THE CORROSION OF DUCTILE TITANIUM

By

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PREFACE

In the last decade the application of fundamental advances in the basic sciences has resulted in tremendous technical progress. With this progress has come the increasing realization of the inadequacy of many of our construction materials. Many of the most recent technical advances are limited severely because of inherent inadequacies in the metals and nonmetals. The modification of existing materials has been rapid, but it is in the nearly virgin field of the so-called "rarer metals" that the greatest promise appears to lie.

The term "rarer metals" has evolved not so much because of scarcity but because of specific processing difficulties. The Bureau of Mines, recognizing the need for exploratory study on relatively neglected metals and nonmetals, initiated, as part of its wartime activities, a broad research program in this field. One of the most promising results of this program was the development of a process for producing ductile titanium metal. Previously, the use of this metal as a structural material was overlooked because of brittleness. The Bureau of Mines Process however, produces a ductile metal with total impurities below 1.0 percent.

Ductile titanium has two very outstanding properties which contribute to its use by modern industry: high strength and light weight. The proportional limit of cold worked titanium is as high as 85,000 pounds per square inch, which is comparable in value to heat treated steels and aluminum bronzes. Its density however is approximately half that of these metals giving titanium very high proportional limits for a stated weight of section.

The ductile metal can be easily worked by cold forging, and the forged ingots can be either cold or hot rolled into sheet.

These attractive features and its potential importance as a construction material of great economic value have inspired a number of industrial laboratories to initiate programs for evaluation of the commercial potentialities of titanium. The Pigments Department of the E. I. duPont de Nemours and Company, Inc., has undertaken an extensive research on the production of the metal and has offered sponge and ingot metal of high purity (99.5%) for sale at $5.00 per pound. This price is low in comparison to the initial offering price of such metals as aluminum and magnesium, now common. Extensive programs designed to determine possible applications and limitations of titanium have been set up by various branches of the armed forces of this country, and many private institutions are employed in cooperative research with the government.

One of the primary considerations in utilizing materials of construction and in developing new products is corrosion. Information on the corrosion of titanium will undoubtedly serve as a guide to other researches and is therefore extremely important. Unfortunately, literature dealing with the corrosion of titanium is rather scattered and questionable because of the variable purity of the metals tested.

The lack of comparative quantitative information on the corrosion of titanium and the very great importance of such information led to the investigation presented in this dissertation. This study is a part of a joint research project on the corrosion resistance of metals by the Metallurgical Division of the Bureau of Mines and the Department of Chemical Engineering of the University of Maryland.

PART I - HISTORICAL

CHAPTER I

GENERAL

In order to attain a thorough understanding of the problem of corrosion of titanium it is desirable to become familiar with some of the more important historical facts concerning the discovery, occurrence, and early attempts to isolate the pure metal. Such a study enables one to understand why titanium did not come to be considered as a material of construction until only recently.

A. Discovery. The presence of titanium was first discovered by W. Gregor (13) in 1791 through a study of the black sands of Menacon near Falmouth, Cornwall. In 1794, M. H. Klaproth (16) found a naturally occurring metallic oxide possessing peculiar properties. He inferred this to be the oxide of a new metal which he called titanium. All of the early investigators were unable to isolate the pure metal, and usually worked with it in an oxide form. It was not until 1825 that the impure metal was isolated by J. J. Berzelius, (2) and again by F. Wohler (33) in 1849.

B. Occurrence. Titanium has been found to be very abundant in the earth's crust, but it is always found in a combined state, never as the free metal. F. W. Clarke (4) has estimated that 0.62% of the lithosphere and 0.58% of known terrestial matter is titanium. Thus it may be seen that titanium is the ninth most abundant element in the

earth's crust, although for many years it has been regarded by many as a "rare element."

Although titanium occurs in a large number of minerals, there are only two which are important from an economic point of view. The first is rutile or titanium dioxide which contains theoretically 59.95% titanium, but usually iron is present in a large amount along with SiO_2 and small amounts of chromium and vanadium. Ilmenite is the second important mineral. This is thought to be ferrous titanate, $FeTiO_3$, isomorphous with pyrophanite, $MnTiO_3$, and geikielite, $MgTiO_3$ (28).

Until recently the world's supply of titanium ores came largely from the beach sand of Travancore, India. A large domestic supply has now been developed in the Adirondack region of New York, and other known deposits occur in Virginia, Wyoming, Arkansas, and several other states. Great deposits of titaniferous magnetite sands have been found in Japan while other titanium ore deposits are found in Russia (5).

C. Early Attempts to Prepare the Metal. After consideration of the knowledge now available it is probable that Berzelius and Wohler (2, 33) never succeeded in preparing pure titanium. They probably had obtained mixtures of the nitride and carbide which possess a metallic appearance and are good electrical conductors.

In 1887 metallic titanium of 95% purity was prepared by Nilson and Pettersson (22) through the reduction of titanium tetrachloride with metallic sodium in a steel bomb. In 1895 metallic titanium of 98% purity was obtained by Moissan (21) through the reduction of titanium dioxide by carbon in an electric furnace. Hunter (15) prepared titanium with a purity of 99.7 - 99.9% by heating titanium tetrachloride with an equivalent amount

of sodium metal in an iron bomb. Similar preparations have been made by many investigators (23, 24, 20). Hunter's process was somewhat modified by Billy (3) who passed titanium tetrachloride vapors over sodium hydride at 400°C. The product contained much hydrogen, as would be expected. This was almost completely removed by heating to 800°C in a high vacuum. Van Arkel (32) treated pure K_2TiF_6 or Na_2TiF_6 by heating with sodium metal in an iron tube. The metal thus obtained was used to prepare pure titanium metal by the iodide process to be described later. The reduction of the fluotitanates does not require as high a pressure as the sodium reduction of titanium tetrachloride, but the fluotitanate must be absolutely free from moisture.

PART I - HISTORICAL

CHAPTER II

PREPARATION AND PROPERTIES OF DUCTILE TITANIUM

Corrosion studies to be of any value in further researches or design applications must be carried out upon materials which are economically available for such purposes. The various processes which hold promise for the commercial production of ductile titanium and the methods of fabrication are now presented so that a complete history of the various metals studied may be defined. A review of these processes suggests where impurities were obtained in the final product and indicates where comparative corrosion studies are necessary.

A. Decomposition of Titanium Iodide. At present there are only two methods for producing titanium metal pure enough to be ductile at room temperature. The first process involves the thermal decomposition of titanium iodide on a heated surface. Iodine is liberated while the metallic titanium deposits upon the surface. This process is usually referred to as the "iodide process." The product is obtained in the form of pencil-shaped rods which are very difficult to work without contamination. This process is therefore not adaptable to large scale production although very pure metal is obtained.

B. Kroll Process. The second method of preparing ductile titanium was developed by Kroll (17). Pure titanium tetrachloride is reduced by magnesium metal in the presence of argon in a molybdenum lined crucible

which is electrically heated to about 1000°C. The titanium so produced is separated from the magnesium salts by water leaching and by acid treatment. The powdered metal may then be compressed into bars and either sintered or melted in an electrically heated vacuum apparatus. The product can be hot-rolled to thin sheet.

C. Modified Kroll Process. The United States Bureau of Mines has recently set up an extensive research program to study the production of ductile titanium metal and its alloys. The Kroll process with certain modifications (5) was used to produce the metal, since it was considered to be the most practical for plant-scale operations. In the development of the modified process the size of the reduction equipment was increased stepwise from 15-pound potsize up to a size which could produce 200 pounds of titanium per batch. The preliminary research with the 15-pound apparatus was carried out at the Salt Lake City station of the Bureau of Mines whereas the 200-pound batch operations have been carried out at the Boulder City, Nevada, pilot plant of the Bureau of Mines.

The pot used in this process was made of iron rather than molybdenum as in the Kroll process. After careful cleaning the top of the pot was welded in place. The assembly was then heated to 500°C and filled with hydrogen. This operation reduced any oxide formed during the welding. The pot was then cooled and the necessary quantity of very clean magnesium ingots was added. The system was then heated to 150°C and evacuated to about 0.005 mm. to degas the charge. Tank helium was next bled into the system until the pressure was slightly above atmospheric. The temperature was raised to 750°C and very pure liquid $TiCl_4$ was admitted to the chamber. The heat given off by the reaction was found to maintain the temperature of the system at the desired point without external heating for approximately two-thirds of the run. After the rate of reaction had slowed so that there

was no longer enough heat from the reaction to maintain the desired temperature, it became necessary again to use external heating. This was continued for one-half hour after the last of the $TiCl_4$ was added. During the run the temperature was increased from 750°C to 900°C.

After the system was cool the pot was cut open, and the charge was removed as chips by boring out the residue. These chips were freed of $MgCl_2$ and Mg by cold leaching with HCl. The chips were then washed, dried, and ground to the desired size. The product was given a second leaching with 10% HCl, washed, and dried. Any iron which was picked up by boring or grinding was removed magnetically.

The grenular metal prepared by this process contained about 25 cc. of H_2 and 0.050% Mg per gram of metal. Both of these impurities were removed by sintering at 1000°C in a high vacuum. The powder may contain up to 0.1% Fe and several tenths of one percent O_2 as the oxide.

D. Dry Purification of Sponge Titanium. A second method of purifying the reaction product is by heating in a vacuum retort (29). The greater part of the unused magnesium and magnesium chloride either melts and drains off or evaporates to leave behind a relatively pure sponge titanium. The principal advantage in a method of this type is the fact that the sponge titanium so produced is never exposed to aqueous solutions, and has no opportunity to retain moisture and hydrated magnesium compounds in the pore structure which thereby increase the oxygen content of the metal. Sponge titanium prepared by leaching the reaction product should have a slightly higher oxygen content than that prepared by vacuum purification.

E. Fabrication. At present there are two processes being used to consolidate the purified reaction product. The first process employs powder metallurgy technic and the other uses melting as a means of consolidation. A comparison of the corrosion of the metals made by these

two processes would be advantageous to determine whether or not the reactivity of the metal is affected by the method of consolidation employed. It would seem that the metal produced by melting should be a trifle more dense than that produced by powder technics and thus the possibility of a difference in corrosion arises. Actually, the density of a sintered compact is 4.30 and the density reported by E. I. Dupont de Nemours and Company (6) is 4.5 which is presumably the value for their metal ingot produced by melting.

F. Consolidation by Powder Metallurgy. The granular metal produced by the modified Kroll process is fabricated by powder metallurgy technics. The metal powder is pressed into compacts at a pressure of 50 tons per square inch. These "green" compacts are sintered for sixteen hours at a pressure of 2×10^{-4}mm. of mercury and at a temperature of 950-1000°C. The sintered compacts are ductile and are easily cold worked. They are best worked by cold forging, and may be reduced as much as 50% in thickness.

The sintered compacts have a density of 4.30, tensile strength of 83,000 psi, 10% elongation, and a Rockwell hardness of G54. After a 25% reduction by cold working they have a density of 4.42, tensile strength of 115,000 psi, 6% elongation, and a hardness of G81. Annealing in vacuum at 1000°C reduces the strength and hardness to values approximating those of the sintered compact.

G. Consolidation of Titanium by Melting. A second method by which the metal in the granular or sponge form may be consolidated is by melting. Such a process possesses several advantages over the previously mentioned powder metallurgy technics. Pressing and sintering operations require very expensive equipment and have definite size limitations.

The raw material for such a process must be in powder form which requires a costly grinding step. A process of consolidation by melting which can use the sponge or granular metal as feed would do away with the extra grinding process.

The melting of titanium presents many difficult problems. The metal has a very high melting point (1725°C) and at this temperature it is extremely reactive. Kroll (17) has reported that Al_2O_3, Y_2O_3, ZrO_2, and MgO react quite readily with titanium at the melting point. The molten metal in contact with refractories of this type is contaminated by both the oxygen and the metallic element. In a recent publication by the Bureau of Mines a brief reference was made to the melting of titanium in a graphite resistor vacuum furnace (18). It was found that the small amount of carbon picked up during the melting operation affected the physical properties of the metal only very slightly.

The duPont Company has carried out research upon the melting of titanium by induction heating in graphite (26). The melting and casting operations are conducted in an atmosphere of argon. It was found that the molten metal flowed through the pores of very pure graphite. The denser less pure forms have been found to be satisfactory after a preliminary high temperature bake at 2000°C. The charge used in this process was titanium sponge. Ingots obtained by this process contain 0.4 - 0.7% carbon and 99.0% titanium. The impurities which were present in the sponge make up the remainder of the ingot impurities. These ingots are said to machine like 18-8 stainless steel and can be readily forged at 1700-1900°F. The bars prepared by hot forging can be hot rolled with 10% reduction per pass at 1200-1600°F.

PART I - HISTORICAL

CHAPTER III

THE CORROSION RESISTANCE OF TITANIUM

There is very little information available on the corrosion properties of titanium, and that which is available, is almost wholly of a qualitative nature. In all of the literature cited it was found that the history of the metal under study was omitted and the methods of testing were not described. It is therefore difficult to piece together the scattered information into any kind of readily understandable picture.

A. Comparison of Titanium with Other Metals. Gillett (11) has suggested the use of titanium and zirconium in chemical equipment since these two metals are resistant to many acids and alkalies. He also stated that the general behavior of these metals to corrodants is very reminiscent of that of tantalum. Kroll (19) also has stated that the corrosion stability of titanium is comparable to that of zirconium. In another article Kroll (17) stated that the uses of titanium in chemical equipment are more limited than the application of zirconium because of lower stability. During attack by acids, zirconium forms on its surface a lower oxide which is stable toward most acids, but in the case of titanium, the monoxide formed is soluble in acids. Dean, et al., (5, 7) have reported that titanium metal has excellent corrosion resistance, being very similar to the type 18-8 stainless steels.

B. Sulfuric Acid. Dean, et al., (5, 7) reported that concentrated H_2SO_4 rapidly attacked titanium, but a 5% solution of H_2SO_4 produced a weight loss corresponding to only 0.40 milligrams per square decimeter per day (m.d.d.). Kroll (19) has stated that sulfuric acid (1:3) has an effect, even in the cold, whereby hydrogen is evolved. He further states that concentrated H_2SO_4 reacts with titanium to give SO_2, and that when dilute H_2SO_4 attacks titanium the solutions are colored violet after a short time due to the trivalent stage of the metal ion.

C. Hydrochloric Acid. Dean, et al., (5, 7) have found that concentrated HCl rapidly attacked titanium, but that a 5% solution of HCl did not cause losses in excess of 0.05 m.d.d. Gillett (11) found titanium to be attacked by concentrated HCl at 100°C. Kroll (19) has written that cold (1:5) HCl acts upon titanium only very slowly but gentle warming to 60°C is sufficient to cause an active disintegration of the metal, and that after attack by dilute HCl the solutions are colored violet.

D. Solutions of Bases. Gillett (11) has found that titanium was much less attacked by 50% NaOH at 100°C than type 18-8 stainless steel. Kroll (17) has stated that titanium is stable in KOH solutions and can therefore be used in place of aluminum in wet rectifiers. It was found by Dean, et al., (5, 7) that 5% solutions of NH_4OH did not cause losses in excess of 0.05 m.d.d.

E. Sulfide Solutions. Dean, et al., (5, 7) have found that a specimen of titanium showed no weight change and was not discolored after exposure to a dilute solution of Na_2S. Gillett (11) has observed that both zirconium and titanium appear unaffected by H_2S and alkali sulfides.

F. Hydrofluoric Acid. Gillett (11) states that the only reagent that is used when one seeks rapid dissolution of titanium is HF, although H_2SiF_6 also shows rapid attack. Kroll (19) found that both titanium and zirconium corrode actively in HF at large dilutions.

G. Solutions of Sodium Chloride. Dean, et al., (5, 7) have found that titanium did not tarnish on exposure to laboratory atmospheres or during a 30-day exposure to salt spray tests. Its physical properties were also unaffected by these tests. It was further pointed out that the resistance to corrosion in these tests was probably due to a protective film of the metal oxide. Gillett (11) found that 20% NaCl slowly attacked 18-8 stainless steel but had only a slight tarnishing effect on titanium or zirconium.

H. Solutions of Nitric Acid. Dean, et al., (5, 7) have found that concentrated HNO_3 and a 5% solution of HNO_3 did not cause losses in excess of 0.05 m.d.d. Kroll (19) has observed that concentrated HNO_3 passivates and treats the metal in such a way that HCl and H_2SO_4 when dilute, corrode the metal very slightly. This information suggests that further research should be carried out to investigate the mechanism by which titanium is rendered passive. Much work has been done toward studying the passivity of iron and stainless steel in nitric acid, and several theories have been proposed. These are discussed in the following chapter to afford an approach to the study of the passivity reported to be shown by titanium when treated with nitric acid.

