nothing occurs to interrupt the growth of the body-centered cubic crystals. In fact, conditions are ideal to promote their growth to relatively large size. In this way a coarse-grained plate is produced. Hume-Rothery and Wyllie showed that such plates consist of a considerable proportion of randomly oriented crystals. Therefore, such plates have two reasons to be dull; coarse crystals, and lack of orientation.

It should be pointed out that orientation in itself means little unless the crystals present a planar surface at the plate surface. Plates were produced during this investigation in which many of the crystals had a (111) orientation. However, the crystals were apparently growing on the (100) planes. When examined under a microscope, three sides of each crystal could be seen rising toward the observer. The plate surfaces were actually composed of a myriad of such pyramids. In order to obtain a bright planar surface, it would be necessary to shear each crystal along a (111) plane.

Plates deposited at a current density above the bright plating range are dull because the cathode film pH is too high. Such conditions foster production of relatively stable hydrides. These hydride crystals grow to large size unless decomposition occurs to interrupt such growth. Figure 3 of Chapter II is an example of extremely coarse-grained hydrides. Under normal chromium plating conditions, a slightly too high current density produces dull plates by producing grains of considerably larger size than are produced in the bright range. These comparatively large grains may still be considerably smaller than those encountered in most other plating processes except bright nickel.

The probable breaking up of hydride crystals into a number of smaller metal crystals was discussed previously. It is considered that the orientation of the product crystals must logically bear some relation to the orientation of the parent crystals. Thus, the forces which create the rupture of the forming, body-centered cubic, crystals might pull them somewhat askew but still leave them in a position to indicate their origin. If the size of the parent crystal is increased, the degree of skewness of the product crystals might be expected to increase. The data of Hume-Rothery and Wyllie(11) support this view as plating above the bright range produced a greater divergence from exact (111) orientation in the plates.

All indications are that the hexagonal hydride is normally deposited with the 001 plane parallel to the plate surface. The face-centered cubic hydride is believed normally to deposit with a (111) orientation. However, exceptions were noted, and it is believed that a further study of this matter is necessary before the significance of the available data can be fully interpreted.

Fine-grain size and near-perfect preferred orientation remain as the basic factors accounting for the brightness of chromium plate.

Structural Characteristics of Chromium Plate

The structural characteristics of chromium plates produced under various conditions were introduced in the preceding chapter to illustrate the effect of sulphate in the plating bath. Various structural characteristics were also mentioned in the preceding sections of this chapter. The discussion in this section is undertaken with the aim of correlating all the information available concerning the structure of chromium plate produced under different conditions.

The work of Hume-Rothery and Wyllie(11) is a fitting introduction to the subject of the structure of chromium plate. Figure 12 is reproduced from their work.

Zone I of Figure 12 indicates a set of plating conditions which maintain a cathode film pH above the bright plating range. Plates produced under these conditions are predominantly, or entirely, relatively stable hydrides as deposited, and are therefore dull. The statement that they are soft is believed a misnomer. Rather, they are extremely brittle and therefore susceptible to scratching. Their tendency to turn green when exposed to air is believed an indication of the inclusion in the plate surface of chromous oxides or hydroxides which oxidize to Cr_2O_3 on exposure to the atmosphere. These low valence forms of chromium are really part of the cathode film and may be removed by scrubbing the plated specimen immediately upon lifting from the plating bath.

Zone II is of more practical interest. In this zone, the plates are predominately the hexagonal hydride of decreasing stability as the zone is traversed from left to right. The plates produced at the left of the zone have deep cracks indicating slow decomposition of the hydride. At the right of the zone the cracks become closer spaced and more shallow, indicating less stability in the hydrides.

The shaded boundary between Zones II and III shows the range in which a very unstable hydride is the major portion of the deposit. Plates produced in this range are the brightest, the hardest, and contain the most inclusions, all as a result of the instability of the hydrides.

Zones III is the range in which the film pH is not raised high enough, under the plating conditions, to produce a plate in which

