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A STUDY OF TITANIUM DIFFUSION COATINGS
BY X-RAY FLUORESCENT METHODS

BY

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A

THESIS

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in partial fulfillment of the work required for the

Degree of

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1955

Approved by - M. E. Straumanis.
Professor of Metallurgical Engineering

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INTRODUCTION

A. The Importance Of Titanium

With the development of commercially feasible processes of extracting titanium from its naturally abundant compounds, it has become possible to utilize titanium in many applications where its desirable properties are required. One of the more important properties of titanium is its ability to withstand the corrosive attack of all common acids except hydrofluoric acid, hydrochloric acid and concentrated sulfuric acid. Hydrofluoric acid is the only acid that is able to appreciably dissolve the protective oxide layer that is formed on titanium and to attack the metal rapidly. It would be very desirable to plate a corrosion-resistant titanium layer on other metals. However, the work of all early investigators was relatively unsuccessful. According to a literature search made by Schlechten, Straumanis and Gill,(1) there has been no successful method developed for electroplating titanium from aqueous or organic solutions. It is possible to electrodeposit titanium from a fused salt bath, but the resultant thin coating is covered by titanium powder and flakes; hence, it tends to be of poor quality.(2) The process is further complicated by the necessity of obtaining highly purified salts and operating the cell under a protective atmosphere.

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(1) Schlechten, A. W., Straumanis, M. E. and Gill, C. B., "Deposition of Titanium Coatings from Pyrosols", J. Electrochem. Soc., Vol. 102, p. 81, 1955.

(2) Cordner, G. D. P. and Worner, H. W., Austral. J. Appl. Sci., Vol. 2, p. 358, 1951.

An alternative to electroplating a protective titanium layer on the base metal would be a process which would apply a diffusion coating of titanium to the base metal. A diffusion coating may be defined as a cementation process that operates by a diffusion mechanism.(3) A diffusion coating produces a smaller dimensional change than an electroplated layer and adheres more strongly to the base metal. Although corrosion-resistant diffusion coatings of such metals as chromium and silicon have been studied in detail and commercial processes such as "chromizing" and "Ihrigizing" have been evolved, little work has been done on titanium diffusion coatings or "titanizing" processes. In 1927, Laissus(4) produced titanium coatings on iron and steel by means of a cementation process using ferrotitanium powder. However, the corrosion resistance of the base metal was only slightly improved. Other investigators were able to produce coatings but with no increase in corrosion resistance.(5)(6)(7)

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(3) Dovey, D. M., Jenkins, I. and Randle, K. C., "Diffusion Coatings", Properties of Metallic Surfaces, Institute of Metals Monograph No. 13, pp. 213-236, 1952.

(4) Laissus, J., "Contributions to the Study of Metallic Cementation: Cementation of Iron Alloys by Titanium and Zirconium", Revue de Metallurgie, Vol. 24, p. 764, 1927.

(5) Kase T., "Metallic Cementation VIII — Cementation of Some Metals (Iron) by Means of Titanium (Ferrotitanium) Powder", Kinzoke No Kenkyu, Vol. 13, p. 50, 1936.

(6) Travers, A., "Coating of Iron with Titanium", Chemie et Industria, special number March 1932, p. 345, 1932.

(7) Cornelius, N. and Bollenrath, F., "The Effect of Carbon on the Diffusion of Some Elements in Steel", Arch. Eisenhuttenw., Vol. 15, p. 145, 1941.

Alexander (8) and Chapin and Hayward (9) developed a process for coating steels with a copper-titanium alloy of composition of 5 to 37.5 percent titanium. These coatings resisted attack by sodium chloride.

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(8) Alexander, P. P., "Coating Metal Articles", U. S. Patent 2,351,798, 1944.

(9) Chapin, E. J. and Hayward, C. R., "Copper-Titanium Coatings on Mild Steel", Trans. A. S. M., Vol. 38, p. 909, 1947.

All the previously mentioned processes were rather ineffective and there existed a definite need for the development of a process which would produce an acid resistant titanium coating.