Although scattered information was available on the corrosion resistance of titanium to other chemicals, the above presentation has been limited to those presented above because existing materials of construction have failed in many applications to these chemicals, and it is hoped that titanium will prove satisfactory.

PART I - HISTORICAL

CHAPTER IV

THEORIES OF PASSIVITY

A. Film Theory. Many theories have been postulated for the passivity exhibited by iron and stainless steels in nitric acid. The earliest theory was proposed by Faraday (9) who considered the passivity of iron in nitric acid to be due to the formation of an oxide film. This theory has been generalized until today it is known as the so-called film theory. Evans (8) has said that most cases of passivity can be attributed either directly or indirectly to a protective film. He stated further that this film is not necessarily an oxide film. Glasstone (12) has pointed out that the passivity produced with stainless steel on exposure to air is probably due to oxide films. The generalized film theory also covers the possibility that passivity can be caused by a protective film of adsorbed oxygen, rather than the oxide. Tammann (27) has suggested that the passivity shown by iron, nickel, cobalt, and chromium is due to a film of adsorbed oxygen.

B. The Electron Configuration Theory. The Electron Configuration Theory was developed to explain the passivity exhibited by stainless steels and iron (30, 31).

This theory makes use of the fact that the elements in the transition groups of the Periodic Table (e.g., chromium, nickel, cobalt, iron, molybdenum, and tungsten) possess incomplete inner shell energy levels and unfilled (d) energy bands in the free metallic state. The Electron

Configuration Theory assumes that these unfilled lower energy levels tend to fill with electrons. The state of passivity is attributed to the existence of unfilled (d) energy bands in the metal, whereas the active state is attributed to the situation that fills these (d) bands with electrons. It is thus contended that adsorbed oxygen or adsorbed oxidizing substances bring about maximum passivity since they tend to absorb electrons rather than supply electrons to atoms of the metal surface. This chemical adsorption brings about the extraction of electrons from the metal surface.

C. Theory of Physically Adsorbed Gas Film. Recently Fontana advanced data which indicated that the passivity exhibited by type 18-8S stainless steel was due to a protective film of physically adsorbed gas (10). It was shown at room temperature that specimens of this alloy show passivity when exposed to the atmosphere but lose passivity upon exposure to very low pressures. It was further shown that this process was reversible, in that the specimen could be passivated, and that the passivity could be destroyed by alternate exposure to air and vacuum. The fact that the passivity can be destroyed by reduced pressure at room temperature indicates that the bonds between the metal and the gas are very weak, and it is very likely that only physical bonds are involved.

In Fontana's method of testing, specimens of 18-8S stainless steel were exposed to boiling 10% H_2SO_4 for three minutes, washed, and exposed to air. The specimens were then exposed to vacuum and subsequently tested for corrosion resistance. It was found that an exposure to a pressure of 0.001 mm. of mercury for six hours was sufficient to assure breakdown of the passivity. Electron diffraction study of the passive 18-8S surfaces indicated no crystalline oxides but did show a diffuse pattern which could have been produced by hydrous oxides of nickel or chromium.

SUMMARY OF FOREGOING INFORMATION AND STATEMENT OF THE PROBLEM

A review of previous researches shows that tremendous progress has been made toward commercial methods of producing and fabricating ductile titanium metal. It has been pointed out that titanium has many desirable properties that are lacking in most of the materials of construction used today, and that in consequence the potential extensions of applications appear extraordinarily promising.

The importance of information on the corrosion of titanium upon further researches on this metal has been discussed and a review of the literature available upon this subject at the time the research in this dissertation was begun has been presented. The examination of this literature revealed that the previous corrosion data on titanium was very incomplete, and a more thorough research of this problem was justified.

It was proposed to design and construct equipment for a total immersion corrosion study on titanium, and to investigate any abnormal results uncovered in this survey. As titanium is rendered passive by treatment with nitric acid, it is proposed to also carry out a research to determine the reason for this behavior.

PART II - EXPERIMENTAL

CHAPTER I

TESTING EQUIPMENT AND CONTROL OF VARIABLES

Before a study of the corrosion of titanium could be made it was necessary to consider the variables which could affect the corrosion, and determine some means of controlling these variables through the design of testing equipment. A discussion of these variables and the equipment designed to permit their control is now presented.

A. Factors to be Considered in Corrosion Testing. A careful examination of the literature on total immersion testing methods and technics has shown that there is no universal laboratory procedure or even apparatus for such work. Laboratory corrosion testing is usually used only in a very preliminary capacity to select materials for use in "on the job" testing. The results of the latter tests receive most consideration in the final analysis and usually control the selection of the material for the particular job being considered. In laboratory testing, however, it is very important to control the several important variables which can affect the selection of materials for "on the job" testing.

The four most important variables to be considered in all laboratory testing are temperature, degree of aeration, ratio of volume of testing solution to specimen area, and preparation of the specimen. Temperature control is obviously important since it has been shown that the rate of

many reactions can be made to double with about a 10°C rise in temperature if all other controlling factors are disregarded. The degree of aeration of the testing solution may alter the whole mechanism of the chemical corrosion occurring at the metal-liquid interface because the presence of oxygen in the testing solution may cause the corrosion products to be in a higher state of oxidation than if no oxygen were present. The physical character of the corrosion product may be changed markedly by this, so that the metal surface may be either protected from or exposed to fresh test solution as the solubility and adhering quality of the product changes. The volume of testing solution for any given specimen must be so chosen as to insure a minimum of variation in the concentration of the testing solution during the progress of the corrosion and still not be so large as to become unwieldy in the laboratory.

The presence of surface oxides, grease, or uneven surface abrasion can cause appreciable variation in the test results of corrosion specimens. These difficulties may be overcome however if a proper surfacing treatment is derived for the metal under consideration. After the method has been worked out, then great care must be exercised so that each specimen has identical treatment before exposure to the corrosive environment.

Broad limiting values have been set forth for the four variables mentioned above by the American Society for Testing Materials (1). They have suggested that the temperature of the test solution be controlled to within 2°F (1°C) of the desired temperature. Toward this end, it has also been suggested that if a water bath is used as a means of temperature regulation, the level of the bath should be at the same height as the test solution within the container. The recommended volume of testing solution to specimen area is given as four liters per square decimeter

of area. This ratio assures a minimum of concentration change as the corrosion of the specimen proceeds and yet keeps the volume of the solution within laboratory limits. The rate of air flow necessary to maintain complete saturation of the test solution depends upon the volume of solution used for testing, the area of the test specimen, and its rate of corrosion. The suggested volume of air per liter of solution is at least 200 cubic centimeters per minute when the volume-area ratio mentioned above is maintained. It has been further suggested that the rate of air flow be controlled within plus or minus 10% of the above value, and also if the rate of corrosion exceeds 300 m.d.d. it may be necessary to increase the rate of air flow. If the tests are to be made under conditions of zero concentration of dissolved oxygen it is advisable to saturate the test solution with an inert gas such as nitrogen which has had all traces of oxygen removed, since elimination of aeration alone will not insure an air-free solution.

It was recommended that the surface oxide and inclusions of some metals could be most satisfactorily removed by a pickling treatment, however this treatment is unnecessary for those metals which will yield reproducible results when ordinary cleaning methods are employed. The final finishing treatment should be with No. 120 abrasive paper. The specimens should then be degreased by scrubbing with pumice paste, followed by a water rinse, and finally a rinse in a mixture of 50% ethyl alcohol and 50% ethyl ether.

B. Determination of Specimen Size. In order to handle a number of specimens conveniently with limited laboratory facilities it was first necessary to determine a specimen size which would be large enough to give a loss in weight at low rates of attack which could be accurately

determined with an analytical balance and yet not so large as to require an unwieldy volume of solution. Another important factor considered at this time was the influence of edge area. It has been recommended that the ratio of edge area to total area be kept as small as possible (Al). The metal, from which the specimens were to be prepared, was furnished in sheets approximately 0.040 inch in thickness. After consideration of the factors mentioned above it was decided to use a specimen one inch square which would give .074 as the ratio of edge area to total area.

C. Determination of Volume of Test Solution. Employing the volume-area ratio mentioned previously would require approximately 500 cubic centimeters of test solution for each sample. As a further insurance it was decided to increase the volume of solution to 750 cubic centimeters, thereby increasing the volume-area ratio by 50 percent of the lower limiting value.

D. Test Solution Container and Sample Holder. The next step in planning the test was to decide upon the type of container to be used for holding the individual samples and their test solution. For this purpose, wide mouth Erlenmeyer flasks of 1000 cubic centimeter capacity were chosen. A flask of this type can be stoppered easily to prevent evaporation and yet has a large enough mouth to admit specimen and holder. The shape of the flask is also such that a reasonable depth of solution is obtained for complete submersion of the sample when 750 cubic centimeters of test solution is used.

It was decided to use specimen supports of the type shown in Figure 1. These were made from 5 mm. pyrex glass rod, and were so constructed that there were three points of contact between the support and the edge of the sample.

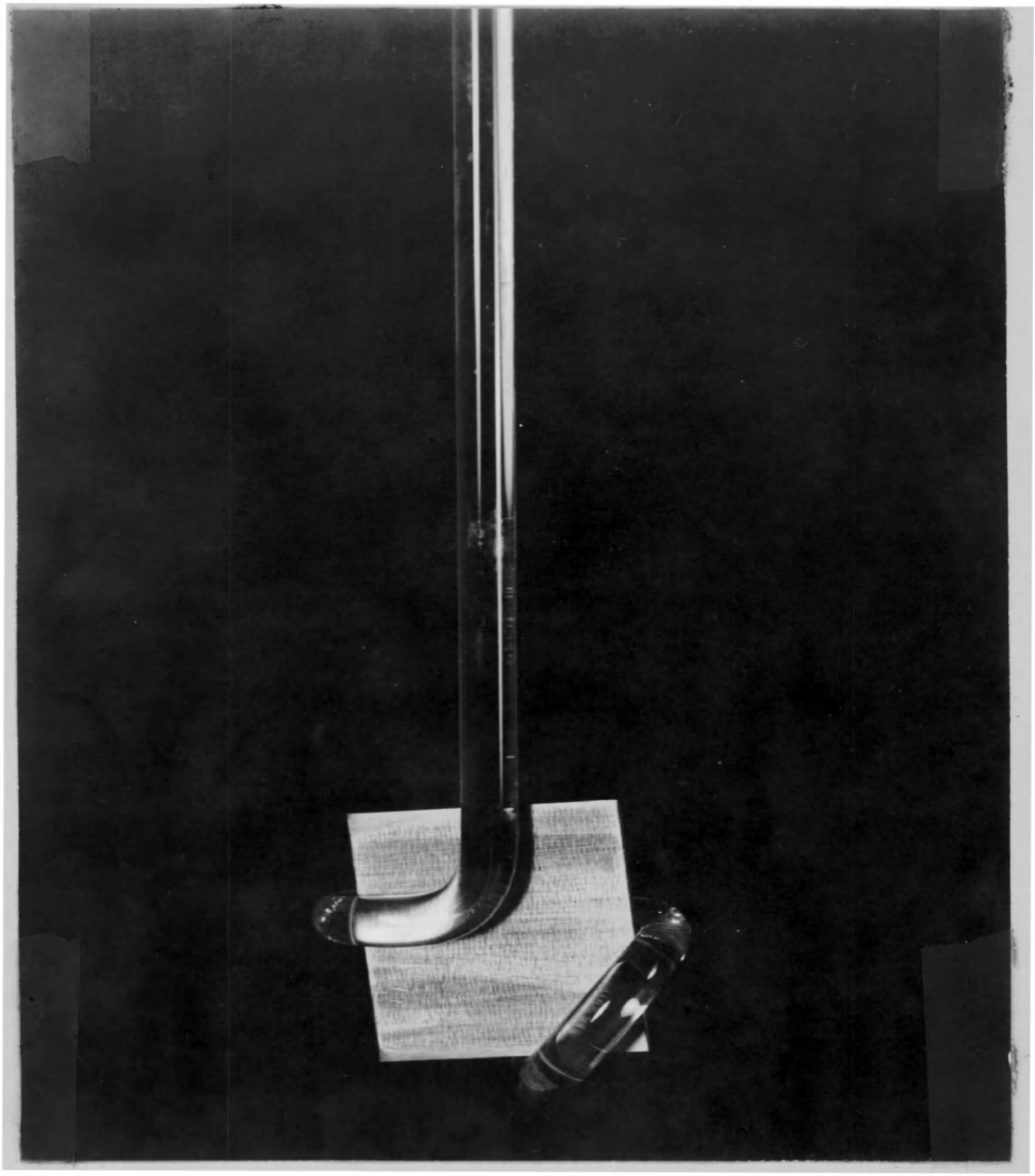


FIGURE 1.
Specimen Support

E. Method of Aeration. In order to saturate the test solution with either air or an inert gas, the aerator shown in Figure 2 was designed. The diffusion instrument in this case was a micro-Buchner funnel with a fritted glass filter disc of coarse porosity. A small glass chimney was mounted about the funnel to prevent the possible impingement of the gas upon the surface of the sample and also as a means of controlling the circulation of the solution within the flask. These chimneys were made from 25 mm. O.D. glass tubing. The complete assembly including the sample holder is shown in Figure 3. For higher temperatures a condenser was added to the assembly as shown in Figure 4.

F. Temperature Control. In order to regulate the temperature of the test solutions it was decided to immerse the test flasks in liquid baths maintained at the desired temperatures. The temperatures chosen for study were 35°C, 60°C, and 100°C. The bath which was to be maintained at 100°C employed type 10-C transformer oil as the medium whereas the other two baths employed water. The temperatures of the baths were controlled by means of mercury type thermo-regulators connected to mercury switch relays which in turn controlled immersion heating elements. By this means of control the bath temperatures did not vary more than 0.2°C. The bath medium was circulated in each tank by means of a small centrifugal pump which was totally submerged in the bath.

G. Control of Aeration Rate. The rate at which air or inert gas was supplied to each testing unit was controlled by Flowrators of the type manufactured by the Fischer and Porter Company. One Flowrator was used to control the rate for four test units by means of a manifold of glass stopcocks sufficiently large in bore to prevent undue resistance to flow. The maximum capacity of these instruments was 400 cubic centimeters of air per minute. It was decided that a rate of not less than