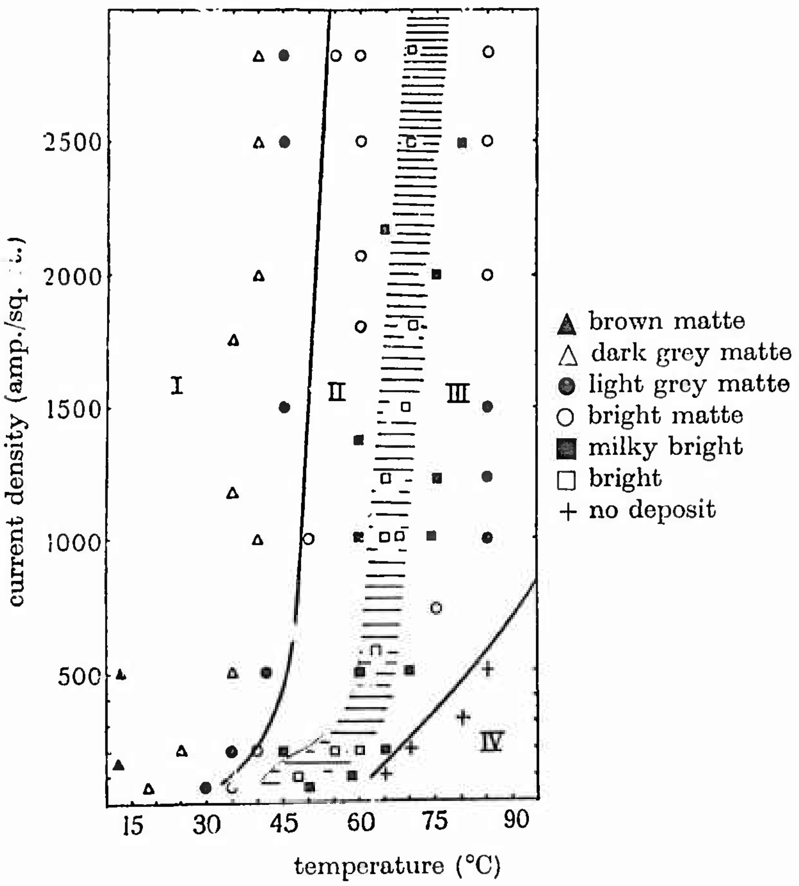

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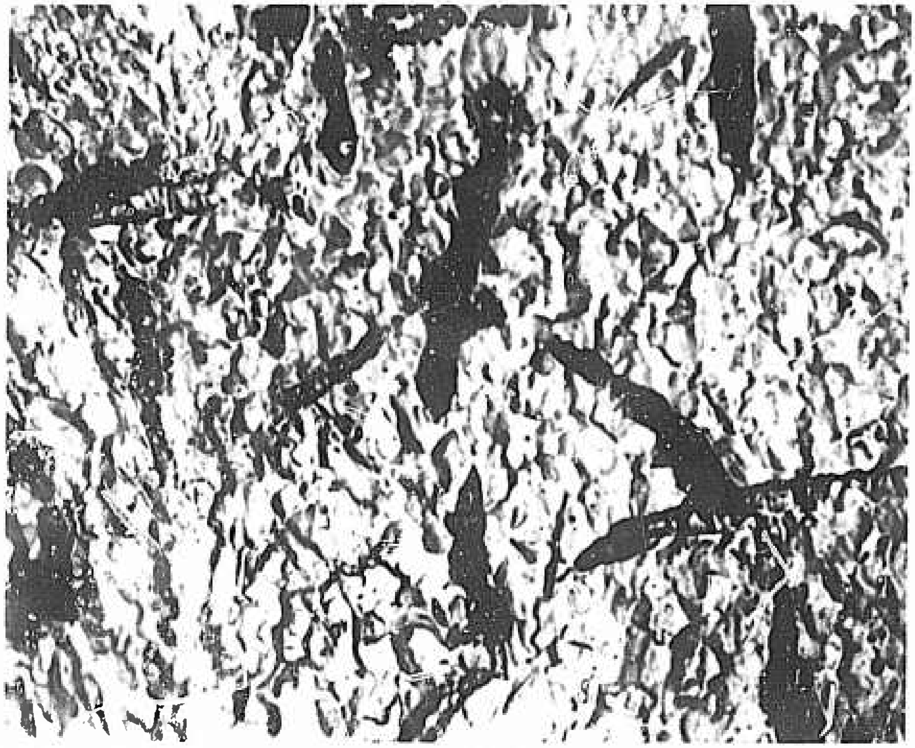
Figure 12. Structure of chromium plated under various conditions (taken from Hume-Rothery & Wyllie, Proc. Royal Soc., 181, (1943), 331). The existence of the various zones shown in the figure is explained in the context. The shaded area represents the rather indefinite boundary between Zones II and III. Most commercial chromium plating is done under conditions shown for the lower portion of the shaded area or just to the left of this area. Bath used in determining points contained 250 g./1. CrO_3 and SO_4 to give an acid ratio $\left(\frac{CrO_3}{SO_4}\right)$ of $\frac{100}{1}$.

hydrides predominate. The high-temperature plates (low contraction) described by Gardam(14), and the plates from baths high in concentration of Fe^{+++} and Al^{+++} as described by Peach(15), fall in this category.

Zone IV is indicative of a cathode film pH too low to permit any plating.

The etchant used in all of the metallographic work described herein was 10 per cent chromic acid solution, used at atmospheric temperature, with the specimen made anodic at 6 volts. The fact that this etching treatment failed to reveal any grain structure in bright hard plates was earlier laid to the fine-grain size of the plate. Another possible contributing factor is the preferred orientation of the plate. By etching a metallographic specimen, it is hoped to show up the grain structure by baring crystal faces of the individual grains so that light is reflected in various directions by the grains and they may then be distinguished each from their neighbors. However, if the crystal faces are essentially coplanar, as is the case in hard chromium plate, then no distinction between grains is likely to be produced by conventional etching methods. Therefore, a combination of these two factors, fine-grain size and preferred-crystal orientation, is probably responsible for the difficulty experienced in revealing the grain structure of hard chromium plate. It is to be emphasized that the size and dispersion of the inclusions should not be confused with the actual grain size of the plate, as is sometimes done.

Upon annealing hard chromium plate, the grain structure is revealed by etching. However, the structure is still so fine that high magnifications are necessary to inspect individual grains. Figure 13



Etched Surface 49461 1000X

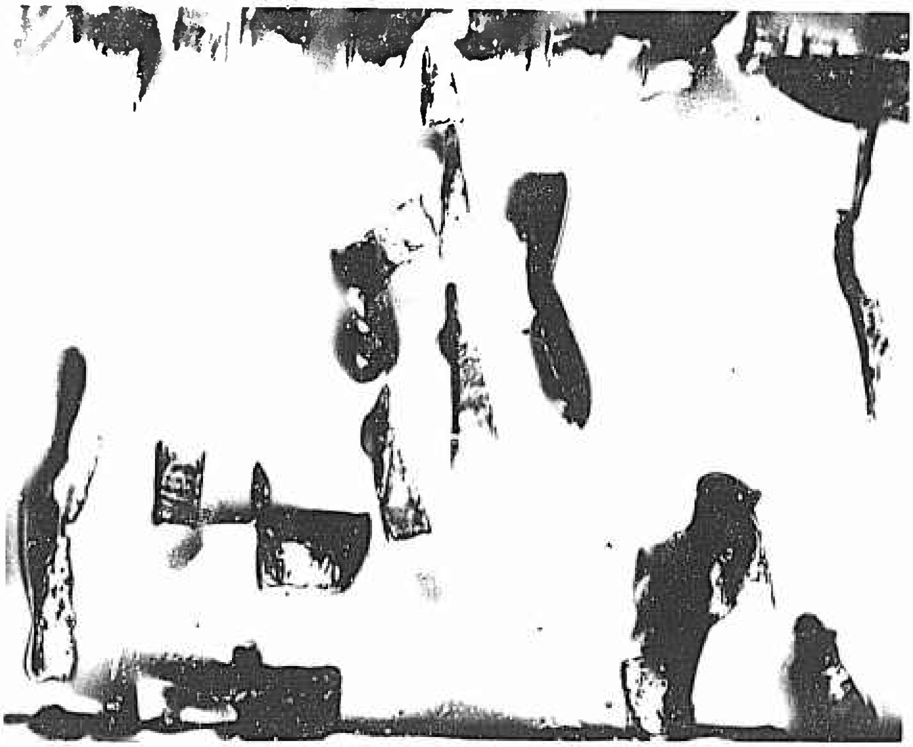
Figure 13. Hard chromium plate after annealing treatment of three hours at 1550°F. Electrolytically etched for five seconds at 6V. in 10 per cent chromic acid solution at room temperature. The surface shown is a cross section of the plate.

illustrates the structure of an initially hard plate which was annealed. It is considered likely that the grains visible in the photomicrograph are either the prior hydride grain outlines or combinations of those grains.

Figure 14 illustrates the inclusion and crack pattern of a normal hard chromium plate as viewed from the cross section. Figure 15 illustrates the structure of a plate produced from a 20/1 acid ratio bath. The inclusions in this plate are much shorter, more numerous, and more evenly dispersed through the plate. Plates produced at bath temperatures near the boiling point of the bath, using procedures similar to those described by Gardam$_{(14)}$, were examined at magnifications up to 1000X. No inclusions or cracks were found in those plates.

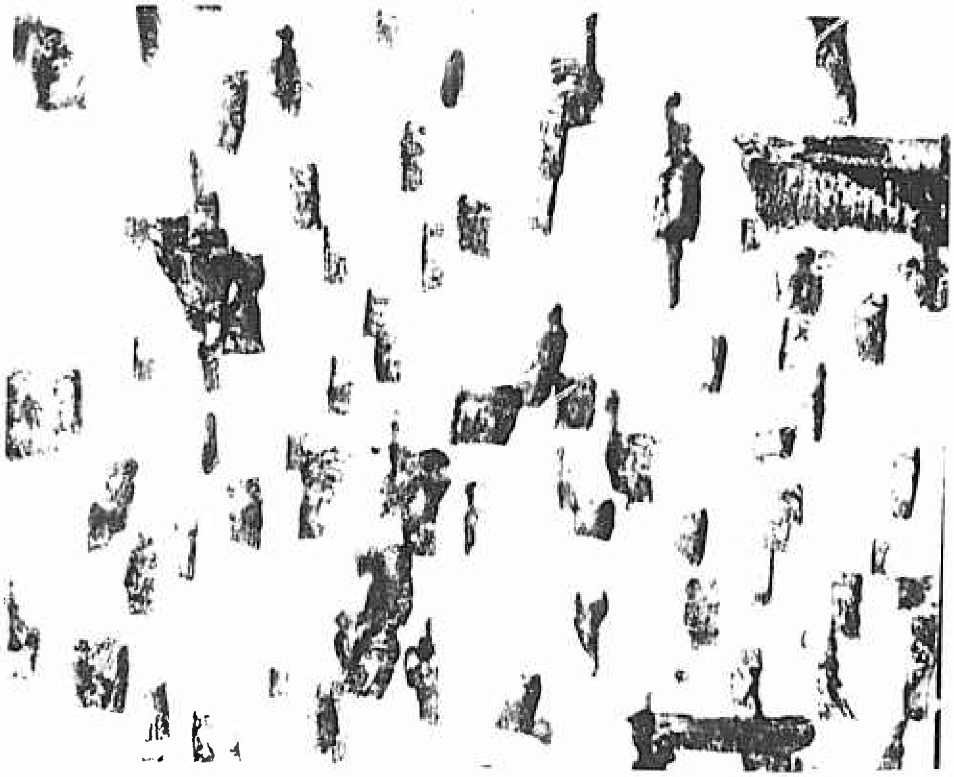
It is shown by these observations, that the number and length of the inclusions in chromium plate indicate the amount and stability of the chromium hydrides in the deposit as laid down. The amount of the hydride is determined by the bath composition and the plating conditions. The stability of the hydride is determined by these factors and by the temperature of the plate immediately after it is deposited. This temperature will be, in general, essentially the same as the plating bath temperature.