B. History Of The Titanizing Process Developed At The Missouri School Of Mines

During experiments on the corrosion of titanium in molten alkali halide baths at the Missouri School of Mines, it was observed that the porcelain crucibles used in the tests were covered below the salt level with a layer which was largely titanium. (1)

A series of experiments were performed which showed that if certain metals are immersed in the molten salt bath containing titanium, the metal will be covered by titanium. The titanium coating originates from some of the corrosion products which have been formed in the salt bath. The corrosion products are mainly finely divided titanium particles similar to the "metal fogs" or "pyrosols" described by Lorenz and Eitel. (10) Copper, iron, nickel, cobalt, and nickel-copper alloys

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(10) Lorenz, R. and Eitel, W., "Pyrosole", Akad. Verlagsges, Leipzig, 1926.

coated by the titanizing process were found to be resistant to attack by nitric acid.

Further experiments were undertaken to determine the influence of the composition of the salt bath, the effect of temperature, the effect of coating time, and the application of an external electromotive force on the characteristics and quality of the coating. These results are described in detail in an article by Schlechten, Straumanis and Gill.(1)

C. Statement Of The Problem

As the only previous determinations of the chemical composition of the titanium coatings had been analyses of the average composition of the entire coating, the determination of the variation in chemical composition throughout the coating was suggested. From this information, it was proposed that a better insight might be gained as to the extent and mechanism of diffusion in the coatings. It was also hoped to correlate the results with concurrent work being done on the phases present in the titanium coatings. From this correlation, it might be possible to show which phases are responsible for the desirable properties of the coating and the minimum amount of titanium in the coating that is necessary to produce an acceptable coating. Finally, it was hoped that the results obtained would verify the accuracy of existing methods for measuring the diffusion coating thickness.

D. Analysis Of Problem

X-ray fluorescent analysis, or x-ray emission spectroscopy as it is preferably called by the analytical chemist, was the method selected to be used in this work. This method of analysis has only recently been developed and shows great potentialities if the proper procedures are followed. Once the initial procedures have been established and the results calibrated with known data, the analysis, although sometimes not as accurate as wet chemical methods, is much quicker and simpler.

As it was necessary to determine composition at many points throughout the coating, fluorescent analysis would seem to be particularly applicable to the solution of this type of problem.

E. Review Of Previous Work

The only previous chemical analyses of titanium coatings produced at the Missouri School of Mines were made by Dr. William H. Webb and the results were reported in a paper by Schlechten, Straumanis and Gill.(1) Titanium and iron were determined by colorimetric methods; the former by using hydrogen peroxide as a reagent (Weller's method) and the latter by the method of Moss and Mellon.(11) In each instance, the sample of iron coated with titanium was immersed in a saturated solution of ferric chloride at a temperature of 60° to 80° C. to separate the coating f the base metal. Final traces of iron on the titanium were removed with 1 to 4 nitric acid. Only the insoluble or corrosion-resistant part of the coating was analyzed and any portion of the coating not containing a sufficient percentage of titanium to resist corrosion was dissolved along with the base metal and was not analyzed. The reported analyses were assumed to represent the average composition of the corrosion-resistant layer. The samples were small disks of low

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(11) Moss, M. L. and Mellon, M. G., "Colorimetric Determinations of Iron with 2,2' -bipyridyl and with 2,2,'2" -terpyridyl", Ind. Eng. Chem., Anal. Ed., Vol. 14, p. 862, 1942.

carbon steel or iron which were plated in a 50-50 molar percent bath of KCl-NaCl exposed to air. The thickness of the coatings analyzed by Webb were much greater than those analyzed in the present work.