FIGURE 2.
Aerator

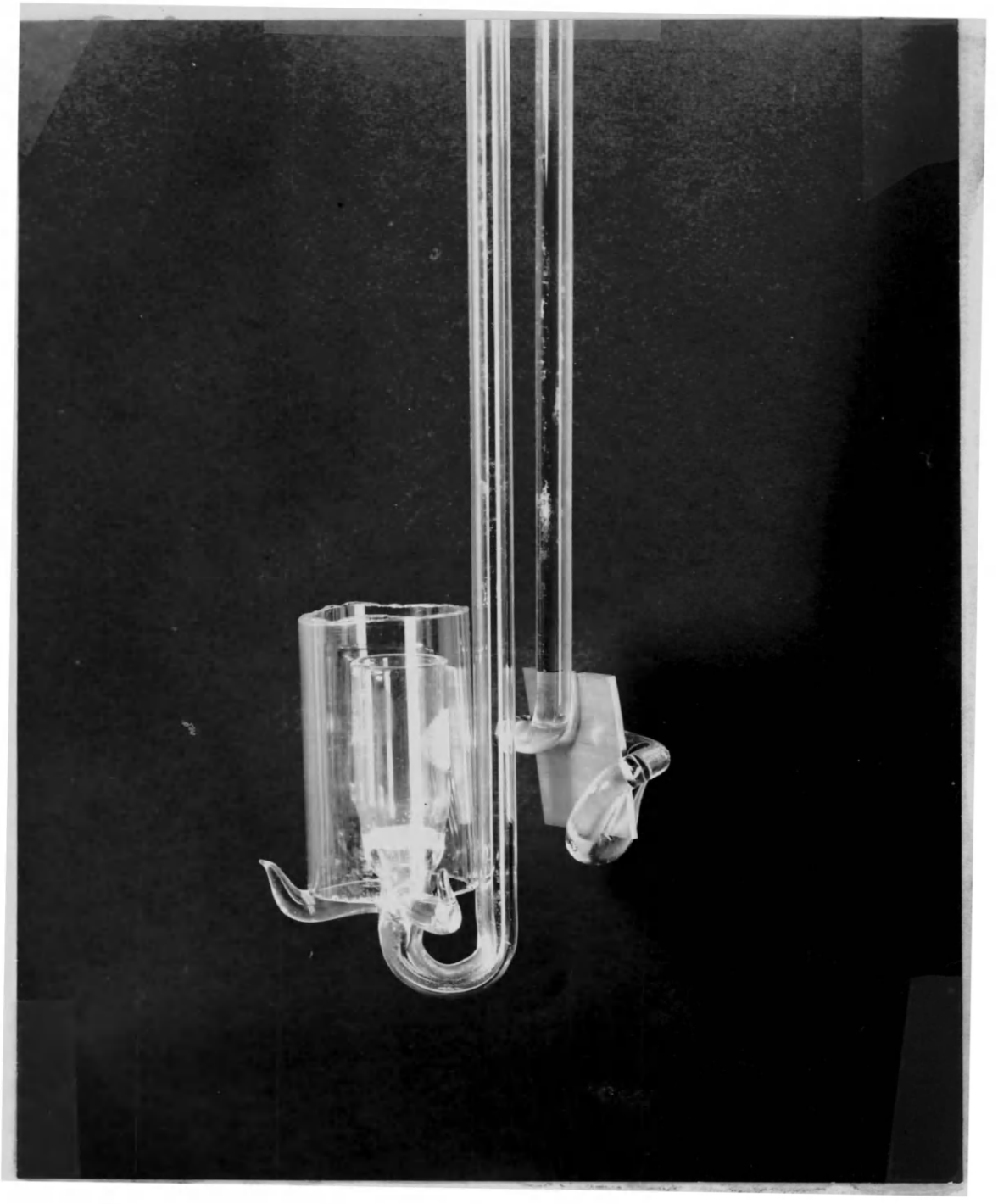


FIGURE 3.
Aerator and Specimen Support

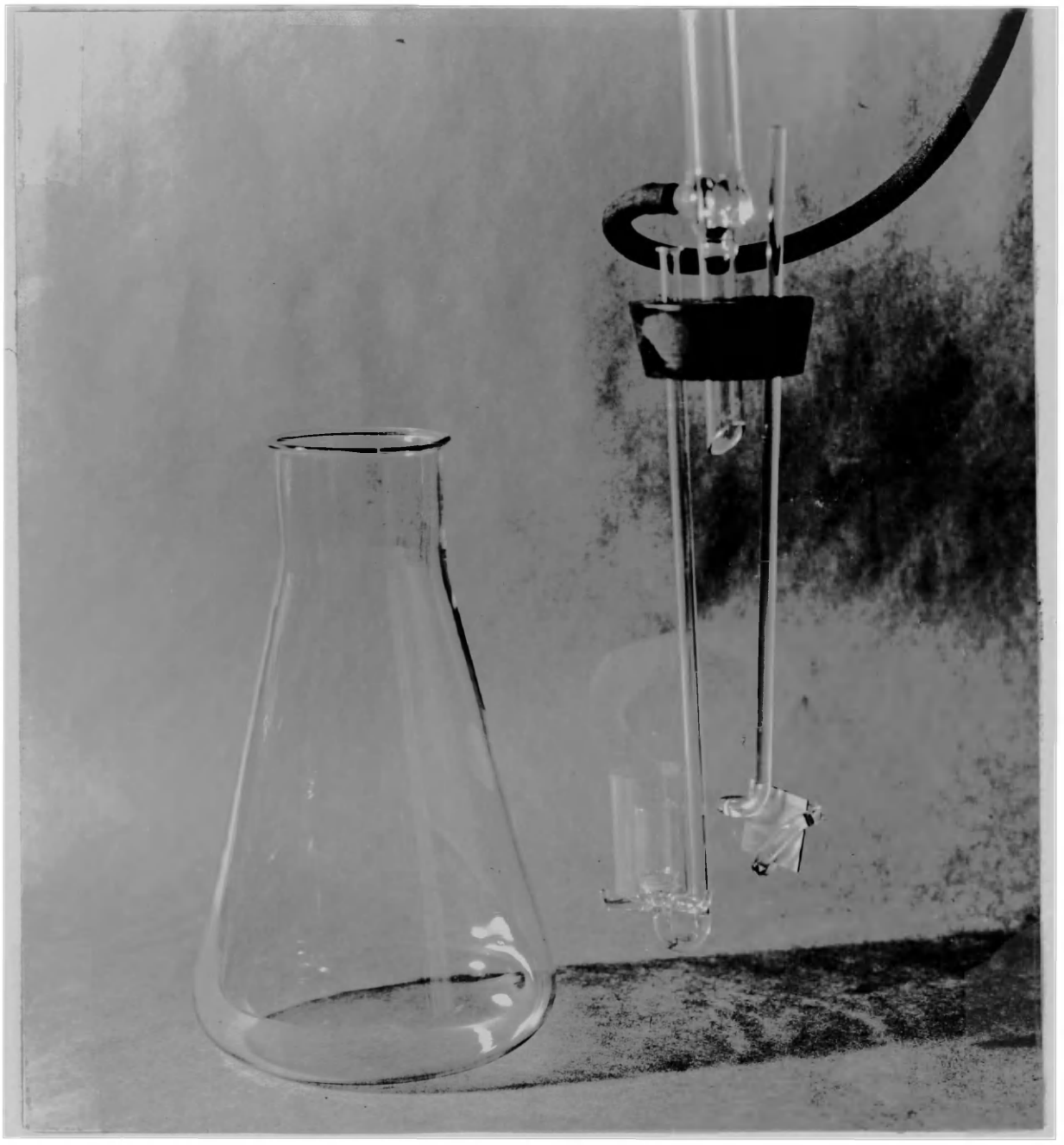


FIGURE 4.
Complete Total Immersion Testing Unit

200 cubic centimeters of air per minute would be introduced into each test solution. This rate is well above that previously mentioned which would be 150 cubic centimeters of air per minute for 750 cubic centimeters of test solution. The air which was used was supplied from the laboratory compressed air supply and was washed with 3% NaOH to remove any CO_2 present. The air was then passed through a water scrubber and finally through glass wool to remove any entrained particles. The complete tank assembly for 35°C or 95°F is shown in Figure 5.

I. Preparation of Samples for Testing. The specimens were cut from sheet stock of 0.040 inch thickness by a Doall saw. The rough samples were machined to +.003 - .005 inch oversize. They were then resurfaced with No. 1/2 emery paper and numbered with a Vibratool. The specimens were then polished by hand with grit No. 3/0 emery paper and degreased with pumice powder. They were next washed with distilled water followed by a rinse in a 50-50 ether and alcohol mixture. After drying they were weighed to within ±0.0001 gram.

J. Number of Specimens for One Test Solution. It was decided to run all tests in quadruplicate since a statistical study of totally immersed specimens in corrosive media has indicated that the average result of four duplicate runs would be within 7% of the true value (14).

K. Cleaning of Specimens after Testing. It was found that the corrosion products could be very easily removed from the surface of the titanium metal simply by scrubbing with a rubber stopper under a stream of running water. The samples were then washed in distilled water, washed in 50-50 alcohol and ether mixture, dried, and weighed.

L. Preparation of Testing Solutions. It was decided that all of the solutions to be used in the testing procedure previously described would

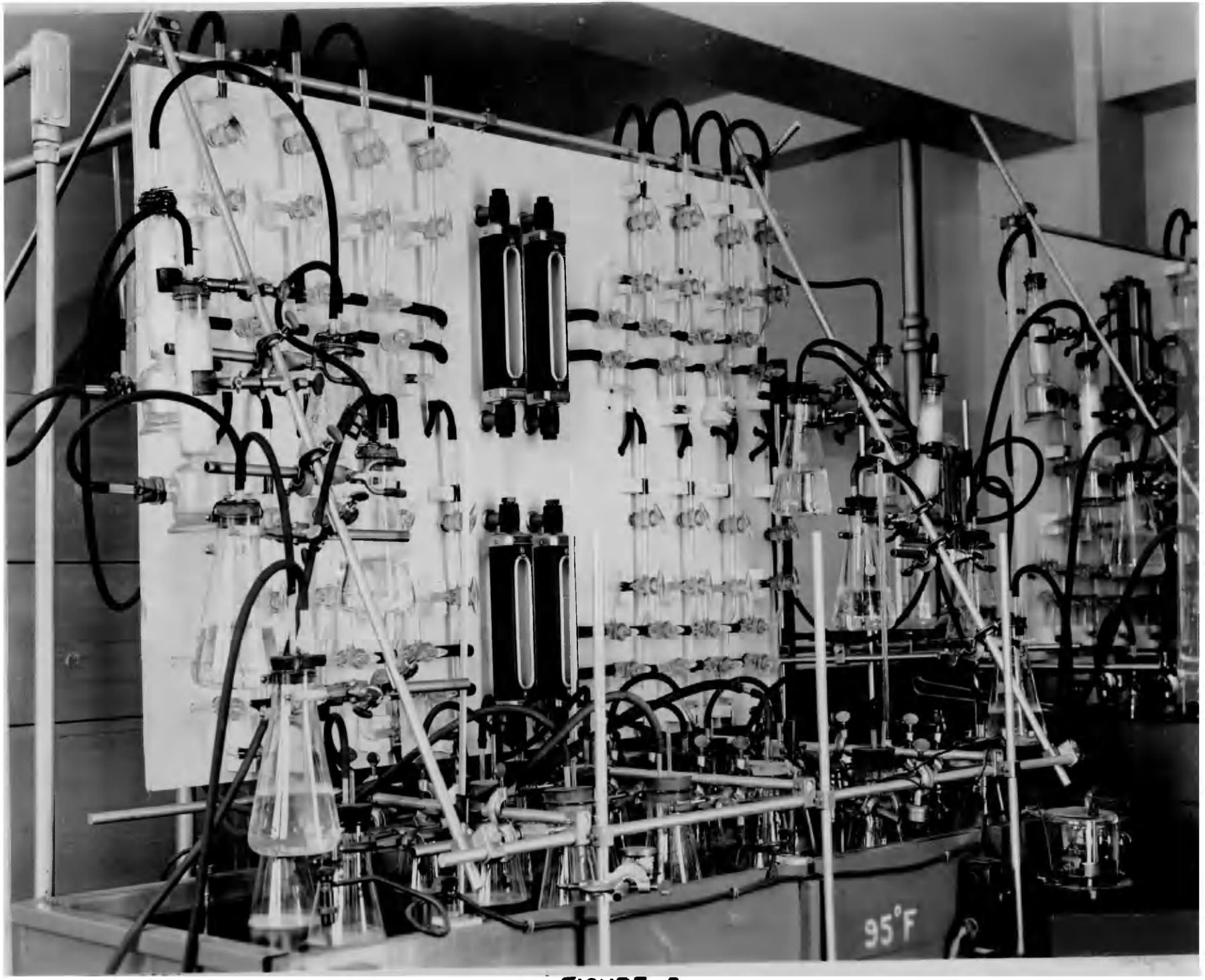


FIGURE 5.
Tank Assembly for Testing at 35°C

be made up by weight percentage. All references to percent solutions made in this paper therefore refer to percent by weight. All chemicals used in testing were of the C.P. grade. The testing solutions were prepared with distilled water which analyzed less than 0.1 p.p.m. salts as NaCl.

M. Metal used in Testing. The titanium used for all tests discussed in this paper unless otherwise specified was prepared by the modified Kroll process and consolidated by the powder metallurgy technic described in Chapter II. The metal was supplied in the cold-worked condition and also in the annealed condition. The cold-worked metal was supplied in sheet which had been cold-rolled to 40% reduction following the last anneal. The annealed metal was cold-rolled with 40% reduction and subsequently annealed at 1000°C in high vacuum. A spectrographic examination of the metal used in this study disclosed the following impurities: Fe(0.1%), Cr, Pb, Mg, Mn, Cu (traces, probably 0.005 - 0.05%). Oxygen and nitrogen which cannot be determined by spectrographic means are probably present as several tenths of one percent.

N. Evaluation of Results. The loss in weight per unit area during the test period was used as the principal measure of corrosion. Since it was found that the titanium did not show any severe pitting or selective corrosion, this method was considered to be valid. The corrosion rates were calculated from the loss in weight suffered by the specimens during the test and were expressed as milligrams per square decimenter per day (m.d.d.) and as mils per year (m.p.y.). The relationship between m.d.d. and m.p.y. is expressed by the equation: $\text{m.p.y.} = \text{m.d.d.} \times \frac{1.437}{\rho}$ where ρ is the density of the metal in grams per cubic centimeter. The latter unit is probably the easiest to interpret since it gives a visual picture of the depth of penetration of active corrosion over a period of time.

PART II - EXPERIMENTAL

CHAPTER II

CORROSION RESISTANCE OF TITANIUM TO SULFURIC ACID

The problem of finding materials which can be used in the storage and handling of sulfuric acid has received attention for many years. For handling concentrated acid, ceramics, duriron, and lead are the only materials which have proven satisfactory. In addition to these materials certain types of stainless steel have been used with dilute sulfuric acid. On the basis of what has been found in the literature (5, 7, 11) it appeared feasible to study the corrosion of titanium in sulfuric acid, and thus determine its range of applicability.

A. Preliminary Testing. Corrosion tests were made upon titanium metal in various concentrations of sulfuric acid employing the procedure and apparatus described in Chapter I. Titanium metal which had been prepared in two different ways was used. The metal in the cold-worked condition was supplied in sheet 0.040 inch thick which had been cold-rolled to 40% reduction in thickness following the last anneal. The metal in the annealed condition was cold-rolled with 40% reduction and subsequently annealed at 1000°C in high vacuum.

The first series of tests was made at 35°C with the test solutions fully aerated. Three sets of four samples each of the annealed metal were tested in each concentration of H_2SO_4 selected for study. The first set was run for 48 hours, the second for 96 hours, and third set for

144 hours. A scheme of this sort was proposed in order to determine if the rate of corrosion changed with increased time of exposure. In order to ascertain if the physical treatment of the metal prior to testing had any effect upon its rate of corrosion, comparative tests were made upon the metal in the cold-worked condition over 144 hour periods only. Duplicate tests in all concentrations of H_2SO_4 were made upon type 316 stainless steel to enable a comparison and correlation of the rates of corrosion for the titanium metal with a well-known structural material possessing good corrosion resistance. The results of this study are tabulated in Table I and are presented graphically in Figure 6.

B. Corrosion of Annealed Titanium. The annealed titanium was found to be attacked rapidly by H_2SO_4 in all concentrations above 5%. The maximum rate of corrosion for the annealed titanium over the range of acid concentrations studied was found to be in the neighborhood of 40% H_2SO_4. Another maximum appeared to be approached somewhere above 96.5% H_2SO_4 which was the upper limit of the range of acid concentrations being studied. A marked decrease in the corrosion rate was observed in the region from 50 to 96.5% with a minimum rate in the vicinity of 65% H_2SO_4.

C. Corrosion of Cold-Rolled Titanium. Examination of the results for the metal in the cold-worked condition shows that its rate of corrosion exceeds only that of the annealed metal in 10, 25, and 40% H_2SO_4. At most of the other concentrations, the rates for the two metals were found to be so nearly identical that their difference is less than the experimental error to be expected in tests of this nature.

D. Effect of Temperature upon Corrosion. In order to determine the effect of temperature upon the corrosion rate for titanium in sulfuric

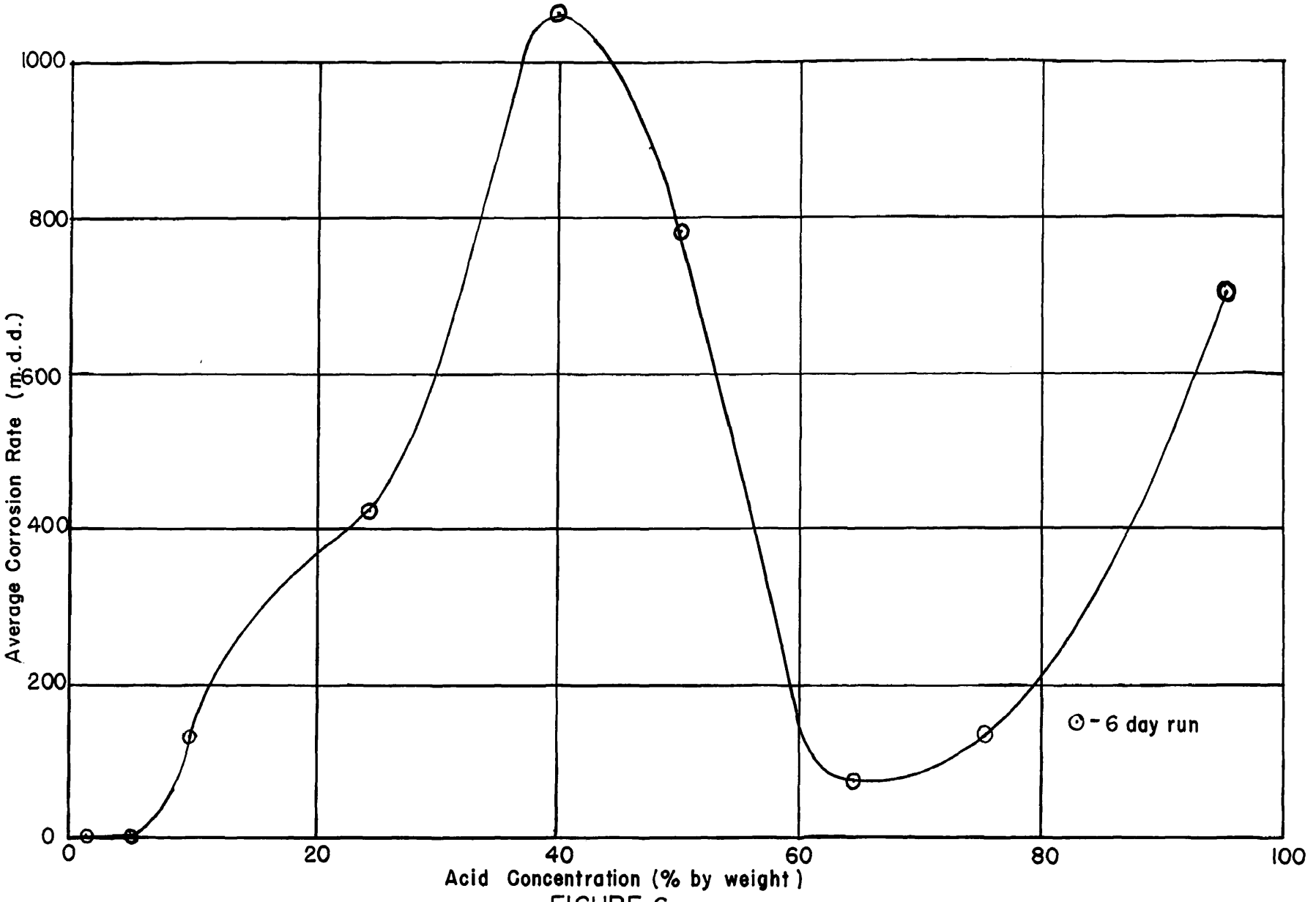


FIGURE 6.