The sulphate concentration of the plating bath is very important in terms of the stability of the hydrides produced. The plate of Figure 15 illustrates the instability of the hydrides produced from baths with higher than normal sulphate concentration. In order to produce bright plates from this 20/1 acid ratio bath, it is necessary to use higher current densities than are used with more normal bath compositions. By such means the cathode film pH is driven into the range producing hydrides.



Etched Surface 49462 600X

Figure 14. Same sample and same view as shown in Figure 9, shown here at greater magnification. Note size, dispersion, and form of the inclusions. Note also the complete absence of any indications of grain structure. This surface was etched electrolytically for five seconds at 6V. in 10 per cent chromic acid solution. The inclusion films left unsupported by this treatment have fallen sidewise and their semitransparency is apparent.



Etched Surface 49463 1000X

Figure 15. Cross section of chromium plate produced from 20/1 acid ratio bath. A current density of 3 amps./sq.in. was used at a bath temperature of 50°C. The bath contained 250 g./l. CrO_3. The sample was electrolytically etched for five seconds at 6V. in 10 per cent chromic acid solution. Note wide dark areas where inclusions were lying in the plane of the etched surface shown or at an acute angle with this surface. Note also that here again the inclusions have fallen sidewise beside the cracks from which they extend.

However, the hydrides produced are very unstable.

Using the principles now available, it should be possible to examine a chromium plate of appreciable thickness under a microscope and approximate rather closely the bath composition and plating conditions employed in depositing the plate.

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CHAPTER IV

THE RELATION OF THE CHROMIUM PLATING PROCESS TO THE USES FOR THE PRODUCT

The common uses of chromium plate may be classified as decorative, wear resistant, and corrosion resistant. Some applications involve combinations of these general classifications. To obtain optimum results in any of these applications, the special characteristics of the chromium plating process should be understood and the plating conditions controlled accordingly.

The decorative uses for chromium plate are most familiar to everyone. Chromium plated automobile hardware and plumbing fixtures are encountered daily, and a surprising number of common household articles bear the lustrous bluish-white hue of "bright" chromium plate. The extreme chemical stability of this bright surface is the real key to the success of chromium plate in decorative use. A contributing factor, though of lesser importance, is the hardness of the plate.

It is believed that the oxide forming characteristic of chromium is responsible for its chemical stability. The surface of the plate is oxidized very quickly when plating stops. This oxide surface is so thin as to be transparent, but is very adherent and continuous. Thus, any appreciable chemical attack may take place only after the oxide surface is destroyed. Chemical stability exists in no other easily available white metal plate to a comparative degree. It should be remembered that the resistance to chemical attack is not due to the intrinsic inertness of the metal, but rather to a particular selectivity for oxygen from the surrounding environment. If environmental conditions do not permit the formation of, or cause the breakdown of, the oxide film, a considerable vulnerability to chemical attack may be expected.

Regardless of the resistance of chromium plate to surface discoloration, it is not a good protector for underlying metals when applied in the thickness usually used for decorative purposes (approximately 0.00002"). Discontinuities in the plate, consisting of pores in such extremely thin plates, expose portions of the basis metal to surface attack. The presence of pores in thin plates is not well explained by the literature or the present work. A possible explanation is related to the surface energy of the various crystal facets composing the surface of the substrate metal. Presumably some of these facets are in an energy condition in which they are more receptive to an electroplate than others. Thus, certain of the least receptive crystal facets simply do not receive a plate and a void in the plate exists over them. Upon continued plating, the edges of the plate grow into this void and gradually cap it over. Such an explanation may not be wholly sound and is merely presented for want of a better one. At any rate, the pores do exist and are extremely deleterious to decorative applications. If the plating is continued to produce a plate of sufficient thickness so that the pores are covered over, then cracking occurs because of the rise in cathode film pH and deposition of hexagonal hydride crystals attendant to continued plating. The cracks expose the basis metal in the same fashion as did the now covered pores.

Since neither of these two evils, porosity and cracking, may be entirely avoided, it has become common practise to provide real corrosion protection for plated steel articles by substrate deposits of copper and nickel. Chromium is then applied over the nickel in a thin coating to impart the prolonged blue-white brightness of chromium to the article. This same procedure is used on other metals such as zinc-base die castings. Brass articles may be plated with nickel, then with chromium, or may be plated with chromium alone, depending on the service requirements. As stated above, the thickness of chromium plate generally used is approximately 0.00002". This thickness of plate ordinarily contains essentially no cracks and a minimum of pores.

The thickness of decorative chromium plates may be increased somewhat with no loss in corrosion resistance by plating in the lower limits of the "bright" range of current densities. In this way, the rate of cathode film pH increase is minimized and a thicker plate may be obtained without the deposition of sufficient hydride crystals to cause cracking. Some sacrifice in brightness may be necessary, however.

The fact that the hardness of decorative chromium plates is much greater than the hardness of annealed chromium has been discussed to some extent. This increased hardness may be attributable to the extremely fine grain size in the plate and to the presence of shrinkage stresses below the stress limit necessary to cause rupture and cracking. Such stresses may arise from the decomposition of a relatively small proportion of hexagonal hydride crystals existing in the original deposit.

The fact that thin, decorative coatings of chromium plate are much softer than thicker coatings is not generally known. It is also not well proven. The reason for this is the difficulty in making accurate hardness measurements on extremely thin metal layers. However, a simple test will serve as a proof. When a very fine piece of emery cloth is rubbed lightly over a surface which bears a decorative chromium plate, the surface will be scratched and dulled by the grits. If a similar test is made on a plate several thousandths of an inch thick, scratches are produced with much greater difficulty. This was tried at intermediate plate thicknesses and it was found, qualitatively, that the plate hardness increases until a thickness near 0.0001" is reached. This may be interpreted as indicative of the proportion of hexagonal hydride in the plate as plating is continued.

The comparative wear resistance of plates of varying degrees of hardness is not definitely known and varies considerably with the application. Presumably, a very hard surface produces optimum wear resistance in a chromium plated surface. In the published literature, industrial hard chromium is often defined as consisting of deposits of bright chromium, 0.001" or over in thickness. It is commonly believed that lesser thicknesses of plate are not inherently less hard but are susceptible to failure by "breaking through" to the usually softer basis metal. It is now apparent that this view may contain an element of truth but does not correctly represent the entire picture. If numerous interconnected cracks reach from the plate surface to the basis metal beneath, the plate is effectively divided into isolated sections. The possibility of failure by "spalling off" of entire sections is then considerable. If the plate is made thicker, so that an individual crack never reaches over more than a small fraction of the distance between the basis metal surface and the plate surface, the entire plate is greatly strengthened. Failure by crushing or spalling is then much less likely to occur. However, a difference in actual hardness may be a major factor in the lesser wear resistance of thin plates as compared to thicker plates.