The results of Webb's analyses are reproduced in figures 1 and 2 on the next page. In figure 1, the average composition of the coating is plotted against plating time for coatings produced in the NaCl-KCl bath at a temperature of 900° C. In figure 2, the average composition of the coating is plotted against the bath temperature at a constant plating time of 7 hours. It may be seen from these graphs that there is no great variation of average coating composition with plating time and only a slight increase in iron content with higher bath temperatures. Webb's results gave the average coating analysis as about 80 percent titanium, 15 percent iron and 5 percent unknown components, which were assumed to be oxygen. It was suggested that the coating varied from almost pure titanium on the outer surface to a very small concentration of titanium at the inner limit of the diffusion boundary. A study of figures 1 and 2 show that as the bath temperature increases, the coating thickness is greatly increased, while the average titanium content of the coating is actually slightly lowered.

The analyses of diffusion coatings produced by commercial processes have been much more extensive. In the case of chromium impregnation or chromizing, there is some disagreement as to the average composition of the coating and the factors which influence composition. Kelley (12) states that the chromium content of the diffused layer varies between

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(12) Kelley, F. C., "Chromium Impregnation", Metals Handbook, American Society for Metals, Cleveland Ohio, p. 706, 1948.

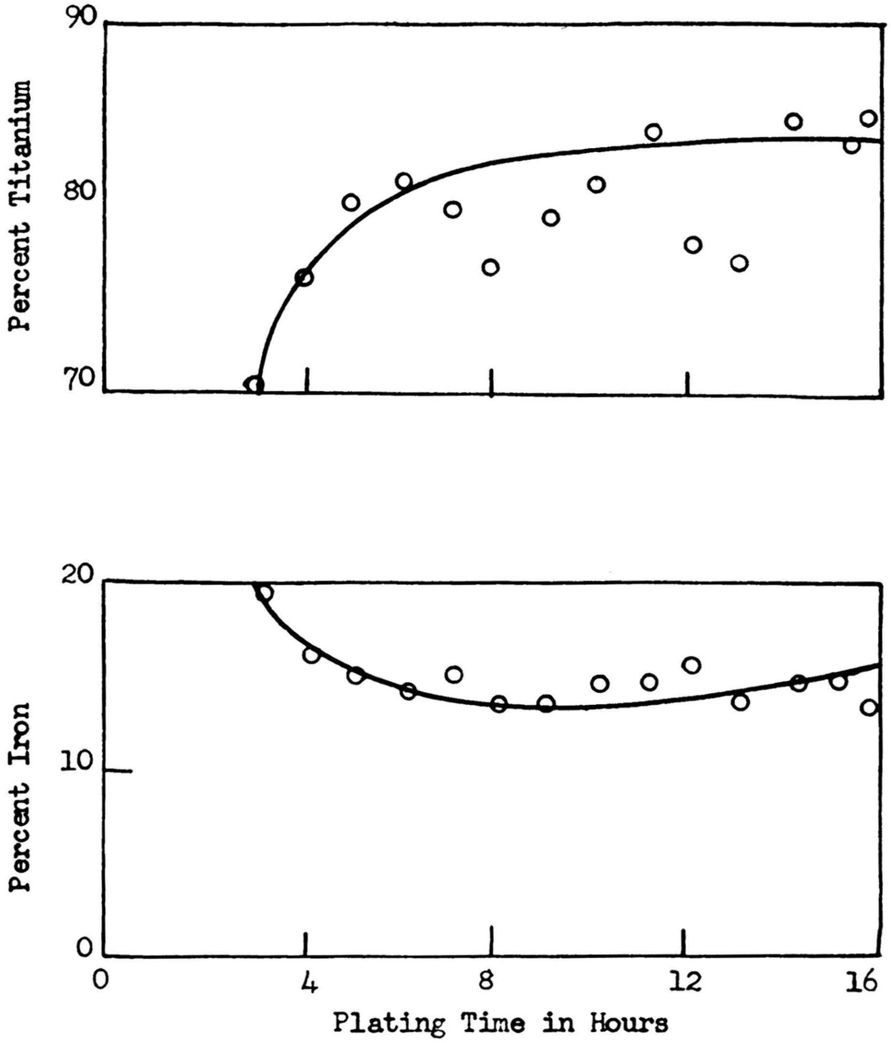

Fig. 1. Titanium and iron contents of titanium coatings vs. coating time; KCl-NaCl bath at 900° C.