CORROSION of TITANIUM in H_2SO_4 at 35°C (aerated)

TABLE I

H_2SO_4 at 35°C - With Aeration

Test Solution, Percent	Time (Hrs.)	Annealed Ti m.d.d.*	Annealed Ti m.p.y.**	Type 316 s.s. m.d.d.	Type 316 s.s. m.p.y.	Cold-rolled Ti m.d.d.	Cold-rolled Ti m.p.y.
1	144	0.42	0.13				
5	48	1.26	.40	0.00	0.00		
	96	.63	.20	.22	.04		
	144	1.53	.49	.41	.07	1.2	0.38
10	48	123.	39.4	1.13	.20		
	96	109.	34.8	.87	.16		
	144	126.	40.4	.72	.13	206.	66.0
25	48	203.	64.8	36.2	6.52		
	96	326.	104.	12.0	2.16		
	144	411.	131.	7.85	1.41	607.	194.
40	48			3078.	554.		
	96			1169.	210.		
	144	1069.	341.	2435.	438.	1331.	424.
50	48	861.	274.	2630.	474.		
	96	652.	208.	2662.	479.		
	144	489.	156.	2287.	412.	334.	107.
65	48	126.	40.2	2064.	371.		
	96	88.1	28.1	1902.	342.		
	144	81.4	26.0	1830.	329.	63.6	20.3
75	48	311.	99.2	609.	110.		
	96	160.	51.0	736.	132.		
	144	131.3	41.9	914.	164.		
96.5	48	556.	177.	11.56	2.08		
	96	556.	177.	9.30	1.67		
(96.5)	144	697.	222.	8.30	1.49	655.	209.
	192	696.	222.				

* Milligrams per square decimeter per day.
** Mils penetration per year.

acid a set of annealed samples was exposed to 5% H_2SO_4 for 48 hours at 60°C. The average rate was found to be 705 m.d.d. as compared to 1.26 m.d.d. for an identical test carried out at 35°C. A similar set of annealed samples was exposed to 5% H_2SO_4 at 60°C for 96 hours. The average rate was observed to be 857 m.d.d. as compared to 0.63 m.d.d. for an identical test at 35°C.

E. Advanced Investigations. An investigation was undertaken to determine the reason for the greatly decreased rate of corrosion exhibited by the titanium metal in 65% H_2SO_4. The first step in this study was to determine the chemical reactions occurring over the concentration range of H_2SO_4 studied at 35°C.

The apparatus diagrammed in Figure 7 was used for this study. Several pieces of titanium metal, which had been finished in the prescribed fashion and whose total surface area was approximately two square inches, were weighed and placed in the reaction flask (a.). 350 ml. of the test solution was then added to this unit and so manipulated that the leg of the reaction flask pictured to the left was entirely filled with the mixture. The leg on the right was then filled with an inert gas in order to blanket the surface of the test solution from the air. When almost 100 cc's. of gas had been evolved, the gas was withdrawn into the jacketed gas burette (b.) over mercury. Unit (a.) was then immediately emptied and the specimens removed from the test solution. They were then scrubbed, rinsed, and reweighed. The total volume of gas collected was measured and then passed into pipette (c.) which contained 0.1 N iodine solution. If any SO_2 were present in the gas it would be removed by this unit. The gas volume was then measured in the burette. The gas was next analyzed for H_2 by passing it over copper oxide at 300°C in unit (e.). The residual

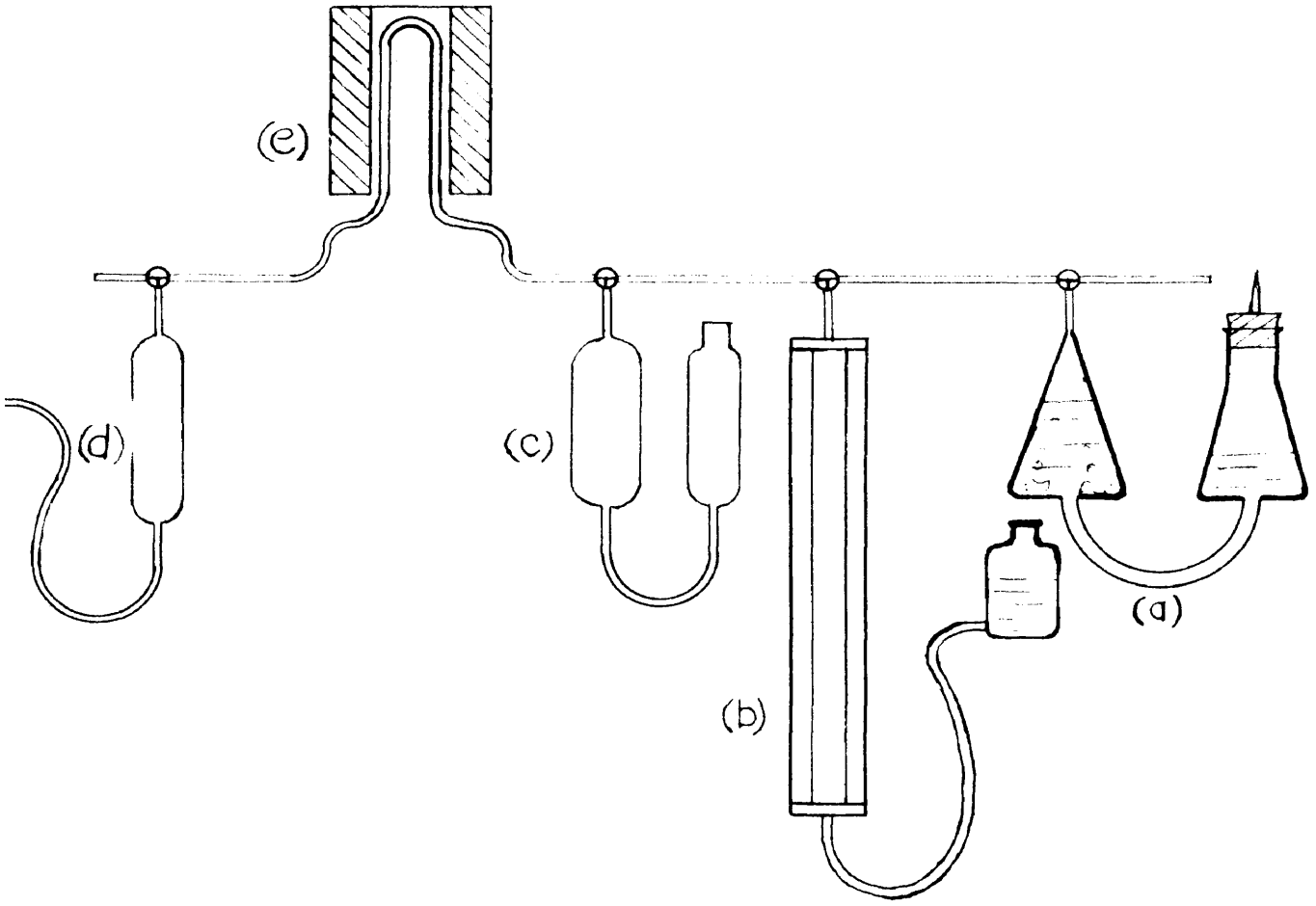


FIGURE 7.

GAS ANALYSIS APPARATUS

gas was collected in (d.). This operation was repeated until the final reading of volume was constant. The residual gas was analyzed spectroscopically by spark emission in a small Geissler tube and was found to be nitrogen. This nitrogen was probably physically adsorbed in the test solution at the start of the tests.

All gas volumes were corrected to S. T. P. and were corrected for the vapor pressure of water in the gas burette. Also the solubility of H_2 was taken into account in the various test solutions under study by approximating data found in Seidel (25). By knowing the weight of titanium which had reacted and the corrected volumes of the gaseous products the stoichiometric equations were readily found. These are presented in Table II.

Examination of these results shows that the reactions as written for 80, 85, 75% acid are very closely followed, however in concentrations of acid below 40% the deviation from the proposed reaction is very marked. The possibility of the formation of Ti++ with 40% H_2SO_4 was investigated since the presence of this ion would account for the large discrepancy noticed.

TABLE II

Determination of Products of Reaction

Conc. of H_2SO_4, Percent	Reaction	Moles Ti by Wt. Diff.	Moles Ti by Gas Analysis	Percent Ti Unaccounted
35	$2Ti+3H_2SO_4 \rightarrow Ti_2(SO_4)_3+3H_2$	0.00182	0.00153	16
40	"	.00296	.00234	20.8
40	"	.00305	.00251	17.7
75	"	.00270	.00270	0
80	"	.00173	.00173	0
85	"	.00125	.00124	0.8

A test was carried out in 40% H_2SO_4, and the solution after the test was analyzed for Ti^{++} by oxidizing all of the titanium to Ti^{++++} with ferric iron and then oxidizing the ferrous iron with dichromate. It was found that there was no Ti^{++} present, and in fact, some of the Ti^{+++} had been oxidized to Ti^{++++} during the testing period.

After it was established that $Ti_2(SO_4)_3$ was the corrosion product when titanium reacted with concentrations of H_2SO_4 from about 60 to 85%, it was thought necessary to investigate the solubility of this compound in the various concentrations of sulfuric acid used. A number of one inch square titanium specimens cut from sheet 0.040 inch in thickness were finished in the prescribed fashion and immersed in separate beakers of 65% H_2SO_4. Each beaker contained 150 ml. of acid and was not provided with any aeration. Gas evolution began immediately from all specimens, but after twenty-four hours the specimens were seen to be covered with a violet film and did not seem to be reacting further. All the samples were then removed simultaneously and individually placed in separate beakers containing the following concentrations of sulfuric acid: 40, 50, 60, 70, 80%. The time was then recorded for gas evolution to begin from each sample. The specimens which were placed in the 40 and 80% H_2SO_4 began to corrode immediately as the film of $Ti_2(SO_4)_3$ went into solution at once. The specimen in the 75% H_2SO_4 began to corrode after four minutes, and the one in the 50% H_2SO_4 after one hour and ten minutes. The specimens in the 60 and 70% H_2SO_4 began to evolve gas very slowly after six hours and fifteen minutes had elapsed. After prolonged exposure of the specimen to the 80% acid the odor of H_2S was perceptible.

On the basis of the foregoing evidence it appears that the very low rate of corrosion found in the 65% H_2SO_4 is due to the relatively insoluble

film of $Ti_2(SO_4)_3$ formed upon the surface of the metal. With a test solution of an oxidizing nature such as was used in the original test, the $Ti_2(SO_4)_3$ is probably oxidized to $TiOSO_4$ which was proven to be only slightly soluble in 65% H_2SO_4 and loosely adhering.

Thus it may be expected that the rate of corrosion would be slightly greater in an aerated solution due to the fact that the protective barrier of $Ti_2(SO_4)_3$ is being continuously removed to a slight extent by the oxidation process.

PART II - EXPERIMENTAL

CHAPTER III

CORROSION RESISTANCE OF TITANIUM TO HYDROCHLORIC ACID

The second most important commercial acid is hydrochloric, and as in the case of sulfuric acid relatively few materials are known which withstand the action of its aqueous solutions. Nickel, certain nickel-chromium-iron alloys, nickel-molybdenum-iron alloys, silver, carbon steel, tantalum and copper are the only metals which can be used to handle aqueous hydrochloric acid. A study was made upon titanium to determine if it could be used in the construction of equipment to withstand this acid.

A. Preliminary Study. Corrosion tests were made upon titanium metal in the annealed condition in various concentrations by weight of hydrochloric acid employing the procedure and apparatus described in Chapter I - Experimental. The first series of tests were made at 35°C in fully aerated solutions. The results of these tests are tabulated in Table III and are graphically illustrated in Figure 8. Like the tests made in sulfuric acid, type 316 stainless steel was exposed to similar tests with hydrochloric acid for comparison purposes.

It was found that the corrosion rate of titanium increased only very slightly with increasing concentration of HCl up to 5%. The rate then increased steadily with acid concentration until ready dissolution of the metal was obtained with 37% HCl which is the strength usually supplied as a laboratory reagent.

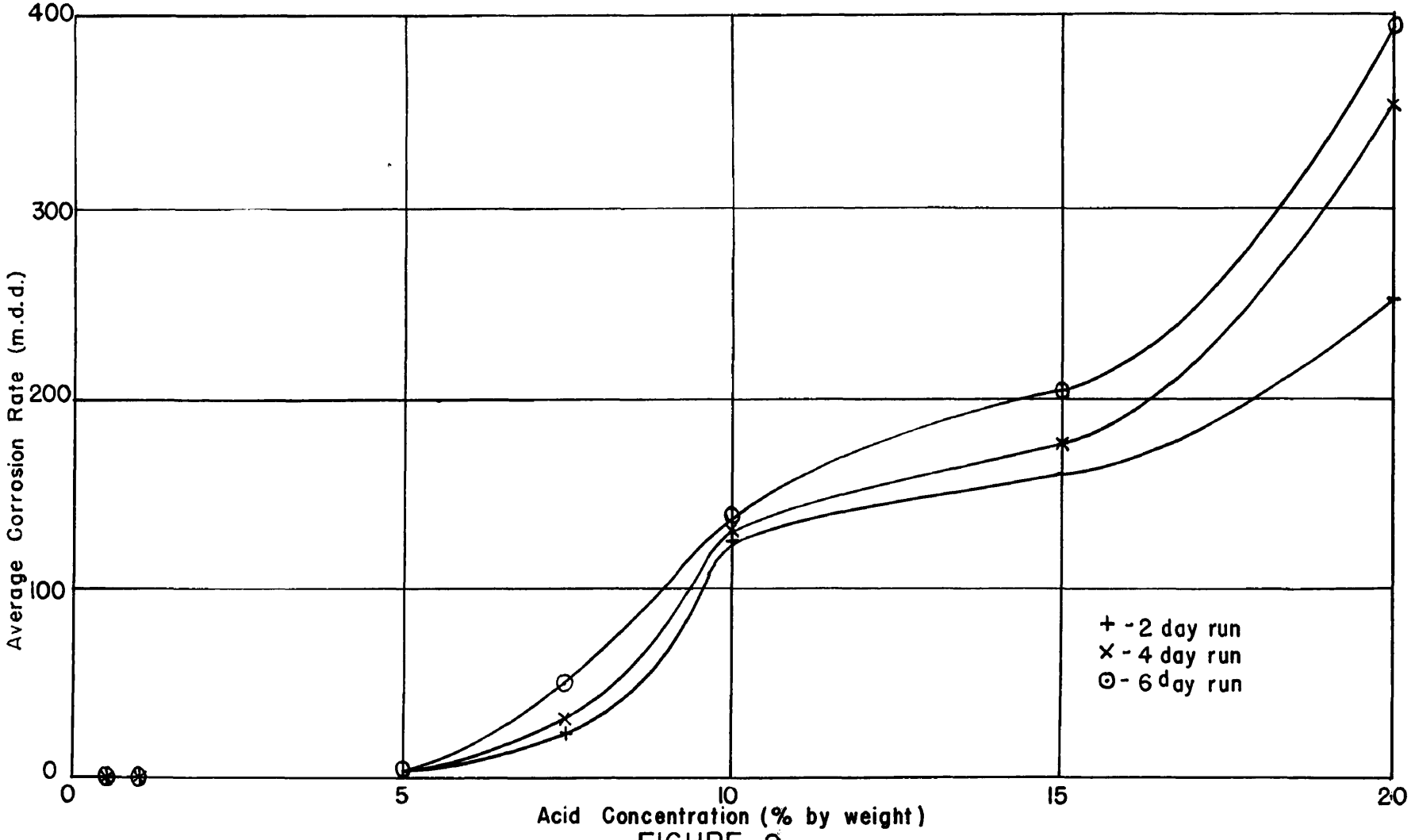


FIGURE 8.
CORROSION of TITANIUM in HCl at 35° C (aerated)

TABLE III

HCl at 35°C - With Aeration

Test Solution, Percent HCl	Time (hrs.)	Annealed Ti		Type 316 s.s.	
		m.d.d.*	m.p.y.**	m.d.d.	m.p.y.
0.5	48	0.97	0.31	1.75	0.32
	96	.36	.12	.74	.13
	144	.12	.04	.79	.14
1.0	48	.45	.14	2.5	.45
	96	.49	.16	1.2	.22
	144	.42	.13	.90	.16
5	48	1.40	.45	650.	177.
	96	1.44	.46		
	144	1.20	.38	301.	54.1
7.5	48	21.4	6.82		
	96	24.4	7.78		
	144	47.7	15.2		
10	48	130.	41.4		
	96	129.	41.4		
	144	133.	42.4		
15	48	159.	50.8		
	96	179.	57.2		
	144	203.	64.7		
20	48	253.	80.7		
	96	353.	113.		
	144	394.	126.		
37	48	6250.	1990.		