The strength of a chromium plate may presumably be increased by shortening the average crack depth in the plate. Very short cracks and a very hard plate are produced under the same conditions of bath temperature and current density from the conventional commercial plating bath. These conditions are temperatures in the range between 130°F. and 150°F. and current densities as high as can be used without obtaining a dull plate. Thus, if a plate for wear-resistant service is to be relatively thin, these conditions should be carefully maintained for best properties in the plate. If a plate is to be thick, it will probably be satisfactory regardless of what part of the bright current density plating range is used.

Applications for chromium plating in wear-resistant service have been of industrial importance for a considerable time. A disadvantage in such applications is the poor "wettability" of chromium plate. Apparently the surface energy of the oxide film is such that the surface is simply not wet by oils. This characteristic is reflected in poor lubrication in wear-resistant service which usually involves the use of the plate on new or used machine parts. The so-called "porous chromium", or "Van der Horst", process provides a solution to the "wetting" problem and yet retains the advantages of hardness in the chromium plate. This process was in use before the war but mushroomed to great commercial importance during the period of war-born shortages of replacement parts. This process involves plating thick layers of chromium on a basis metal surface under conditions which produce a desired crack pattern and a desired crack depth in the plate. The plate surface is then etched, ordinarily by merely reversing the current in the plating bath so that the plated part is the anode. The cracks in the plate surface are greatly widened by this procedure and the entire surface is etched to a certain extent. The etched surface is then honed to provide a surface consisting of smooth plateaus surrounded by fairly wide, channel-like voids. These voids serve as oil reservoirs and oil passages so that the poor wettability of the plateau areas is counteracted. Another type of surface termed a "pitted" type is produced in which the voids appear as large pits in the surface rather than as somewhat narrower, long channels. It is not immediately clear why these pit-type voids are formed upon etching. A study of the crack system present in such a plate before etching would probably reveal the answer. A guess in this direction is that the pits represent the meeting points of several cracks.

The porous chromium process has been particularly useful for prolonging the service life of cylinders or cylinder liners for internal combustion engines or for top piston rings in engines not having plated cylinders. The entire cylinder wall is plated with porous chromium. In the case of piston rings, only the top ring is ordinarily plated as the lower rings require no such lubrication aid to function properly over a sufficient service life.

After an engine cylinder is worn to an unserviceable condition, it may be reclaimed by grinding the cylinder walls to a uniform oversize dimension, plating with chromium to a slightly undersize dimension, reverse etching to widen the cracks in the plate, and honing to the desired final dimension. The processing costs attendant to such reclamation operations are ordinarily considerably less than the original cost of the cylinder or cylinder liner, and the reclaimed product may be expected to wear several times as long as the unplated original.

The lack of corrosion resistance of chromium plate was discovered early in the history of chromium plating. This shortcoming did not outweigh the advantages of chromium plate and the use of more corrosion-resistant substrate plates was adopted as described earlier. This procedure is extremely expensive when the volume of total production so treated is considered. There is no indication that a method can be devised to provide more corrosion resistant, decorative chromium plates. The only way in which the corrosion resistance of a bright plate can be improved is to make it so thick that no crack reaches from the plate surface to the basis metal. Such a thick plate is economically out of the question for ordinary decorative service as it is more costly and more difficult to produce than the composite plates now in use. For special service requiring both corrosion resistance and wear resistance, plates several thousandths of an inch thick may sometimes be very practical. This will be especially true if the temperature of the service is somewhat elevated.

Where optimum corrosion resistance is desired and the extreme hardness of bright chromium is not required, a high-temperature chromium plate should be applicable. By plating from the conventional commercial plating bath at temperatures close to 100°C. with current densities in the range from one to ten amps./sq. in., the cathode film pH is maintained so low that a relatively unstressed, body-centered cubic plate is produced. It is believed that the diffusion rates obtaining at such a high bath temperature are so high as to prevent the cathode film pH from rising greatly. The plate so produced contains no cracks or inclusions and is soft by comparison with bright chromium. It has a dull surface, though white, and tends to retain fingerprints as oily appearing areas. It is probably of little use for decorative purposes because of the cost involved in buffing such a plate. The most important feature of this type of plate is its complete lack of cracks and inclusions.

Because of this it has good possibilities as a corrosion-resistant coating. When any chromium plate is heated in air to temperatures in the region of 1000°F., the surface oxide film thickens to the extent that interference colors appear. However, the oxide film is adherent and provides a permanent protective coating. It is believed that the high-temperature plate would constitute an excellent corrosion-resistant coating on steel or other metals for elevated temperature service up to 1000°F. and possibly even higher.

A second application for this high-temperature plate has been found in providing a machineable plate. The plate is sufficiently soft to be machined with a high-speed tool. This is a distinct advantage as all "bright" industrial chromium is so hard and brittle that it may be dimensioned only by grinding with abrasive wheels or by honing.

The present outlook for chromium plate in commercial applications is favorable. While cheaply made plastic articles may replace chromium plated metal articles in the decorative field to a considerable extent, the industrial applications for chromium plate are developing at a considerable pace. It is expected that these applications as an engineering material, specified by technically trained personnel, will be aided by the present work.

CHAPTER V

'The time has come', the Walrus said,
'To talk of many things:
Of shoes - and ships - and sealing wax -
Of cabbages - and kings -
And why the sea is boiling hot -
And whether pigs have wings.'

Lewis Carroll
Through the Looking Glass

The Mechanism of Precipitation of Chromium Hydrides

Since no direct experimental evidence is available, the question as to how a plate of chromium hydride is laid down is purely a speculative one. Two mechanisms are easily visualized. It might be supposed that the cathode surface is practically covered by a layer of hydrogen atoms. Chromium ions discharged near the cathode and precipitating on it then would simply be codeposited with the hydrogen in the same manner in which alloys of two or more metals are considered to be deposited.

A second possible mechanism involves the formation of the hydrides in the cathode film and their subsequent precipitation on the cathode as discrete units of formula Cr_2H to CrH_2. This mechanism is perhaps most easily reconciled with the view expressed earlier that the actual reduction of chromium ions to chromium metal is accomplished by atomic hydrogen.

As hydrogen atoms reduce chromium ions through the successive stages from the hexavalent to the divalent forms, the electron transfer would presumably result in the hydrogen diffusing off through the solution as hydrogen ions. However, it is possible that the hydrogen atoms which then bump into the divalent chromium ions do not merely transfer electrons and detach themselves. A bonded arrangement of hydrogen and chromium might occur in which the hydrogen is inescapably held. This combination would be positively charged and hence yet attracted to the cathode. Upon precipitation at the cathode, the electrons necessary to release the hydrogen-chromium bonds are available. However, a metastable interstitial solid solution now exists and the hydrogen escapes but slowly.

The fact that hydrides are more stable the less acid the environment in which they are formed, or from which they are precipitated, is clearly established by the experimental evidence. This is not readily explained. At first glance it would seem more logical were the hydrides more stable when produced from the more acid cathode films where the hydrogen ion concentration is greatest. This is believed to be an important point in electrochemical phenomena, and will bear detailed study.