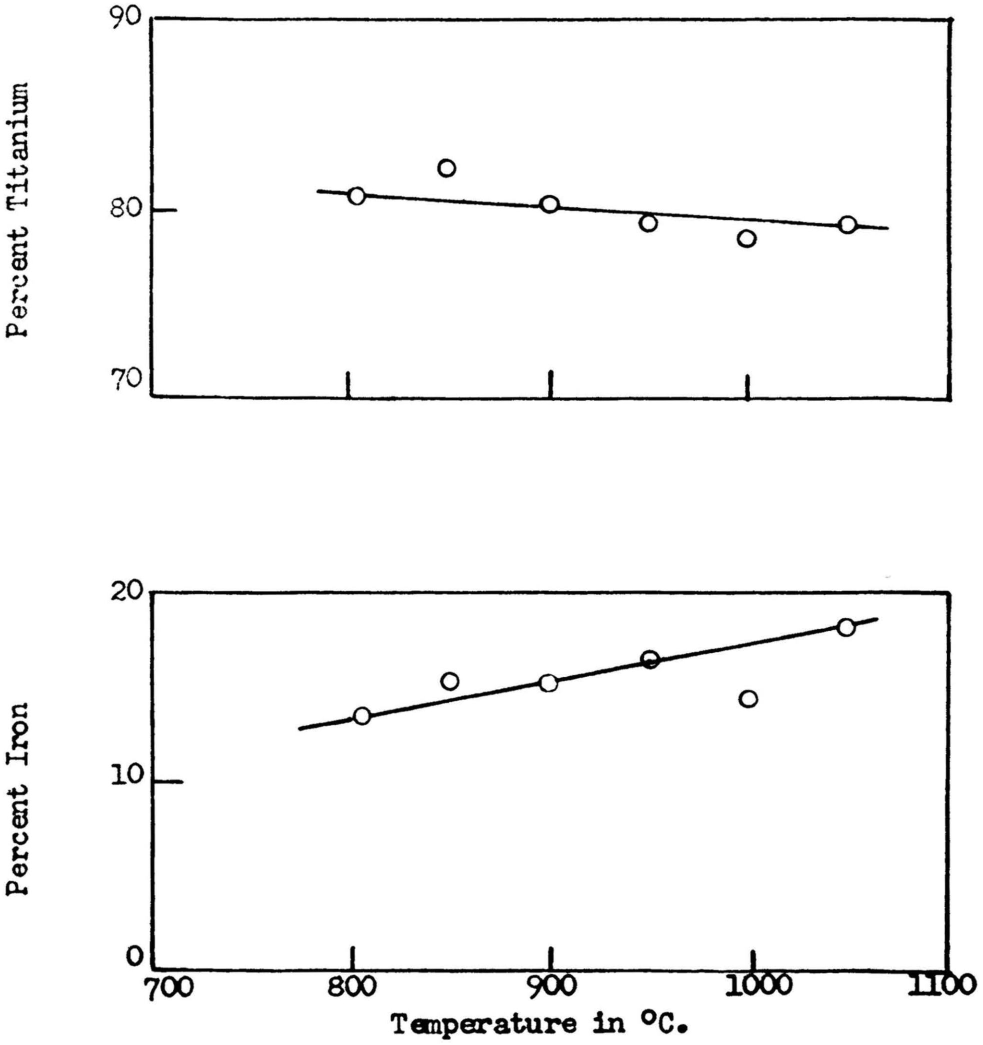

Fig. 2. Titanium and iron contents of titanium coatings vs. temperature; KCl-NaCl bath for 7 hr.