* Milligrams per square decimeter per day.
** Mils penetration per year.

B . Effect of Temperature. A series of tests similar to those at 35°C were made at 60°C with fully aerated solutions. The maximum concentration of HCl studied was 5% since from the data obtained at 35°C, it is obvious that the rates would be very great in hydrochloric acid of any greater concentration. The results of this investigation are tabulated in Table IV and shown graphically in Figure 9.

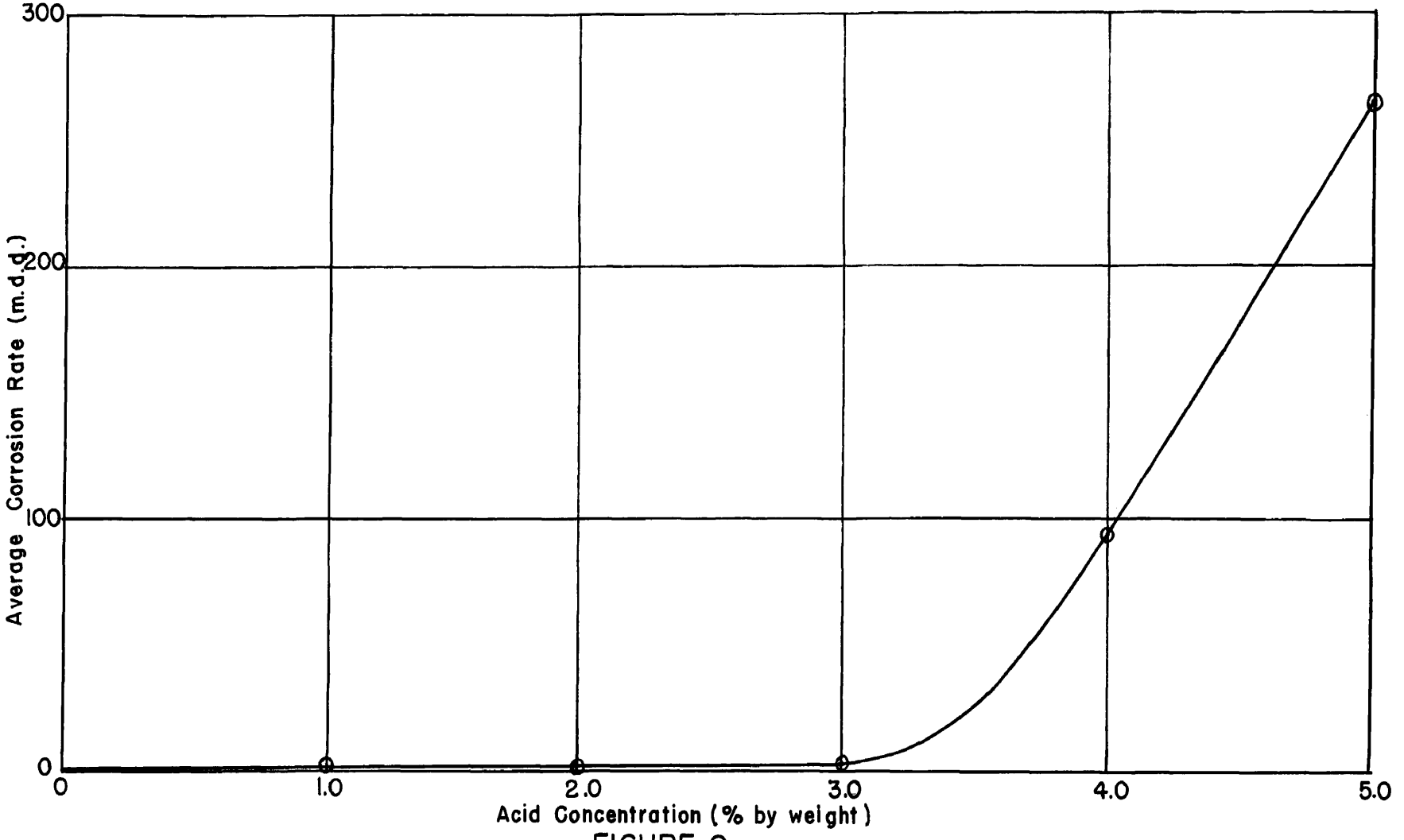


FIGURE 9.

CORROSION of TITANIUM in HCl at 60°C (aerated)

TABLE IV

HCl at 60°C - With Aeration

Test Solution, Percent HCl	Time (Hrs.)	Annealed Ti m.d.d.	Annealed Ti m.p.y.	Type 316 s.s. m.d.d.	Type 316 s.s. m.p.y.
1	96	0.50	0.16	464	83.5
1	144			452	81.4
3	144	0.91	0.29	1408	253.
4	144	94.5	30.2	2177	392.
5	96	263.	84.0		

It was found that a negligible rate of corrosion was shown by the titanium at this temperature in concentrations of HCl up to three percent. When the temperature of testing was increased to 100°C it was found that titanium resisted only concentrations of HCl which were 1 percent or less. These data are tabulated in Table V.

TABLE V

100°C - With Aeration

Test Solution, Percent HCl	Time (Hrs.)	Annealed Ti m.d.d.	Annealed Ti m.p.y.
1	144	1.35	0.43
2	144	963.	307.
3	144	1687.	538.

In every test which was made with HCl no severe pitting was noticed. The corrosion in all cases was very even with no indication of any preferential attack.

C. Corrosion of Titanium Prepared by Melting. In order to ascertain if the fabrication of titanium by melting rather than by powder technic has any effect upon the corrosion resistance a duplicate study was made using 10% HCl as the testing solution. The metal was prepared by the Battelle Memorial Institute by melting titanium prepared by the modified Kroll process in a tungsten arc. The stock furnished was in the form of 0.040 inch sheet in the cold-worked condition. The test was carried out in 10% HCl which was fully aerated at 35°C. The total testing period was 144 hours. Before testing, the specimens were given the prescribed surfacing treatment. It was found that the metal prepared by melting was slightly more resistant to corrosion (at least in 10% HCl) than the metal prepared by the powder technic. The rate of corrosion for the former was 32 mils per year as compared to 38.4 mils per year for the latter.

PART II - EXPERIMENTAL

CHAPTER IV

CORROSION RESISTANCE OF TITANIUM TO NITRIC ACID

Another of the important mineral acids is nitric acid. Its widespread use by industry especially in the manufacture of explosives make it an important item of commerce. It was decided to study the corrosion of titanium in nitric acid in order to determine if it is suitable for use in containers and process equipment handling this acid.

A. Preliminary Testing. Corrosion Tests were made on annealed titanium metal in various concentrations of aerated nitric acid. The metal was first tested at 35°C and the results of this study are shown in Table VI. It may be seen that titanium metal is very resistant to attack in all concentrations of nitric acid up to 69.5% at this temperature. After testing, the surfaces of all specimens were visually unattacked and seemed to be covered by a nearly transparent film with a very slight amber tint.

Tests were also conducted at 100°C using 5% and 10% HNO_3 for periods of 144 hours. A rate of 0.61 mils per year was found in the 5% HNO_3 and 1.29 mils per year in the 10% HNO_3. These are slight increases over the values found at 35°C but are still negligible.

Titanium was tested in non-aerated, boiling 65% nitric acid and was found to have an average corrosion rate of 10.4 m.d.d. or 3.31 m.p.y. Tests were also made in fuming nitric acid (assay 90%) at room temperature over a

240 hour period. There were no visible signs of attack after testing and a negligible loss in weight was found (0.18 m.d.d. or 0.06 m.p.y.).

TABLE VI

HNO_3 at 35°C - With Aeration

Test Solution, Percent	Time of Run (hr.)	Annealed Ti m.d.d.	Annealed Ti m.p.y.	Type 316 s.s. m.d.d.	Type 316 s.s. m.p.y.
5	144	0.24	0.08	0.41	0.07
10	144	.51	.16	.50	.09
20	144	.57	.18	.47	.08
30	144	.84	.27	.38	.07
40	144	.72	.23	.41	.07
50	144	.72	.23	.50	.09
60	144	.87	.28	1.00	.18
69.5	48	1.40	.45	2.46	.44

B. Study of Passivity of Titanium. Kroll has pointed out that concentrated nitric acid passivates and acts upon the titanium in such a way that HCl and H_2SO_4, when dilute, corrode the metal very slightly (19). An investigation was initiated to study this behavior and perhaps provide an adequate explanation. In a preliminary test a specimen of annealed titanium was exposed to boiling concentrated nitric acid for ten minutes, rinsed, and placed in 65% H_2SO_4. After 48 hours active corrosion with gas evolution occurred. It was concluded from this test that the film formed upon the metal during the nitric acid treatment was very thin and offered slight resistance to this test solution.

The possibility of an oxide film being the means of gaining passivity with titanium was first investigated. The passivated surfaces of several specimens of titanium and the surface of an untreated specimen were examined by electron diffraction. The specimen which had received no treatment gave no pattern. A specimen which was coated with an oxide film by exposure to

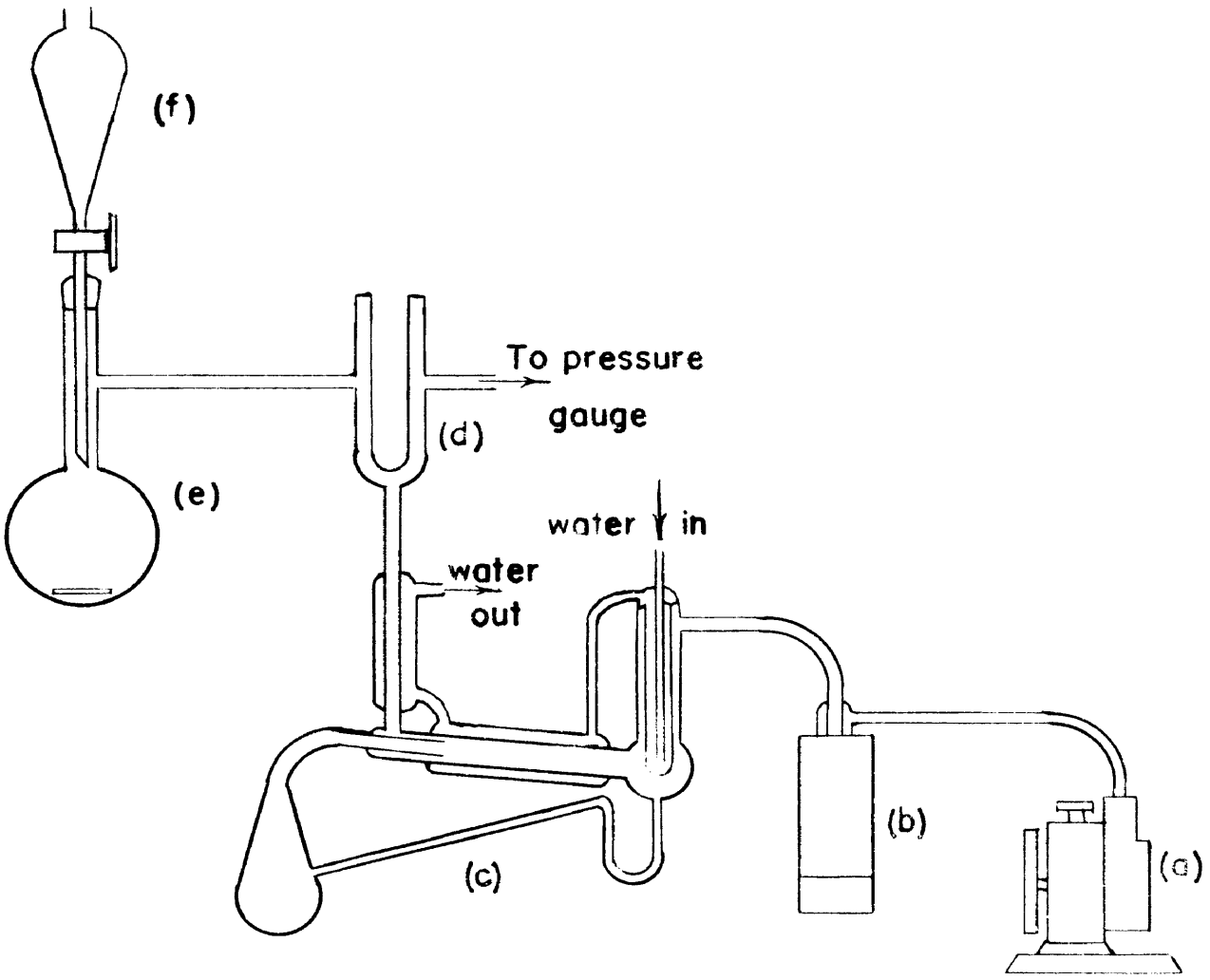
oxygen in a tube furnace gave a very distinct pattern for TiO_2 of the anatase and rutile forms. A third specimen which was treated with boiling HNO_3 for ten minutes gave patterns of anatase and rutile, but the broad, hazy lines obtained indicate that very small crystals were present. A specimen which was treated in a 40% H_2SO_4, 5% HNO_3 for 24 hours at 35°C also gave a pattern for very small crystals of anatase and rutile.

The results of the above study seem to indicate that the passive effect of HNO_3 on titanium is due to a crystalline oxide. It was decided however to investigate the possibility of the presence of physically adsorbed gas within the passive film as a second component aiding the protective action.

The apparatus shown in Figure 10 was constructed for use in this study. A Duo-Seal forepump was used with a mercury diffusion pump to obtain the low pressures necessary. A means of adding the test solution directly to the system was also provided. This enabled the specimen to be exposed directly to the test solution after being evacuated without intermediate exposure to air. The pressure within the system was determined with a McLeod type gauge which was accurate to 0.01 micron.

Before any specimens of titanium were tried in this apparatus, Fontana's experiment was duplicated, using 18-8S stainless steel in order to ascertain if the apparatus was correctly designed. His results were duplicated (9).

The specimens to be tested were given a surfacing treatment as described in Chapter II. After drying they were placed in boiling, concentrated HNO_3 for ten minutes. They were then removed, rinsed with distilled water, and dried. During each run under vacuum with the passivated specimen, a similar specimen was placed under distilled water. At the same time that the test



(a) Forepump
(b) Condensable vapor trap
(c) Diffusion pump
(d) Condensable vapor trap
(e) Specimen container
(f) Test solution container

FIGURE 10.
LOW PRESSURE APPARATUS

solution was added to the specimen under vacuum, the test solution was also added to this control specimen.

The results obtained through this procedure are shown in Table VII.