The relative instability of the chromium hydrides is not surprising in view of their structures. The hydrogen atoms have a coordination number of 4 in both the hexagonal and face-centered cubic hydride arrangements. Pauling states that such structures are ordinarily metastable. It is not entirely clear whether the bonding of the chromium atoms is that of a normal hexagonal close-packed or face-centered cubic lattice simply somewhat expanded by the interstitial hydrogen atoms, or whether the hydrogen atoms are bonded to the chromium atoms in a metallic type bonding arrangement. The latter view is favored. That is to say; the hydrogen is believed present in the hydrides as protons, each of which has contributed an electron to the structure, just as any metal atom contributes an electron or electrons to the so-called "electron cloud" to become a metal ion in the structure.

In this light, the term "alloy" is probably a more exact one. However, the use of "hydride" to describe these metal-hydrogen structures has appeared in the published literature for many years and no attempt to change this practise is likely to be successful.

Hydrides of Other Metals

Nickel and iron plating are, in many ways, similar to chromium plating because of the effects of plating conditions on the properties of the plate. It is believed that a properly directed research would produce hydrides of both of these metals and show that some of the properties of the plates are related to hydride formation. It is well known that iron plates contain large amounts of hydrogen and that they are hard and brittle until this hydrogen is removed by heating. By refrigerating an iron plating bath, a plate was produced during the present work which was extremely hard. It could be scratched with a tungsten-carbide tool, but with difficulty. Similarly, it is well proven that nickel plates commonly contract as they are deposited and that this contraction becomes more noticeable as the pH of the cathode film increases. Nickel plates have also been observed to expand during deposition. It is entirely possible that such phenomena can be explained on the basis of hydride deposition and decomposition. The situation for iron and nickel is much the same today as it was for chromium plate at the start of the present research.

The present work and extensions of it may also be of help in studying electrode reactions such as are of interest to workers in the field of corrosion of metals. It is currently postulated that an inhibitive hydride film forms on many metals when they are exposed to conditions where they tend to replace hydrogen ion in solution. The hydride film is believed to form a barrier to further electrochemical action.

By producing and working with the hydrides of various metals, and determining their properties, information regarding the plausability of the postulates will be obtained.

The Overvoltage of Metals

There are two kinds of overvoltage which are commonly considered in electrochemical work; hydrogen overvoltage, and metal overvoltage. Hydrogen overvoltage is defined for a given system as the numerical difference between the theoretical and experimental values of voltage necessary to produce visible hydrogen evolution at a cathode. Metal overvoltage is defined as the difference between the actual deposition potential and the potential value to be expected for a reversible electrode in the same solution. The present discussion is concerned only with metal overvoltage.

It is considered significant that of the transition group metals, Cr, Mn, Fe, Co, and Ni, all have considerable metal overvoltages. Glasstone has advanced the view that metal overvoltage is a result of deposition of the metal in an active, or unstable state. A rate control phenomenon was considered in which the slowness of conversion from the unstable form to the normal form of metal on the cathode gives rise to the overvoltage.

The present work would indicate that Glasstone's views, which incidentally were conjectural rather than founded on experiment, were probably a step in the right direction. However, the rate control feature is rejected. It is believed more proper to say that the overvoltage of metals is due to the deposition of unstable structures of greater free energy than the normal form of metal composing the cathode. The rate of decomposition of these unstable structures is not seen to have any bearing on the overvoltage. The spontaneous decomposition of chromium hydride is ample proof that its free energy is greater than the combined free energy of the chromium metal and atomic hydrogen which constitute the decomposition products. Whether the decomposition occurs during the plating process or several days later is not seen to have any effect on the metal overvoltage.

It is true that the only direct evidence in support of the above hypothesis is that gathered for chromium plating in the present research. Similar work with at least one more of the transition elements appears necessary before a proper theory can be established.

Properties of Plating Brighteners

So far as is known, the concept of the action of the trivalent dispersoid in the chromium plating bath presented in Chapter II is original with the present work. It is desired to consider the case for carrying over to other types of plating baths the concept of bath constituents operating according to their isoelectric properties.

Attempts at fundamental studies of plating brighteners have not yet met with any appreciable degree of success. The present-day scientist searching for a brightener for a new plating bath is on approximately the same basis as certain Edisonian scientists of the twenties who assembled all the vegetable products they could lay hands on and tested each of them as bath additions. The theories commonly accepted for the functioning of brighteners involve the electropositive character of these materials which are usually colloidal or of high molecular weight. During plating, the brighteners are attracted to the cathode and particularly to the areas of highest current density on the cathode. The theory holds that the brighteners are adsorbed on these areas of highest current density and thus plating on these areas is impeded by the adsorbed material. Since any irregularities projecting from the plate surface constitute high current density areas, these areas are in effect masked, while any depressions in the plate surface are in a position to receive depositing plate at an increased rate.

One of the greatest difficulties with this theory is that the brighteners are brought to the plate surface and adsorbed there, then simply left hanging there. One author, after an extensive discussion of the attraction of the brightener particles to the cathode, and their adsorption there, states that "the cycle is then repeated". However, the complete cycle cannot be repeated until the cathode surface is back in its original condition without the adsorbed material.

It is true that certain indications of the inclusion of brighteners in plates have been noted. Cathode efficiencies of over 100 per cent have been explained on this basis. In other cases, the appearance of striations in plates, similar to Liesegang bands in minerals, have been ascribed to the periodic adsorption of brighteners which are supposedly covered by the subsequently deposited plate. However, these are exceptional cases. In general, the inclusion of brighteners in plates is not established as a usually occurring phenomenon.

Consider the possibility that the above theory is correct to the point where adsorption occurs at the cathode surface — really as far as the theory goes. Then alter the conditions at the solution-cathode interface so that the adsorbed brightener is detached from the cathode surface and leaves the cathode area. Then again revert to the interfacial conditions favoring adsorption, and the theory is at least logically complete.

Changes in pH of the cathode film may be the only condition necessary to accomplish these results. If the cathode film pH is brought into the region of the isoelectric point of the brightener, then the brightener can be viewed as moving toward or away from the cathode according to the pH value existant in that region. There is a strong possibility that increase in solution pH may serve to release adsorbed materials from a surface. The work of Taggart and his collaborators, and of others in the field of mineral dressing, has illustrated the importance of the solution pH in adsorption phenomena. In many cases, materials will be adsorbed from a solution at a solid surface under certain condition of pH in the solution. Under other conditions of pH (usually higher pH) the adsorption does not occur. Adjustment of pH, or other conditions, at the solution-solid interface to obtain the desired results, is termed "conditioning" in the field of mineral dressing.

Drawing further from the studies of Taggart and others, the whole concept of adsorption of brighteners becomes suspect. The possibility of direct chemical bonding of brighteners and the surface atoms of the cathode is suggested. There is little ground for conclusive argument on the data yet available. However, a course of study is indicated and also a method of experimentation.

The classification of brighteners into groups has been attempted by several authors. Certain types are believed to function as brighteners only after reduction at the cathode. Others are used in combination. For instance, a metal brightener is always complemented by an organic brightener.

It is noteworthy that the metal brighteners, which have been used in acid plating baths at various times in plating history, are metals which readily hydrolyze to form oxides or hydroxides of a colloidal nature. Among these metals are Se, Te, Zn, and Co. It is also considered significant that the organic materials used in conjunction with these metals are known to "protect" the hydroxides from precipitation at their respective isoelectric points. It appears that the case for cathode film pH control by brighteners operating at their isoelectric points to control diffusion to and from the cathode area is most likely to find substantiation in this class of materials. When such substantiation is found, the rest of the brightener groups can be studied from the same point of view with more hope of success than is now apparent.