10 and 20 percent, depending on the time and temperature of heating. From the results of another series of analyses, Samuel and Lockington (13) report that the average composition of the coating varies from 18 to 23 percent chromium and is not dependent on time or temperature of heating. Campbell, Barth, Hoeckelman and Gonser (14) state that the surface layer is never pure chromium, but actually varies from 40 to 70 percent chromium. Bever and Floe (15) report that the chromium content of the surface layer varies from 35 to 50 percent. However, they also note that the sigma phase (45 percent chromium) is not usually found in chromized cases.

The earliest chemical analysis of chromium coatings was done in 1926 by Grube and Fleischbein. (16) Their results were obtained from the chemical analysis of thin layers turned off on a precision lathe. Although the accuracy of their method is questionable, they did observe a pronounced change of slope, corresponding to the position of the boundary of the columnar diffusion grains, on the plot of depth of

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(13) Samuel, R. L. and Lockington, N. A., "The Protection of Metallic Surfaces by Chromium Diffusion", Metal Treatment and Drop Forging, Vol. 18, p. 407, 1951.

(14) Campbell, I. E., Barth, V. D., Hoeckelman, R. F., and Gonser, B. W., "Salt Bath Chromizing", Trans. Electrochem Soc., Vol. 96, p. 263, 1949.

(15) Bever, M. B. and Floe, C. F., "Diffusion Treatments for Wear Protection", ASM Surface Protection Against Wear and Corrosion, p. 123, 1952.

(16) Grube, G. and Fleischbein, W., "Die Oberflächenveredelung der Metalle durch Diffusion", Ztsch. f. anorg. u. all. Chem., Vol. 154, p. 314, 1926.

penetration versus concentration of chromium. In 1934 Hicks,(17) by means of an x-ray diffraction method, found the surface layer contained about 66 percent chromium. Hicks also observed that the chromium content gradually decreased with increasing depth from the surface until a depth was reached at which there was a sudden discontinuous decrease of from 12 to 1 percent chromium. He concluded that this abrupt drop in concentration coincided with the limit of the gamma loop at the particular diffusion temperature. Hicks' work verified the observation of Bannister and Jones,(18) that in all cases where columnar growth was observed the metal that was diffusing into iron had the property of preventing the formation of the gamma solid solution when a definite percentage of the alloying element was reached. Hicks also suggested that the method employed by Grube was not delicate enough to pick up the abrupt concentration change. Hicks' method consisted of determining unit cell dimensions and then by comparison with a chart of unit cell dimensions of various iron-chromium alloys the composition of the alloy corresponding to a particular value of the unit cell could be determined. This method is particularly applicable to chromium because of the continuous solid solution between iron and chromium and also because values of the unit cell for various iron-chromium alloys are available from the literature. After each x-ray determination, the sample was ground down on No. 1 emery paper and 2/0 polishing paper and then its thickness

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(17) Hicks, L. C., "An X-ray Study of the Diffusion of Chromium into Iron", Trans. AIME, Vol. 113, p. 163, 1934.

(18) Bannister, C. O. and Jones, W. D., "The Diffusion of Tin into Iron", J. of the Iron and Steel Inst., Vol. 124, p. 71, 1931.

measured with a reputable ordinary micrometer.

Determinations have been made for the average composition of coatings produced by the other commercial processes. Ihrig (19) has found the composition of the outer two-thirds of a silicon coating to be about 15 percent silicon and to be substantially constant, while the inner one-third decreased to 5 percent silicon. Analyses were made of successive surface slices of 0.01 inches from a 0.12 percent carbon steel with the resulting silicon content varying from 14.02 to 13.54 percent for the outer two-thirds of the coating.

According to Sayles, (20) the surface layer of a calorized coating contains about 25 percent aluminum. The surface coating produced by the old method of calorizing contained as much as 60 percent aluminum at the surface and caused the layer to be too brittle. To eliminate brittleness, either pack calorizing is used or the old method is modified to include a 12 to 48 hour heat treatment at 800 to 1000° C. This heat treatment causes the aluminum to diffuse and thus produce a thicker coating and also decrease the concentration of aluminum at the surface of the layer.