TABLE VII

Effect of Vacuum on Passive Film

Test No.	Pressure, (Microns)	Time in Vacuum, Hours	Test Solution, Percent	Temperature of Test, °C	Time Before Evacuated Sample Corroded, Hours	Time Before Control Corroded, Hours
1	1.0	5-1/2	40 H_2SO_4	Room	16	48
2	0.2	5	50 H_2SO_4	Room	12	48
3	0.15	6	40 H_2SO_4	35	16	48

Figure 11 shows two specimens of titanium which were passivated in HNO_3 and then subjected to 40% H_2SO_4 for 24 hours. The specimen which shows attack (2) was subjected to a pressure of 0.2 micron prior to treatment with 40% H_2SO_4. The unattacked specimen (1) was placed directly in the 40% H_2SO_4 after being passivated.

These results indicate that the passive nature of the film in part at least must be dependent upon physically adsorbed gas within the film of oxide.

It was believed possible, however, that gas could be adsorbed by the metal prior to the treatment with HNO_3 and when exposed to low pressure would escape through the film of oxide leaving a damaged protective layer. In order to ascertain if this were the case, a specimen of titanium was degassed for 5 hours in the apparatus at 0.2 micron before being treated

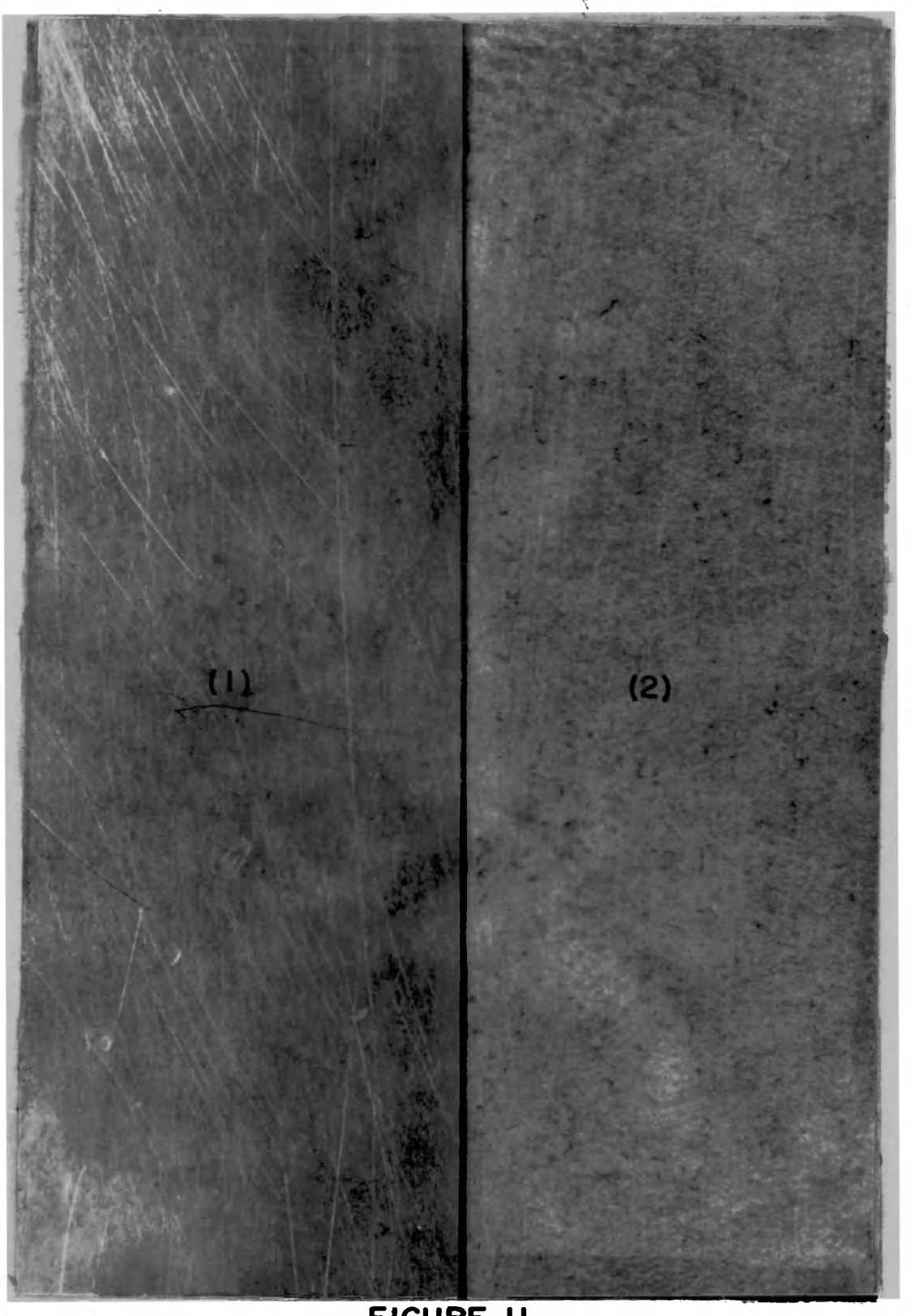


FIGURE 11.
Effect of Low Pressure on Passivity of Titanium

with HNO_3 which was bled directly into the vacuum. After 10 minutes in boiling HNO_3 the specimen was rinsed, dried, and kept under 0.2 micron pressure for 5-1/2 hours. At the end of this time 50% H_2SO_4 was bled into the vacuum. Active corrosion was noted after 12 hours at room temperature. The results of this test indicate that any physically adsorbed gas affecting the passivity of the metal was adsorbed either during the treatment with HNO_3 or during the time between treatment and placing in the vacuum.

An investigation was next made to determine if the exposure of the specimen to air after the treatment with HNO_3 caused the physical adsorption of gas upon the surface. A specimen was treated with boiling HNO_3 for 10 minutes, rinsed, and placed under vacuum while still wet. A pressure of 0.1 micron was maintained for six hours at room temperature. At the end of this time 40% H_2SO_4 was bled into the system and maintained at 35°C. After 22 hours the specimen showed active attack. An identical test was performed upon another specimen with the exception that this one was dried before being placed under vacuum. It was found that it also took 22 hours for active corrosion to start on the second specimen.

From these results it appears that the physically adsorbed gas present in the film must be acquired during the treatment with nitric acid.

Although it was strongly suspected that the adsorbed gas is oxygen or oxides of nitrogen, it was decided to confirm this belief by experimental evidence. If the gas were oxygen or oxides of nitrogen, the protective effect of the passive film should be greatly decreased in a test solution saturated with hydrogen gas. The adsorbed gas would be removed by the reaction with the atomic hydrogen in equilibrium with the hydrogen

dissolved in the test solution. Although the concentration of atomic hydrogen in equilibrium with molecular hydrogen at this temperature is very low a noticeable difference in the passive nature of the film in this solution and one in a solution saturated with an inert gas, such as nitrogen, should be detected. Accordingly, two specimens of titanium were surfaced and treated with boiling HNO_3 for 10 minutes. They were then rinsed and each placed in 200 ml. of 40% H_2SO_4 at room temperature. One solution was saturated with hydrogen by bubbling in hydrogen gas. The other solution was saturated with nitrogen by bubbling in nitrogen gas. It was found that after 23 hours, corrosion of the specimen in the solution saturated with hydrogen had begun. The solution appeared to have a blue tint indicating the presence of Ti^{++}. The specimen in the solution saturated with nitrogen, however, showed no evidence of attack. It was therefore concluded that the adsorbed gas present in the film was either oxygen or oxides of nitrogen.

A study was next made in an effort to draw a comparison between the passive film prepared by liquid means and an oxide film prepared by dry means. A specimen of titanium was surfaced and exposed to boiling HNO_3 for 10 minutes while a second specimen was surfaced and exposed to an atmosphere of pure oxygen at 800°C for a short time. Both specimens were placed in non-aerated 40% H_2SO_4. After 48 hours the specimen treated in HNO_3 began to corrode. The specimen treated at 800°C began to corrode 5-1/2 hours later. A control specimen of untreated titanium reacted immediately upon exposure to non-aerated 40% H_2SO_4. It was very evident by visual examination before exposure to H_2SO_4 that the film prepared by direct action of oxygen with titanium at 800°C was much thicker than the film prepared in HNO_3. If this were true it would appear that the thickness of the TiO_2 film was not the controlling factor in the protective nature of the film.

In order to determine if the film prepared by dry means contained any adsorbed gas the following study was carried out. Two specimens of titanium metal were surfaced and exposed to an atmosphere of oxygen at 780°C for a short time. One specimen was then placed in the vacuum apparatus and maintained under a pressure of 0.3 micron for six hours. The other specimen was stored in a desiccator during this time. Both specimens were then exposed to 40% H_2SO_4 at room temperature. After 12 hours the specimen which had been degassed showed active corrosion whereas the other specimen did not show active corrosion until after 48 hours. This evidence indicates that adsorbed oxygen is of great importance to the protective qualities of a film of TiO_2 prepared by exposure to a controlled atmosphere.

In summary it may be said that the passivity imparted to titanium by nitric acid is due to a definite film barrier. This film has two components, namely TiO_2 (anatase and rutile), produced by chemical reaction with the HNO_3, and physically adsorbed gas which is bound to the surface by some physical attraction rather than by an exchange of electrons. It has been shown that the passivity exhibited by the film is seemingly independent of the thickness of the oxide layer but is dependent upon the presence of physically adsorbed gas. It has been further shown that physically adsorbed gas is an essential component of a protective film prepared by the action of oxygen upon titanium at elevated temperatures. The protection furnished by the oxide is probably due only to a layer of molecular dimensions in direct contact with the metal interface. The previous statement is in agreement with the Electron Configuration Theory (30, 31). However, the presence of a physically adsorbed gas is not covered by this theory. The fact that a physically adsorbed gas contributes

to the passivity of titanium is in direct agreement with the theory of passivity for type 18-8S stainless steel as proposed by Fontana (10). The presence of an oxide film as a contributing factor to passivity is not covered by this theory.

PART II - Experimental

CHAPTER V

A STUDY OF MEANS OF INCREASING THE CORROSION RESISTANCE OF TITANIUM IN SULFURIC AND HYDROCHLORIC ACIDS

In the previous chapter it was shown that titanium was rendered passive to the action of sulfuric acid by a pretreatment with boiling, concentrated nitric acid. It was found, however, that this passivity was effective for only about 48 hours when the metal was exposed to 40% sulfuric acid at 35°C. In order to prolong this period of passivity it was thought advisable to investigate the effect of adding small quantities of nitric acid to sulfuric acid. Such additions of nitric acid to sulfuric are of interest in tests of this nature because a large percentage of the sulfuric acid used by industry contains a considerable amount of nitric acid. It was planned also to study the effect of additions of nitrates and also perchloric acid as means of inhibiting the corrosion in solutions of sulfuric and hydrochloric acids. In addition to the formation of a protective oxide film on titanium by inhibitors it was also believed that a similar film could be prepared by anodic oxidation, and it was therefore proposed to investigate this possibility.

A. Additions of HNO_3 to Sulfuric Acid. As the previous tests involving passivity employed 40% sulfuric acid it was decided to use this concentration of acid in the present study. A specimen of annealed titanium was exposed to an acid mixture containing 40% H_2SO_4 and 10% HNO_3. The solution was not aerated and was maintained at 35°C for six days. At the

end of this time the specimen was removed and examined. The specimen was found to be slightly discolored by an extremely thin, adherent, amber-colored film. There was no evidence of any type of attack upon the specimen. In order to determine the least possible amount of nitrate ion which is effective in bringing about passivity, a similar specimen was exposed to a mixture of 40% H_2SO_4 and 1% HNO_3. An examination of the specimen after an exposure to this mixture for six days at 35°C indicated that no attack had occurred. The surface of the specimen was found to be amber colored just as in the previous test. Specimens of titanium were then exposed to the following solutions: 40% H_2SO_4 and 1% $NaNO_3$, 40% H_2SO_4 and 0.5% $NaNO_3$, 40% H_2SO_4 and 0.1% $NaNO_3$. The tests were made with no aeration at 35°C for six days. The specimens which were exposed to the first two solutions mentioned above showed no corrosion and were covered with a thin amber film. The specimen which was exposed to the 40% H_2SO_4 and 0.1% $NaNO_3$ was severely attacked. The corrosion was uniform, however, with no obvious pitting.

Similar additions of NO_3^- to sulfuric acid were studied at a higher concentration of sulfuric acid. A specimen of titanium was exposed to 96.5% H_2SO_4 and 1% HNO_3 for six days at 35°C with no aeration. The specimen was unattacked at the end of this period. A similar test was made using 96.5% H_2SO_4 and 1% $NaNO_3$. After six days a very slight attack upon the specimen was observed.

B. Addition of Perchloric Acid to Sulfuric Acid. The addition of perchloric acid as an inhibitor for sulfuric acid was next studied. A specimen of titanium was exposed to a mixture of 95% H_2SO_4 and 0.5% $HClO_4$ for a period of six days at 35°C with no aeration. The specimen suffered a very severe, uniform attack.

C. Effect of Temperature on HNO_3 Additions. At elevated temperature the addition of NO_3^- to sulfuric acid was also found to be effective in lowering the rate of corrosion. A specimen of titanium was exposed to 10% H_2SO_4 and 1% HNO_3 for six days. The solution was kept at 60°C and was fully aerated. At the end of the testing period the specimen was examined and found to show no evidence of attack. Ordinarily at this temperature titanium is attacked very severely by this concentration of sulfuric acid.

D. Quantitative Tests. In order to compare quantitatively the effect of adding nitric acid to sulfuric acid a set of four specimens of annealed titanium was tested in a solution of 40% H_2SO_4 and 1% HNO_3. The tests were made at 35°C in fully aerated solution over a six day period. Similar tests were made upon type 316 stainless steel. It was found that the annealed titanium in this mixture of acid gave an average corrosion rate of 0.92 m.d.d. or 0.29 m.p.y. When annealed titanium was exposed to 40% H_2SO_4 under the same conditions the average rate of corrosion was found to be 1,069 m.d.d. or 341 m.p.y.

E. Addition of HNO_3 to Hydrochloric Acid. The effect of adding nitric acid to hydrochloric acid was next investigated. Four specimens of annealed titanium were exposed to a solution containing 20% HCl and 1% HNO_3. The tests were made at 35°C with full aeration for a six day period. The average rate of corrosion was found to be 1.44 m.d.d. or 0.46 m.p.y. as against 395 m.d.d. or 126 m.p.y. for annealed titanium in 20% HCl at 35°C.

The results of all tests are tabulated in Table VIII.

F. Previous Studies on Anodic Films. In the past several years the anodic oxidation of aluminum has become extremely important. When aluminum is exposed to air it soon becomes covered with a thin layer of oxide

TABLE VIII

Effects of Inhibitors

Solution	Temperature °C	Degree of Aeration	Results
40% H_2SO_4, 10% HNO_3	35	none	no attack
40% H_2SO_4, 1% HNO_3	35	none	no attack
40% H_2SO_4, 1% $NaNO_3$	35	none	no attack
40% H_2SO_4, 0.5% $NaNO_3$	35	none	no attack
40% H_2SO_4, 0.1% $NaNO_3$	35	none	severe attack
96.5% H_2SO_4, 1% HNO_3	35	none	no attack
96.5% H_2SO_4, 1% $NaNO_3$	35	none	slight attack
95% H_2SO_4, 0.5% $HClO_4$	35	none	severe attack
10% H_2SO_4, 1% HNO_3	60	aerated	no attack
20% HCl, 1% HNO_3	35	aerated	no attack
40% H_2SO_4, 0.5% HNO_3	35	aerated	no attack

which protects the surface from further corrosion. Such a film may be prepared by chemical treatment, especially by anodic oxidation. Oxide films prepared by such treatment have the property of only allowing the passage of current in one direction, that is, from the metal into the oxide. Thus, when aluminum is made the anode in a cell containing a weakly basic solution and a given potential impressed upon the cell from an external D.C. source, it is found that the current will rapidly decrease to an extremely low value. If the voltage is further increased, only enough current will flow to increase the film thickness until its resistance is great enough to allow only an infinitely small current to flow for the voltage impressed. Such coatings have found use in electrolytic rectifiers, lightning arrestors, and for applications where improved resistance toward corrosion is desired. The anodic film prepared on aluminum and its alloys is transparent but can be colored for decorative applications by dyeing with organic dyes.

It was pointed out by Kroll (17) that a film of titanium oxide on titanium also allows current to flow in only one direction. He also suggested the use of titanium in place of aluminum in wet rectifiers using KOH as the electrolyte. This effect was also found in dilute sulfuric acid solution.

It was decided to investigate the conditions under which the oxide film on titanium could be prepared and its effect upon the corrosion resistance of titanium to acids. It was found in the preliminary tests that the oxide film so formed exhibits a broad range of very brilliant colors which is dependent upon the following factors: The composition of the electrolyte, temperature, source of current (A.C. or D.C.), and the rate of voltage increase with time.