Pickling Inhibitors

The mechanism by which pickling inhibitors operate is not presented in entirely convincing arguments in the literature. Here, as in the case of plating brighteners, extensive studies have led to amazing conclusions. A recognized expert on inhibitors states that the outstanding property of these materials is that they all can take up hydrogen. The inference is that the inhibitor takes up the hydrogen being displaced from solution by dissolving metal. The way that further attack on the metal is prevented is not made clear. Other authors seem to have done little better.

It has been pointed out that plating brighteners are usually pickling inhibitors and vice versa. This leads to an examination of the two processes, brightening plates, and inhibiting pickling, to see what similarity exists between them. Most inhibitors operate by cathodic control (i.e.,by polarizing the cathodic areas in the metal surface). Therefore inhibitors, like brighteners, operate at the cathode. The pH tends to rise at the cathode when hydrogen is discharged there. Therefore, both brighteners and inhibitors operate in media somewhat less acid than the solution proper.

The similarities in the materials used in these two applications and the similarities in the conditions under which they operate are such that any study of brighteners is also a study of inhibitors. It appears that experimental evidence obtained in either of these separately considered fields can be correlated with the other field. A tremendous volume of empirical information has now been accumulated. It but remains to devise a theory to encompass this information. The undefined field of "surface chemistry" certainly offers opportunity for far-reaching theoretical developments at this time.

The Periodic Phenomena at Cathodes

The periodic cathode phenomena reported in Chapter II remain to be discussed. It will be remembered that iron and copper wires were made cathodic in a chromic acid solution. As the potential across the cell was slowly raised, the cell potential was observed to undergo periodic fluctuations between a high and low limit and the cell current likewise fluctuated. The high cell potential was accompanied by a low cell current and the low cell potential by a higher cell current. The two conditions are illustrated by the following listings:

H_2 evolved	No H_2 evolved
Cell current low	Cell current high
Cell voltage high	Cell voltage low

The explanation logically advanced to explain these phenomena is that hydrogen bubbles partially mask the cathode during the periods of hydrogen evolution. This effectively decreases the cathode area and operates to lower the total cell current and increase the cell voltage. When hydrogen evolution stops, the entire cathode area passes current and the cell voltage accordingly is low.

The above explanation is but superficial, however, and explains some of the effects of the periodic performance but not the basic causes of this phenomenon. Also unexplained are the facts that the voltage fluctuations are gradually reduced to a point of equilibrium, and that a cathode brought to an equilibrium condition retains that condition even upon exposure to air, but loses it upon rubbing with a cloth.

Some have postulated the formation and breakdown of an oxide film as the cause of the periodic phenomenon. Others visualize the formation of a metal hydride layer on the cathode as the cause. It is difficult to understand why such films should form and then break down almost completely before reforming, and why, after some time, an equilibrium condition should arise. A possible explanation of the formation and breakdown of an oxide film might be advanced as follows: The initial period of hydrogen evolution is accompanied by a considerable pH increase in the cathode film. When this pH becomes sufficiently high, a relatively stable oxide suddenly forms on the cathode. The atomic hydrogen being generated at the cathode is then used up in reduction of this oxide. At the completion of the reduction reaction,each individual hydrogen atom is back in solution as a hydrogen ion. Therefore, there is no drain of hydrogen ions out of the cathode film. Diffusion effects occurring during this film reduction period reduce the cathode film pH to the approximate level of the pH of the solution proper. When the oxide film reduction reaction is complete, gassing again commences and continues until a new oxide film is formed.

This hypothesis meets with difficulty when the attainment of equilibrium is considered. Why should equilibrium be attained at intermediate cell current and voltage values? The experimental evidence gives no direct support to the idea that an incomplete oxide film is formed on the metal, allowing hydrogen evolution to proceed at the breaks in the film. However, it might be suggested that, during the initial oxidation — reduction cycles, preferential etching occurs at the metal surface. This leaves the surface roughened or pitted to a considerable extent. Now the solution in the pits remains more alkaline than that around the projections in the metal surface. Therefore, gassing continues at the surface and the pits remain filled with high pH solution so that the oxide on the pit surfaces is not reduced. It is certain that etching of the cathode surface does occur at potentials between the bubble potential and the metal deposition potential. Several times, during the present research, it was noted that brass cathodes were severely attacked after several hours in this potential range in a chromium plating solution. The attack was considerably greater than that occurring by chemical action during simple immersion tests.

Some authors have attributed the extensive polarization at cathodes to the formation of metal hydrides at the electrode surface. This concept would relate the hydrogen overvoltage of an electrode to hydride formation. It is difficult to visualize a hydride film forming and breaking at the cathode surface as a cause for the periodic phenomena. It appears that here, too, additional work is indicated.

The Future of the Electroplating Field

It is hoped that the discussions of this chapter will serve to emphasize the importance of a new, undefined, branch of science, related to the phenomena occurring at solution-metal interfaces. It would appear that study of such phenomena offer the best possibilities for advancement in the understanding of electroplating. It has been apparent for some time that a similar situation exists in the field of ore dressing and in several other not otherwise related fields.

The present research has provided answers to more questions than the original plans encompassed. However, like most researches, it has stirred up many questions which remain to be answered. These represent a challenge to continue the search for the reasons underlying the phenomena concerned. Let us attack from all directions.

APPENDIX

APPENDIX SHEET I

Calculation of a_o for Face-Centered Cubic Chromium Hydride
Copper Radiation

2θ	θ	$\sqrt{\Sigma h^2}$	$\log\sqrt{\Sigma h^2}$	$\log\sqrt{\Sigma h^2}+\log\frac{\lambda}{2}$	$\log \sin\theta+10$	$\log a_o$	a_o
40.7	20°21′	$\sqrt{3}$	0.23856	0.12468	9.54127	0.58341	3.832A
47.25	23°40′	$\sqrt{4}$	0.30103	0.18715	9.60359	0.58456	3.842
68.8	34°24′	$\sqrt{8}$	0.45155	0.33766	9.75202	0.58563	3.851
83.1	41°33′	$\sqrt{11}$	0.52070	0.40682	9.82169	0.58512	3.847
87.2	43°36′	$\sqrt{12}$	0.53959	0.42571	9.83861	0.58710	3.864

Avg. = 3.85A

$V_{F.C.C.} = a_o^3 = 3.85^3 = 57.07A^2$ = volume of a 4-atom unit cell of F.C.C. hydride.

$\frac{57.07}{2} = 28.53A^2$ = volume of a 2-atom unit of F.C.C. hydride.

a_o for B.C.C. Cr = 2.878A.

$V_{B.C.C.} = a_o^3 = 2.878^3 = 23.84A^3$ = volume of 2-atom cell of B.C.C. Cr.

$28.53 - 23.84 = 4.69A^3$ = volume of shrinkage during decomposition of F.C.C. hydride to B.C.C. metal.

$4.69A^3$ = 16.4% of $28.53A^3$.

Shrinkage during decomposition is 16.4% of the volume of the hydride.

$n\lambda = 2d\sin\theta$ $\quad d = \frac{a_o}{\sqrt{\Sigma h^2}}$ $\quad a_o = \frac{\lambda}{2}\frac{\sqrt{\Sigma h^2}}{\sin\theta}$

APPENDIX SHEET II

Calculations for Hexagonal Close-Packed Chromium Hydride
Copper Radiation

Crystal Plane	θ	2θ
100	19°5'	38.2°
002	20°23'	40.8°
101	21°44'	43.5°
102	28°32'	57.4°

$$\sin\theta = \frac{\lambda}{2}\sqrt{\frac{4}{3}\cdot\frac{h^2+hk+k^2}{a^2}+\left(\frac{l}{c}\right)^2}$$

$a = 2.717$

$c = 4.418$

$V_{H.C.P.} = 0.866\ a^2c = 0.866 \cdot (2.717)^2 \cdot 4.418 = 28.24^3$

= volume of a 2-atom unit cell of H.C.P. chromium hydride.