Mc Culloch (21) has determined that the average zinc content for a sherardized coating produced by heating at 350 to 370° C. for three

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(19) Ihrig, H. K., "Silicon Impregnation", Metals Handbook, American Society for Metals, Cleveland, Ohio, p. 708, 1948.

(20) Sayles, B. J., "Aluminum Impregnation", Metals Handbook, American Society for Metals, Cleveland, Ohio, p. 703, 1948.

(21) Mc Culloch, L., "Experiments with Sherardizing", Trans. AIME, Vol. 68, p. 757, 1923.

hours is about 90 to 92 percent. Kelley(22) mentions that a sherardized coating containing more than 15 percent iron is not corrosion resistant.

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(22) Kelley, F. C., "Zinc Impregnation", Metals Handbook, American Society for Metals, Cleveland, Ohio, p. 716, 1948.

The results that have been mentioned showed that there is considerable variation between the compositions of different types of diffusion coatings and also considerable variation in the composition required to withstand corrosion. It would appear that the predominant factor in determining the properties of diffusion coatings is the nature of the layers which are present. Under ideal conditions, the phases present in a layer may be predicted from a consideration of the phase diagram; therefore, the phase diagram is of fundamental importance in determining the properties of a diffusion layer.

F. Theory Of X-Ray Fluorescent Analysis

The radiation produced when highly accelerated electrons strike a metal target in an x-ray tube may be of two types, continuous and characteristic. The continuous spectrum is produced by successive decelerations of the impinging electrons and consists of x-rays of various wave lengths. The minimum wave length of the continuous spectrum may be determined by applying the relationship: $eV = \frac{h\lambda}{c}$

where: $V =$ the accelerating potential between the cathode and the anode,

$e =$ the electronic charge,

$h =$ Planck's constant,

$c =$ the velocity of light,

$\lambda =$ the minimum wave length.

When an x-ray of minimum wave length is produced, it is assumed that the impinging electron has been decelerated in one collision. The shape of the continuous spectrum is independent of the target material. If the accelerating potential is greater than a certain minimum value which is dependent on the target material, the characteristic spectrum is superimposed on the continuous spectrum. When the energy of the accelerated electron is great enough to knock one of the inner electrons of the target material out of its orbit, the orbit is immediately filled by an electron drawn in from an outer shell. As the outer shell electron moves into an inner shell of lower energy, the excess energy is given off in the form of a characteristic x-ray photon. The most common characteristic x-ray is known as the K-alpha radiation and is produced when an electron drops from the L to K shell. In a similar manner, the K-beta x-ray is produced when an electron drops from the M to K shell. However, since the probability of this transition is less than the L to K transition, the intensity of the K-alpha x-rays will be greater than the K-beta. According to the quantum theory, each L shell is actually composed of three sublevels, so it might be expected that there would be three slightly different K-alpha characteristic x-rays for each element. Actually there are only two because the third transition is forbidden according to the selection rules that have been developed. The K-alpha doublet which was used in this work is composed of the two K-alphas which are of very nearly the same wave length for any given element. The wave length of any characteristic x-ray is dependent on the target material from which it is excited. This relationship, known as Moseley's law, states that the wave length of a characteristic x ray is inversely proportional to the square of the atomic number of the target material. By the use of an analyzing crystal, each of the characteristic x rays can be diffracted at a different angle defined by the Bragg equation: $n \lambda = 2d \sin\theta$

where: λ = the wave length of the characteristic x-ray,

d = the interplanar spacing of the analyzing crystal,

θ = the angle between the incident characteristic beam and the lattice planes in the analyzing crystal,

n = the order of the Bragg reflection and is usually taken as one.

From a determination of the intensity of the diffracted beam at each of the "Bragg reflections" predicted by Bragg's law, it is possible to determine the amount of each element present in the target or specimen.

If the target is bombarded by a continuous spectrum of x-rays rather than electrons, characteristic x-rays still may be produced provided that the energy of the bombarding x ray photons meets the minimum energy required to remove an inner target electron from its orbit. The x-rays produced by this mechanism are known as secondary or fluorescent x-rays. Hence, the only differentiation between normal characteristic x-rays and fluorescent x-rays is in the mode of production.