C. Film Formation with Alternating Current. A series of experiments was made to determine suitable electrolytic solutions for this process, and to determine the limitations of the other variables previously mentioned. In these tests a source of 60 cycle alternating current was used with a Variac in series with the cell to control the voltage across the cell. Both electrodes in every test were of cold-rolled titanium polished to a bright finish and pre-cleaned in a mixture of 50% ethyl alcohol and 50% ethyl ether.

The solutions found to be most satisfactory are as follows: (1) Saturated $NaHCO_3$ with addition of 1.25 c.c. of 30% H_2O_2 per liter. (2) Saturated $NaHCO_3$ with additions of CrO_4^{--}. (3) 3% KIO_3 with slight addition of 30% H_2O_2. (4) 3% solution of $Na_2WO_4.2H_2O$. (5) K_2CrO_4 solutions of all strengths above 3%. It was found that the additions of H_2O_2 and CrO_4^{--} to the saturated $NaHCO_3$ greatly decreased the current requirements of the process and increased the ease with which the color

of the film could be controlled. Without these additions the film which was formed appeared to have many minute breaks which served to leak current and not only impaired the effectiveness of the film as a protective device but also increased the temperature of the electrolyte due to the increased I^2R loss. The most satisfactory results were obtained with the electrolytes at room temperature (22°C). As the temperature was increased it was increasingly difficult to form the film.

When a 3% solution of $Na_2WO_4.2H_2O$ was used as the electrolyte with two titanium electrodes and an A.C. current the following optimum conditions were found. A maximum potential of 20 volts was reached in 38 minutes when the temperature of the electrolyte was 22°C. During the test the potential was increased in small encrements so that the current density of either electrode never exceeded 4.65 amperes per square decimeter. The color of the film when first formed was yellow but gradually changed through gold to crimson at the end of the test.

It was found that when a 3% solution of K_2CrO_4 at 22°C was used the potential could be increased to 13 volts in 30 minutes. The film obtained was gold in color and was found to be 0.30 mils thick by means of a filmeter developed by the Naval Research Laboratory and manufactured by the American Instrument Company of Silver Spring, Maryland. A further increase of potential to 24 volts at the same current density as before caused the film to change to a blue color. The thickness of this film was also found to be 0.30 mils by the filmeter. It is doubtful if the sensitivity of the filmeter is great enough to measure accurately the small increase in film thickness indicated by the color change of the film.

A satisfactory film was obtained with a solution of saturated $NaHCO_3$ with slight additions of H_2O_2 or CrO_4^{--} at room temperature when the voltage was increased gradually so that the current was kept below 46 amperes per square decimeter at all times.

A solution of 3% KIO_3 at room temperature was found to give very satisfactory results. A small quantity of free iodine was liberated during the electrolysis, but this effect was made negligible by the addition of a small amount of H_2O_2.

The results of tests with the electrolytes previously mentioned and also the other electrolytes studied are presented in Table IX.

TABLE IX

Electrolytes Studied for Anodizing Titanium with Alternating Current

Electrolyte	Temperature °C	Time, Minutes	Maximum Voltage	Current Amps./dm.^{2}	Final Color (Remarks)
Sat. $NaHCO_3$ + H_2O_2	22	185	32	4.65	light blue
Sat. $NaHCO_3$	23	16	14	38.0	burnt amber
3% KIO_3 + H_2O_2	22			1.55	light blue
3% $Na_2WO_4 \cdot 2H_2O$	22	38	20	4.65	rose
3% $NaNO_3$					above 15 V. film broke
3% K_2CrO_4	22	30	13	19.4	gold
3% $C_2H_2O_4$	20	12	11	9.92	film dissolved
5% HNO_3	22	22	16		above 16 V. film broke
Sat. Na_2HPO_4	22	surface was readily attacked to form thick gray film			

H. Film Formation with Direct Current. A study was next made to determine suitable electrolytes and the time-voltage relationships for the anodic oxidation of titanium using a direct current source. In these tests cold-rolled titanium was used for the anodes and lead for the cathodes. A variable resistance was placed in series with the cell to provide a means of regulating the cell voltage. The titanium electrodes were polished to a bright finish and washed with a mixture of 50% ethyl alcohol and 50% ethyl ether before the anodizing operation. The following solutions were found to be very satisfactory for the anodic oxidation of titanium with direct

current: (1) Saturated $NaHCO_3$. (2) Saturated Na_2PPO_4. (3) 15% H_2SO_4. (4) 3% $C_2H_2O_4$. At 22°C it was found that in all of the electrolytes mentioned above, a corrosion resistant oxide film was produced by gradually increasing the potential to 40 volts over a 55 minute period.

I. Corrosion Resistance to Sulfuric Acid. Each of the specimens which was anodized was exposed to a solution of 5% H_2SO_4 at 35°C with no aeration. A specimen of titanium which had received no treatment was also exposed to 5% H_2SO_4. It was found that the specimens which had been anodized showed absolutely no corrosion over a 28 day period. The specimen which had not been treated was attacked at the rate of 67.5 m.d.d. or 21.5 m.p.y. over the 28 day period. The results of this test are shown in Table X.

A specimen of "anodized" titanium also was tested in 40% sulfuric acid at 35°C. Over a six day testing period the corrosion rate was found to be 150 mils per year, whereas the untreated metal was found to corrode at the rate of 425 mils per year. It was observed that the "anodized" specimen did not start to corrode actively until after about 48 hours. At the end of the testing period, however, active corrosion was occurring, and the surface was found to be very evenly attacked. It is very likely, therefore, that if the period of testing were extended the rate of corrosion of the treated metal would approach in value the rate of the untreated metal.

In order to determine the maximum concentration of sulfuric acid in which the anodizing treatment would offer satisfactory protection to titanium the following tests were made. Three specimens of titanium were surfaced in the usual fashion and oxidized anodically in a saturated solution of sodium bicarbonate at 22°C. The potential was increased at such a rate that after seven minutes the potential across the cell was 25 volts. At no time was the anode current above 0.39 amperes per square decimeter. The specimens

were then rinsed, dried, and weighed. They were exposed to 10%, 15%, and 20% sulfuric acid respectively at 35°C with full aeration for 11 days. It was found that 10% sulfuric acid did not attack the "anodized" titanium, however, in 15% sulfuric acid the treated metal was found to exhibit a rate of 86.0 m.d.d. or 27.4 m.p.y. In 20% sulfuric acid the rate was increased to 304 m.d.d. or 96.8 m.p.y. These tests indicate that at 35°C the strength of sulfuric acid which is fully resisted by titanium may be increased from 5% to 10% by the process of anodic oxidation.

J. Corrosion Resistance to Hydrochloric Acid. In order to determine if the anodic oxidation produces a film upon titanium which is resistant to hydrochloric acid a set of specimens which were anodically treated by the method described immediately above were exposed to 10% hydrochloric acid at 35°C with full aeration for 21 days. At the end of the testing period the specimens were found to have been attacked at the rate of less than 0.35 m.d.d. which may be considered full protection. The rate for untreated titanium in 10% hydrochloric acid was found previously to be 133 m.d.d. Thus, the useful range of hydrochloric acid with titanium at 35°C can be increased from five percent to ten percent by use of anodic oxidation. The results of all corrosion tests on anodized titanium are tabulated in Table X.

TABLE X

Corrosion Resistance of "Anodized" Titanium

Test Solution	Temperature °C	Aeration	Length of Test, Days	Remarks
5% H_2SO_4	35	none	28	no attack
40% H_2SO_4	35	none	6	attacked, 158 m.p.y.
10% H_2SO_4	35	full	11	no attack
15% H_2SO_4	35	full	11	attacked, 86 m.d.d., 27.4 m.p.y.
20% H_2SO_4	35	full	11	attacked, 304 m.d.d., 96.8 m.p.y.
10% HCl	35	full	21	no attack

PART II - EXPERIMENTAL

CHAPTER VI

STRESS CORROSION OF TITANIUM

In almost all applications of materials of construction the problem of stress corrosion occurs. Applied stress in addition to residual stresses in a metal sometimes causes corrosion phenomena which would not occur to the metal under ordinary conditions. It is therefore very important to understand the mechanism by which such attack proceeds in order to determine processes of fabrication which would eliminate this attack. Before titanium can be considered for use in the construction of chemical equipment it is necessary to have some information on what type of stress attack is to be expected. To the knowledge of the author there was no information available on this subject at the time this research was begun.

A. Testing Procedure. The specimens to be studied were cut to the following dimensions: 0.9 cm. x 10 cm. x 0.112 cm. The specimens were then bent in a U shape as shown in Figure 12. The distance across the open end of the U was 2.5 cm. A glass clamp was fitted over the ends of the specimen bringing the distance across the ends to 1.0 cm. The specimens were then given the standard surfacing and cleaning treatment, and exposed to 750 ml. of a solution of absolute methyl alcohol containing 0.33% by weight of bromine. The solution was heated during the study and allowed to reflux. The boiling point of this mixture was 64.7°C. After failure, the specimens were removed and studied microscopically.

FIGURE 12.

Battelle Ti (consolidated by melting) tested under stress in a 0.33% Br_2 solution in methyl alcohol at b.p. Failure occurred after 1/2 hour exposure.

B. Annealed Titanium. A specimen of annealed titanium prepared by powder metallurgy consolidation and subsequent rolling and annealing was stressed and subjected to the testing solution. After 23 hours the specimen was removed and examined, although failure had not occurred. The surface of the specimen was darkened. The specimen had become weakened at the bend and could be moved easily whereas before the test it offered considerable resistance.

The structure of the stressed section after the test is shown in Figure 13, and the structure of the unstressed section is shown in Figure 14. The attack in both cases was intergranular, but appears to have been much worse in the stressed section. The annealed grain structure outlined by the intergranular attack was seen to be typically polyhedral.

A second specimen of annealed titanium with the same deformation was exposed to the test solution for 18 hours without failure. The structure of the stressed and unstressed sections of this specimen are shown in Figures 15 and 16. In both cases the metal underwent intergranular attack. The extent of attack was not as great as that observed in the first specimen due to 20% less exposure time.

C. Cold Rolled Titanium. A specimen of cold-rolled titanium prepared by powder metallurgy consolidation and subsequently rolling with 40% reduction was stressed and exposed to the standard testing solution. Failure occurred at the stressed section after two hours exposure. The structure at the point of failure is shown in Figure 17. The attack at this point was extensive. The structure of the unstressed section is shown in Figure 18. The corrosion at this point was moderate. In both cases the attack was intergranular.

The effect of stress on the extent of intergranular corrosion was greater in the case of the cold-rolled titanium than for the annealed

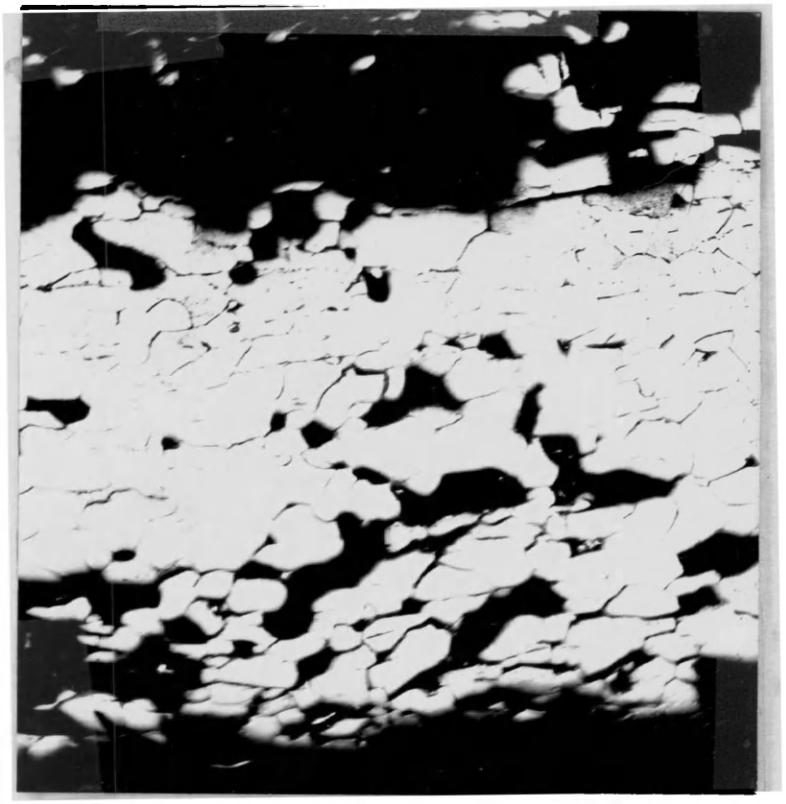


FIGURE 13.

Annealed Ti(consolidated by powder technic) tested 23 hours under stress in a 0.33% Br_2 solution in absolute methyl alcohol at b.p.

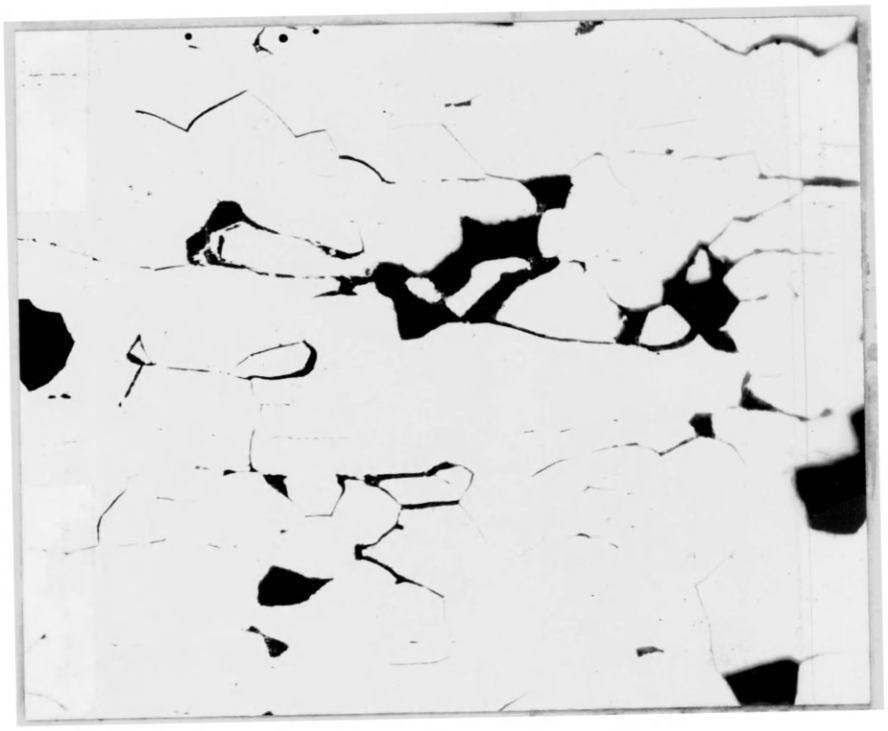


FIGURE 14.

Same sample as FIGURE 13, long section through unstressed end of sample.

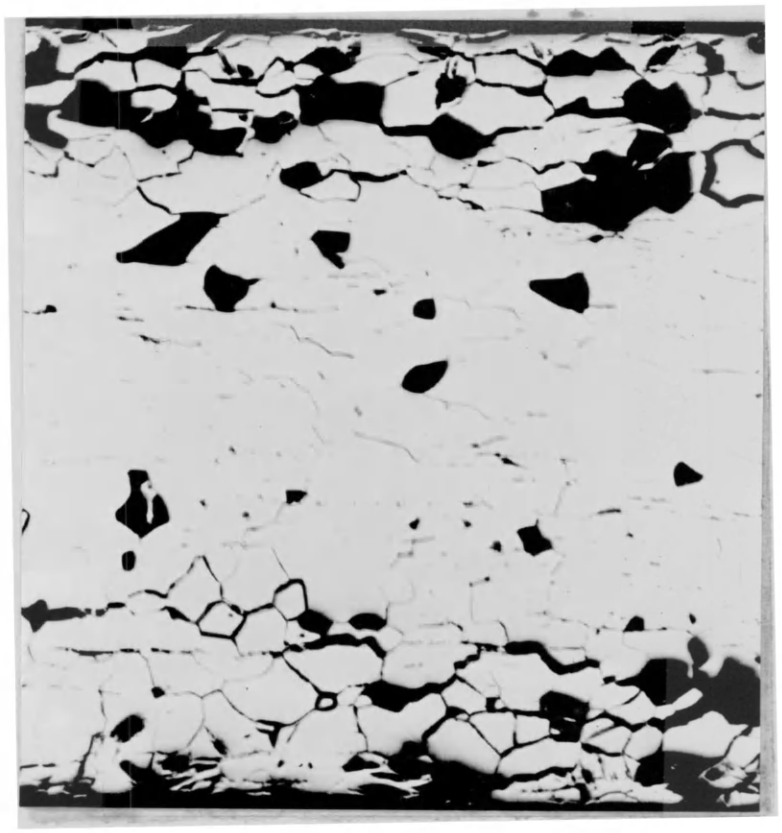


FIGURE 15.