$V_{B.C.C.} = 23.84A^3$ from Appendix Sheet I

$28.24 - 23.84 = 4\ 40A^3$ = volume of shrinkage during decomposition of H.C.P. hydride to B.C.C. metal.

$4.40A^3 = 15.6\%$ of $28.24A^3$

APPENDIX SHEET III

Body-Centered Cubic Chromium X-ray Data
Copper Radiation

Plane	Σh^2	$\frac{\log \Sigma h^2}{2}$	$\log \sin \theta$	θ	2θ	2θ
110	2	0.15051	$\bar{1}.57754$	22°13′	44°26′	44.4°
200	4	0.30103	$\bar{1}.72806$	32°19′	64°38′	64 6°

$\frac{\lambda}{2} = 0.76934 \qquad \log \frac{\lambda}{2} = 1.88612$

$a_o = 2.878 \quad \log a_o = 0.45909$

$\sin 6 = \frac{\lambda}{2} \cdot \frac{\sqrt{\Sigma h^2}}{a_o}$

Calculation of Ratio of H Atoms to Cr Atoms for Sample of F.C.C. Hydride

0.0329 gms. = weight of Cr

12.21 ml. = volume of H_2 (S.T.P.)

$\frac{0.0329}{52.01} \times N = 0.0006326N$ = No. of Cr atoms

$\frac{12.21 \times 2}{22,400} \times N = 0.0010902N$ = No. of H atoms

$\frac{0.0010902}{0.0006326} = 1.7+$ = No. of H atoms for each Cr atom.

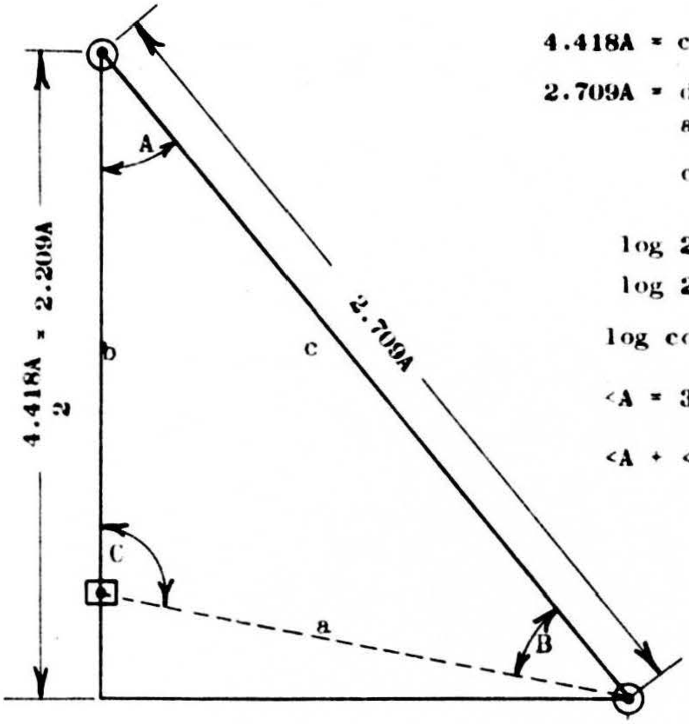
52.01 = atomic weight of Cr

22,400 = volume of 1-gram mol. of gas

N = Avagadro's No.

APPENDIX SHEET IV

Calculation of Size of Hydrogen-Filled Interstices in Hexagonal Close-Packed Chromium Hydride



4.418A = c distance of unit cell

2.709A = distance of closest approach of chromium atoms

$\cos\angle A = \frac{2.209}{2.709}$

$\log 2.209 = 0.34420$

$\log 2.709 = 0.43281$

$\log \cos\angle A = \overline{1}.91139$

$\angle A = 35°14'14''$

$\angle A + \angle B = 2\angle A = 70°44'28''$

Note:

⊙ = centers of chromium atoms

⊡ = center of hydrogen atom

$180° = 179°\ 59'60''$

$70°\ 44'28''$

$\angle C = 109°\ 15'32''$

Sine law

$a = \frac{c \sin A}{\sin C}$

$\log c = 0.43281$

$\log \sin A = \overline{1}.76257$

0.19538

The radius of Cr for a coordination number of 6 is 1.28A

$\log \sin C = \overline{1}.97503$

$\log a = 0.22035$

$a = 1.66A$

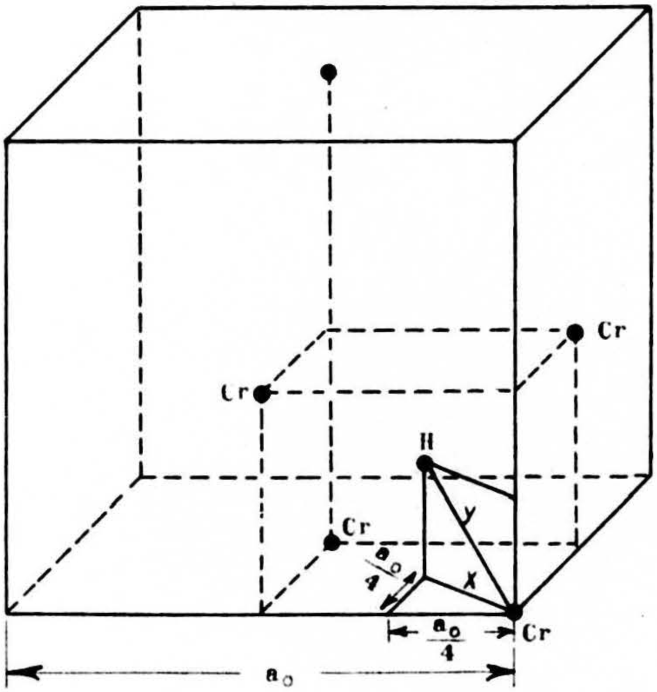
-1.28

$0.38A = r_H$

Radius of the H atom in the hexagonal close-packed chromium hydride is 0.38A

APPENDIX SHEET V

Calculation of r_H in F.C.C. Chromium Hydride



$$x^2 = \left(\frac{a_o}{4}\right)^2 + \left(\frac{a_o}{4}\right)^2$$

$$y^2 = x^2 + \left(\frac{a_o}{4}\right)^2$$

$$y = \sqrt{3\left(\frac{a_o}{4}\right)^2}$$

$$a_o = 3.85\text{A}$$

$$y = 1.67\text{A} = r_H + r_{Cr}$$

The radius of the chromium atom with a coordination number of 12 is 1.28A.

1.67A - 1.28A = 0.39A = radius of hydrogen atom in face-centered cubic chromium.

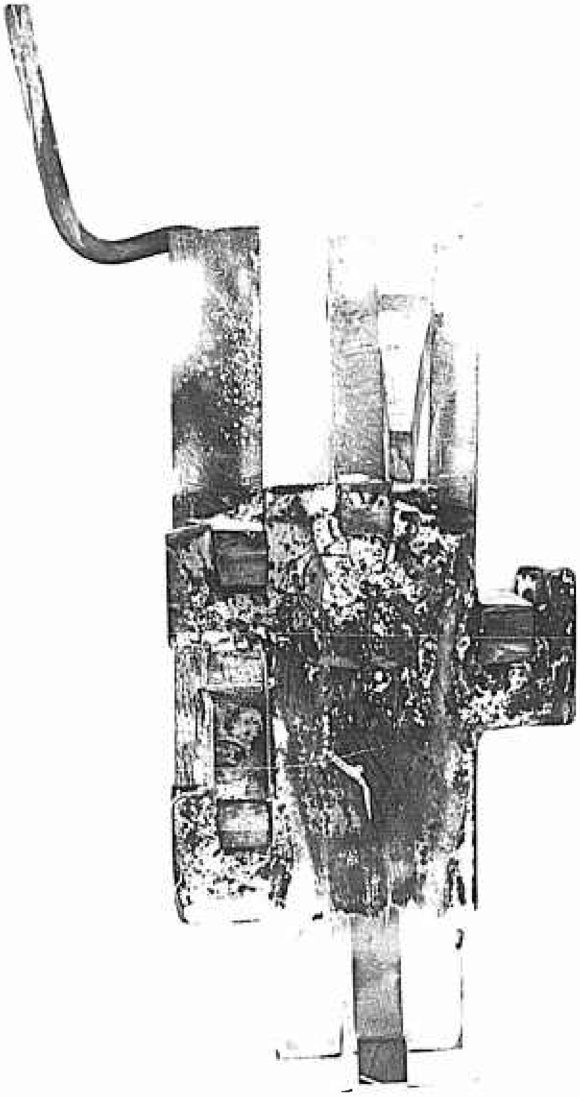
APPENDIX SHEET VI

Apparatus Used for Chromium Plating

The apparatus used in the production of plates for this study consisted of only two special items. These were a simple arrangement for cooling the plating bath, and an equally simple fixture for holding the plating anode and the sample being plated.

The plating baths were held in glass beakers of from 400-ml. to 1-liter capacity. When the baths were to be heated, this was done on an electric hot plate equipped with a temperature control. When the baths were to be cooled below atmospheric temperature, the glass beakers were suspended in a "refrigerator" consisting of a tinned can insulated on the outside with several layers of corrugated cardboard. The can measured approximately 7 by 7 inches on the bottom, and 6.5 inches high. Cracked dry ice was used as the refrigerant and was added through a hole in the top of the can beside the suspended beaker. The bath temperatures could easily be maintained within a range of ± 4°C. by this method and closer control was possible through constant surveillance.

The plating fixture was constructed of plastic (methyl methacrylate) sheet. The assembled fixture and its component parts are shown in the photographs of Figure 1 and Figure 2. The anode was made of antimonial lead and the electrical connection to the anode was carried through the plastic anode holder. The brass slug cathodes ($\frac{1}{2}$" in diameter) were held in a 7/16" hole, countersunk to $\frac{1}{2}$" diameter. A cathode slug was in position in the cathode holder as shown. The electrical connection to the cathode was accomplished through a platinum wire in the cathode contact member. This member was wedged into the countersunk hole against the cathode, thus masking the back of the cathode while holding it at the bottom of the countersunk portion of the hole.



47634

Figure 16. Plating fixture — assembled

APPENDIX SHEET VIII

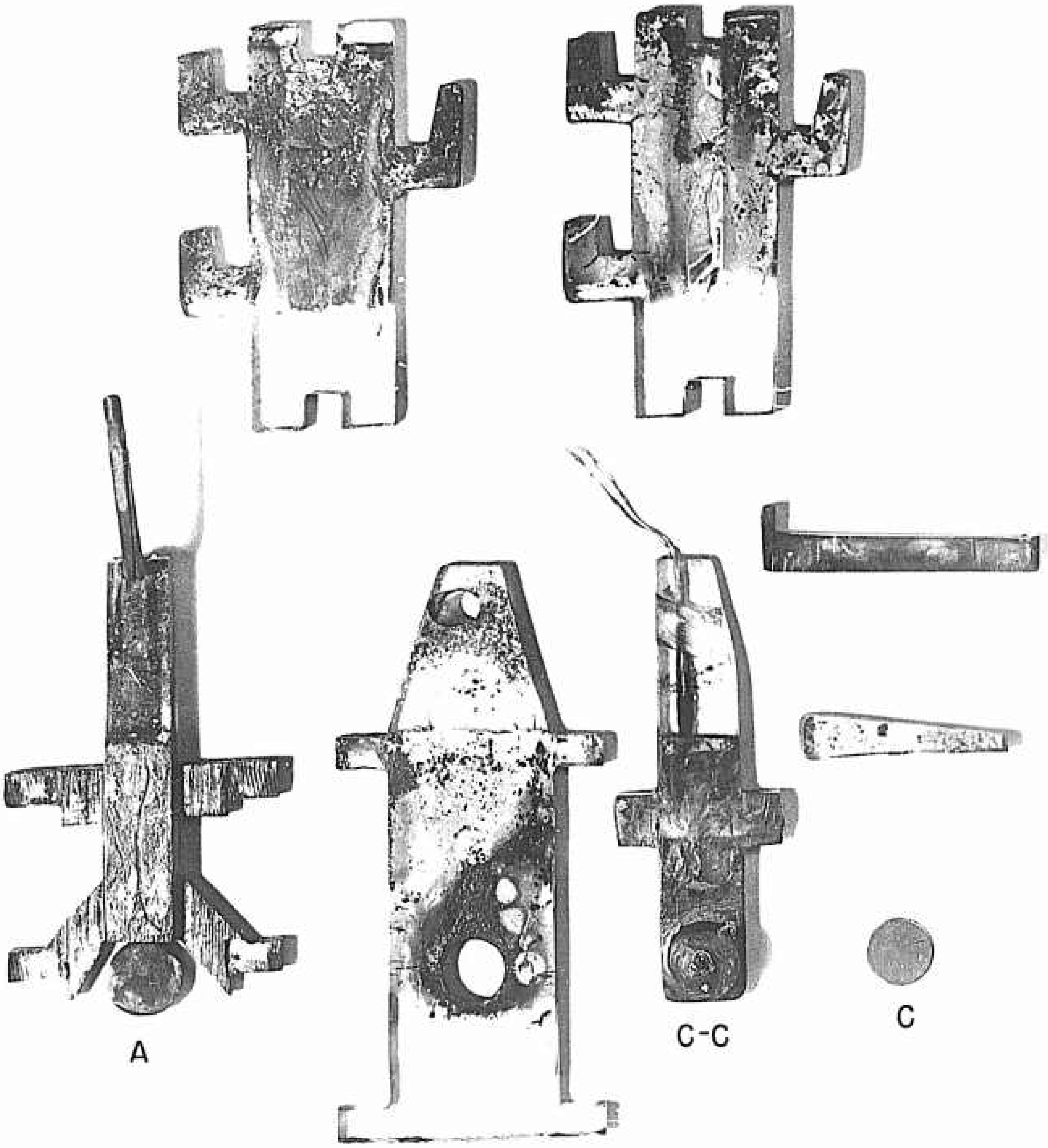


Figure 17. Plating fixture disassembled to show component parts. A — Anode. C-C — Cathode contact member. C — Sample cathode slug.

AUTOBIOGRAPHY

I, Cloyd Arten Snavely, was born [redacted] [redacted] [redacted] [redacted] [redacted] I received my secondary school education in [redacted] [redacted] [redacted] [redacted] My undergraduate education was obtained in Columbia College of Columbia University from which I received the degree Bachelor of Arts in 1939. I then entered the Engineering School of Columbia University, receiving the degree Bachelor of Science in 1940, and the degree Master of Science in 1941. I was called to active duty in the U. S. Navy in June, 1941, and remained in that status until September, 1945. In October, 1945, I was appointed a Battelle Fellow at The Ohio State University, which appointment I held while completing the requirements for the degree Doctor of Philosophy.

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