Long section of annealed Ti specimen (consolidated by powder technic) after exposed 18 hours in a 0.33% Br_2 solution in methyl alcohol at b.p.

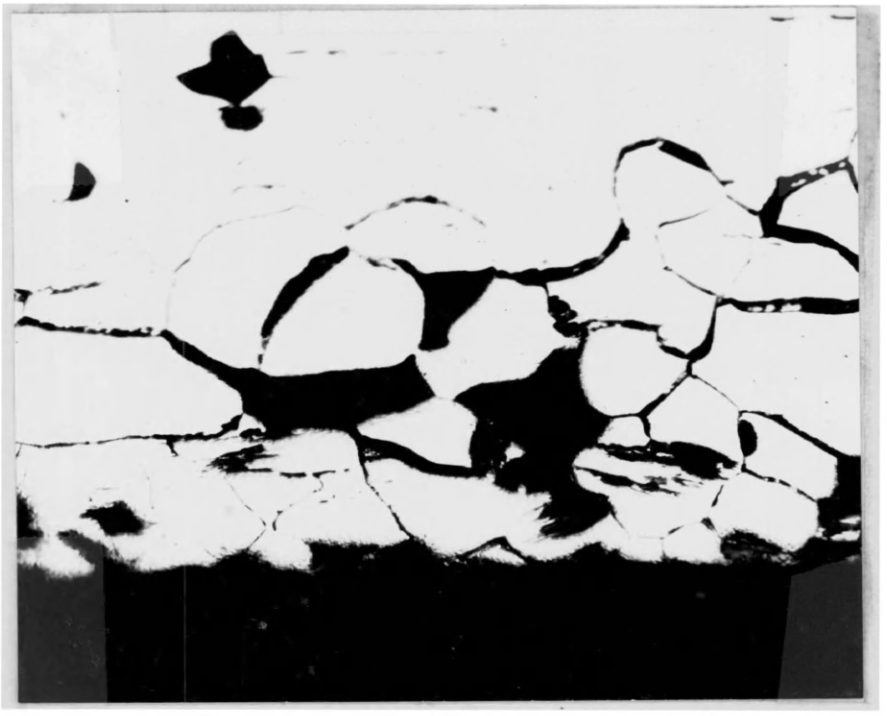


FIGURE 16.

Same specimen as FIGURE 15. Longitudinal section taken through unstressed end of sample.

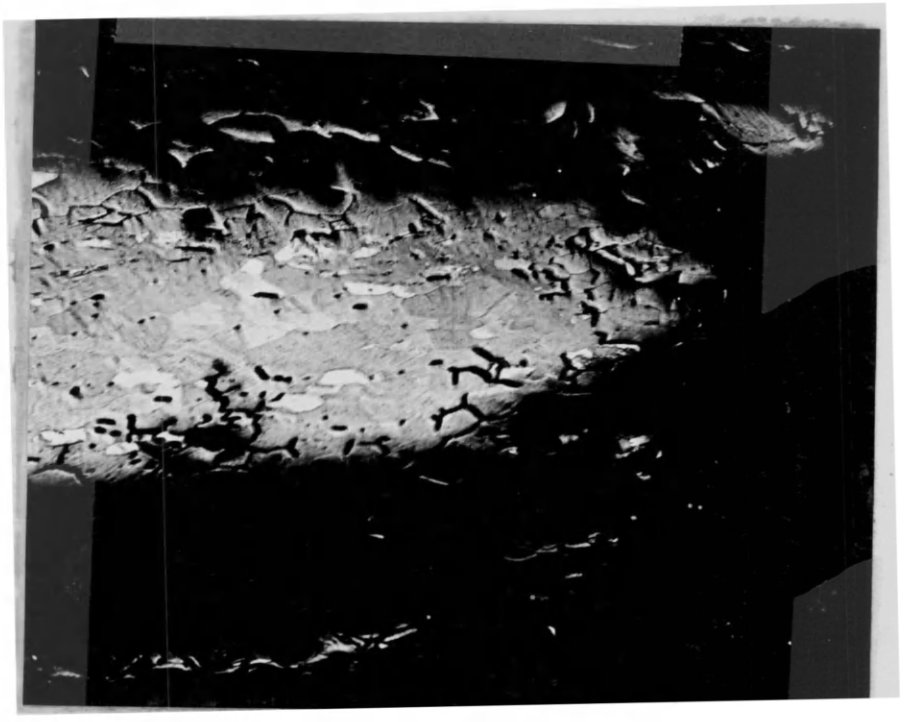


FIGURE 17.

Cold rolled Ti(consolidated by powder technic) exposed to a 0.33% Br_2 solution in methyl alcohol at the b.p. Corrosion extensive.

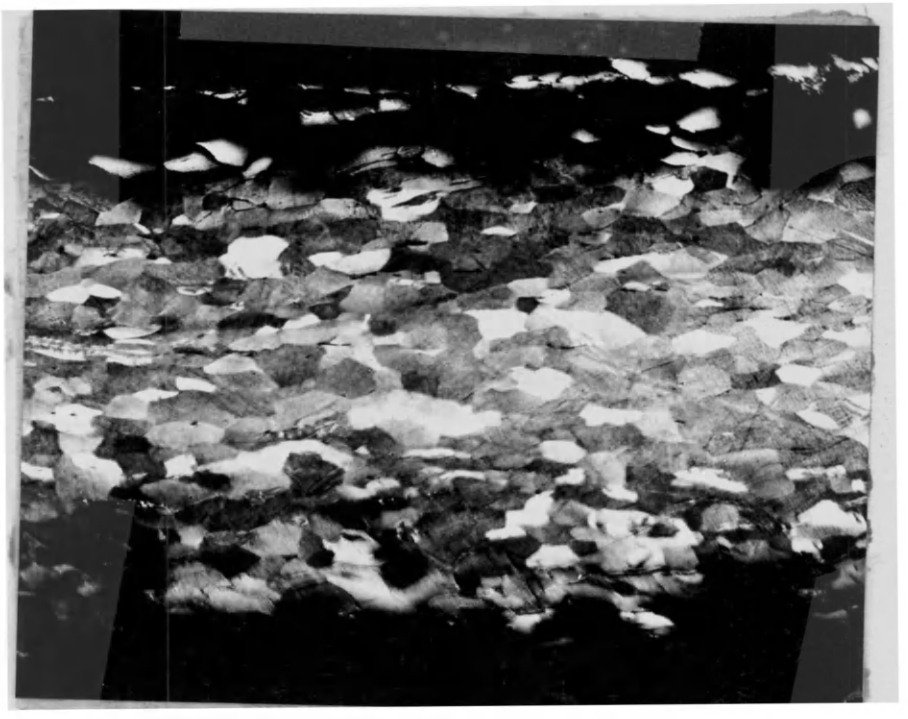


FIGURE 18.

Same specimen as FIGURE 17, longitudinal section through unstressed end of sample. Corrosion moderate.

titanium in the same medium. This can be readily observed by comparing Figures 17 and 18 with Figures 15 and 16.

The rapid intergranular attack upon both the annealed and cold-rolled titanium by the Br_2-CH_3OH reagent suggests a possible method of converting scrap titanium to a powder form which could be re-consolidated by powder technics.

D. Cold-Rolled Titanium Consolidated by Melting. A specimen of titanium prepared by a melting procedure with subsequent 40% reduction by cold-rolling was stressed and placed in the .33% Br_2 solution of absolute methyl alcohol. Failure occurred after 1/2 hour exposure. The appearance of the specimen after failure is shown in Figure 12. The early failure of this specimen was attributed to the occurrence of tension stress cracks along the outside radius of the bend, which were propagated to failure in the corrosive medium. The intergranular character of the failure together with a typical tension stress crack may be seen in Figure 19.

The results of this research indicate that failure of titanium due to stress corrosion can be minimized by an annealing operation after the cold rolling step in the manufacture of sheet material. It also appears that the metal consolidated by powder metallurgy may be stressed much more than the titanium prepared by melting without danger from stress corrosion.

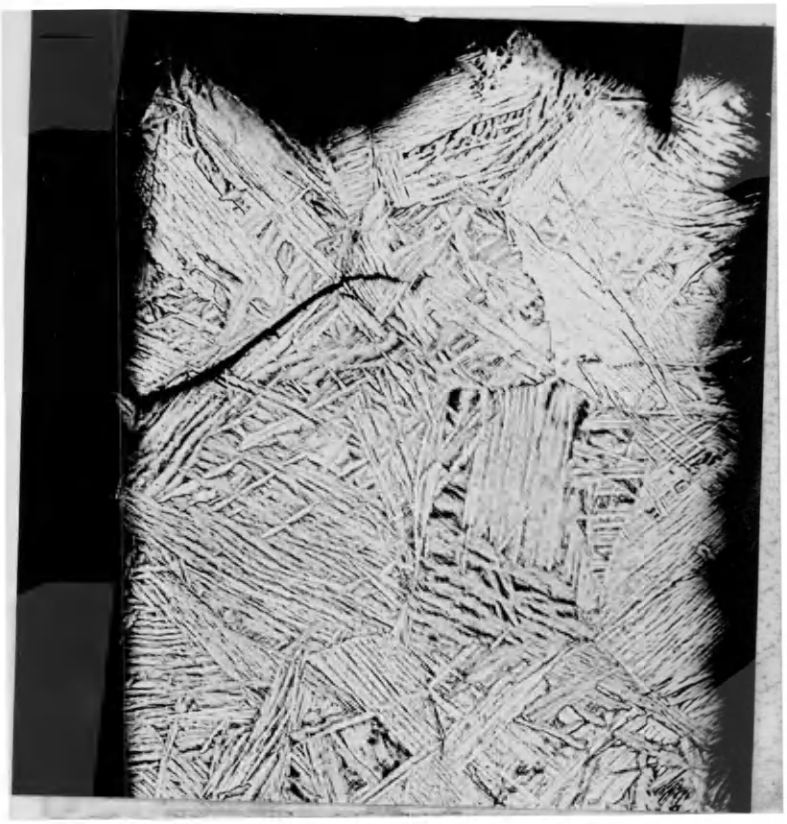


FIGURE 19.

Long view at failure point of specimen shown in FIGURE 12. Note tension stress crack near break.

SUMMARY

Equipment was designed for investigating the corrosion of ductile titanium in sulfuric, nitric, and hydrochloric acids. It was found that titanium can withstand concentrations of sulfuric acid up to 5% at 35°C, but an increase in temperature to 60°C increased the rate to such an extent that the use of the metal under these conditions is impossible. The reaction mechanism of titanium in sulfuric acid was investigated, and it was concluded that the decrease in corrosion rate observed in 65% sulfuric acid at 35°C was due to a protective film of $Ti_2(SO_4)_3$ that is insoluble in this concentration of acid. The corrosion of annealed titanium and cold-rolled titanium in sulfuric acid was compared and was found to be identical.

As in the case of sulfuric acid, titanium was found to resist hydrochloric acid up to 5% at 35°C. An increase in temperature to 60°C was found to lower the maximum permissible concentration of hydrochloric acid to 3%, and a further increase in temperature to 100°C lowered this concentration to 1%. Titanium metal consolidated by melting was compared in hydrochloric acid against titanium prepared by powder technics and was found to be slightly more resistant to corrosion than the latter.

The corrosion resistance of titanium to nitric acid of all concentrations was found to be excellent at all temperatures up to, and including the boiling point of 65% acid.

An explanation was sought to account for the passivity exhibited by titanium in nitric acid. Experimental data relating suggested theories and an interpretation of these have been presented to throw some light upon the mechanism of this phenomena. It was concluded that the passivity was due both to the presence of an oxide film and to the physical adsorption

of a gas (either O_2 or oxides of nitrogen) upon the surface of the metal. The protection offered by the film prepared by exposure to oxygen at elevated temperatures was shown also to be dependent upon physically adsorbed gas.

Various means of increasing the corrosion resistance of titanium to hydrochloric and sulfuric acids were investigated. The uses of inhibitors and anodic oxidation were examined and comparative data developed.

The stress corrosion of titanium metal prepared by several different technics was investigated, and an effort was made to correlate the methods of consolidation to the susceptibility to stress attack. A set of micro-photographs illustrating stress corrosion was presented.

BIBLIOGRAPHY

(1) Tentative Method of Total Immersion Test of Non-Ferrous Metals. A. S. T. M. Designation: B185-43T (1943).

(2) Berzelius, J. J. Pogg. Ann, 4 (1825) p. 1.

(3) Billy, M. (Titanium) Ann. Chem., vol. 16 (1929) pp. 5-54.

(4) Clarke, F. W. U. S. Geological Survey Bulletin 770, (1924) p. 36.

(5) Dean, R. S., B. Silkes (Metallic Titanium and its Alloys) Bureau of Mines Information Circular No. 7381, (1946) p. 1.

(6) Technical Information, Pigments Department, E. I. duPont de Nemours and Company, Wilmington, Delaware.

(7) Dean, R. S., J. R. Long, F. S. Wartman, and E. L. Anderson (Preparation and Properties of Ductile Titanium) Metals Technology (1946) 13 No. 2, Technical Publication No. 1961, pp. 12-13.

(8) Evans, U. R. Metallic Corrosion, Passivity and Protection: Edward Arnold and Co., London (1937) p. 4.

(9) Faraday, M. Experimental Researches in Electricity, vol. II: University of London (1844) p. 243.

(10) Fontana, M. G. Industrial and Engr. Chem. 39, No. 9 (1947) pp. 103A-104A.

(11) Gillett, H. W. (Some Features of Ductile Zirconium and Titanium) Foote Prints, 13, No. 1 (June, 1940) pp. 5-7.

(12) Glasstone, S. Textbook of Physical Chemistry: D. Van Nostrand and Co., New York (1940) p. 1011.

(13) Gregor, W. Crell's Ann., i, 40, (1791) p. 103.

(14) Humes, C. H., R. F. Passano, and A. Hayes, (A Study of the Error of Averages and Its Application to Corrosion Tests) Proceedings of American Soc. Testing Materials 30 (1930) Part II, p. 448.

(15) Hunter, M. A. (Metallic Titanium) Journ. Am. Chem. Soc., vol. 32 (1910) pp. 330-336.

(16) Kloproth, M. H. Beitrage zur Chemischen Kenntiss der Mineralkorper.

(17) Kroll, Wilhelm (The Production of Ductile Titanium) Trans. Electro-Chemical Society, vol. 78 (1940) pp. 35-47.

(18) Kroll, W. J., et. al. Metals Technology, Jan., 1948.

(19) Kroll, W. J., (Einige Eigenschaften des Reinen Titans) Metallwirtschaft, 18 (1939) pp. 77-80.

(20) Lely, D., and L. Hamburger (Herstellung der Elemente Thorium, Uran, Zirkon und Titan) Ztschr. anorg. Chem., 87 (1914) pp. 208-228.

(21) Moissan, Henri (Preparation and Properties of Titanium) Compt. rend., vol., 120 (1895) pp. 290-296.

(22) Nilson, L. F., and Otto Petterson (Several Physical Constants of Germanium and Titanium) Ztschr. physikal. Chem. vol. 1 (1887) pp. 27-28.

(23) Patterson, R. A. (Crystal Structure of Titanium and Chromium) Phys. Rev., vol. 26 (1925) pp. 56-59.

(24) Podgus, Emil (Reindarstellung sehr reaktionsfahrivgen Metalle und Metalloide) Ztschr. anorg. Chem., vol., 99 (1917) pp. 123-131.

(25) Seidell, A. Solubilities of Inorganic and Metal Organic Compounds Third Edition 1 (1940) p. 557.

(26) Sutton, J. B. (Induction Melting of Titanium Metal in Graphite) Titanium Symposium, Paper 9, Washington, D. C., Dec. 16, 1946.

(27) Tammann, G. Z. anorg. Chem. 107 (1919) p. 104, 236.

(28) Thornton, W. M. Jr., Titanium: A. C. S. Monograph Series No. 33, (1927) pp. 26-29.

(29) Production of Titanium Powder at Boulder City: Titanium Symposium, Paper 4: Washington, D. C., Dec. 16, 1948.

(30) Uhlig, H. H., and J. Wulff. Trans. Am. Inst. Mining Met. Engrs. 135 (1939) pp. 494-521.

(31) Uhlig, H. H. Trans.Electrochemical Society, 85 (1940) pp. 307-333.

(32) Van Arkel, A. E. (Production of High-Melting Metals by the Thermal Dissociation of their Compounds) Metallwirtschaft, vol. 13 (1934) pp. 405-409, 511-514.

(33) Wohler, F. Liebig's Ann., 73 (1849) p. 34.