Fluorescent x-ray spectroscopy was applied to quantitative analysis as early as 1922. Early experiments by Hadding, Coster, von Hevesy and other workers are mentioned in the book by von Hevesy (23) entitled "Chemical Analysis by X-rays and Its Applications". Early workers used

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(23) von Hevesy, G., Chemical Analysis by X-rays and Its Applications, New York, McGraw-Hill, p. 86, 1932.

both primary and secondary x-ray radiations for their analyses. The sample was actually placed inside the x-ray tube. Because of this, such problems arose as the operation of a demountable x-ray system with replaceable targets and the effects of localized heating on the sample material. These problems were overcome by using samples mounted outside of the x-ray tube; however, the resultant reduction of intensity remained a nearly insurmountable problem in the early days.(24) With the development of higher powered x-ray tubes to increase intensity and efficient Geiger tubes to replace the old photographic plate as a recorder of intensity, analysis by x-ray fluorescence became practical. The work begun in 1946 at the United States Naval Research Laboratory y Friedman and Birks(25) led to the construction of the first modern practical instrument for x-ray fluorescent analysis. The North American Philips Company introduced x-ray fluorescent analysis equipment on a commercial scale shortly thereafter. The General Electric Company has also developed a similar machine.

G. Previous Applications Of Fluorescent Analysis

In the seven years that the fluorescent analysis unit has been available commercially, it has been used for three main types of analysis. One type of analysis has been the determination of minor constituents in substances as exemplified by the analysis of

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(24) Friedman, H. and Birks, L. S., "A Geiger Counter Spectrometer for X-ray Fluorescence Analysis", Rev. of Sci. Instr., Vol. 19, p. 323, 1948.

(25) Friedman, H. and Birks, L. S., Ibid., p. 323.

tetraethyllead in gasoline.(26) Other determinations of minor constituents have been lead in aviation fuel,(27) nickel flashings in porcelain enamels,(28) sulfur in oil,(29) and uranium in aqueous solutions.(30) The main application of x-ray fluorescent analysis has been in the analysis of major constituents of substances. Examples of applications of this type are the analysis of high temperature alloys,(31)(32) stainless steels(32-36) and elements in minerals and ores.(37-40)

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(26) Lamb, F. W., Niebylski, L. M. and Kiefer, E. W., "Determination of Tetraethyllead by X-ray Fluorescence", Anal. Chem., Vol. 27, p. 129, 1955.

(27) Birks, L. S., Brooks, E. J., Friedman, H. and Roe, R. M., "X-ray Fluorescence Analysis of Ethyl Fluid in Aviation Gasoline", Anal. Chem., Vol. 22, p. 1258, 1950.

(28) Patrick, R. F., "Some Applications of the Fluorescent X-ray Spectrometer in Ceramics", Am. Ceram. Soc. Journal, Vol. 35, p. 189, 1952.

(29) Birks, L. S., "Apparatus for Vacuum X-ray Fluorescent Analysis of Light Elements", Rev. of Sci. Instr., Vol. 22, p. 891, 1951.

(30) Birks, L. S. and Brooks, E. J., "Analysis of Uranium Solutions by X-ray Fluorescence", Anal. Chem., Vol. 23, p. 707, 1951.

(31) Brissey, R. M., "Analysis of High Temperature Alloys by X-ray Fluorescence", Anal. Chem., Vol. 25, p. 190, 1953.

(32) Koh, P. K. and Caugherty, B., "Metallurgical Applications of X-ray Fluorescence Analysis", J. of Appl. Phys., Vol. 23, p. 427, 1952.

(33) Abbott, J. L., "X-ray Fluorescence Analysis", The Iron Age, Vol. 162, p. 58, Oct. 28, 1948 and p. 121, Nov. 4, 1948.

(34) Cordovi, M. A., "Rapid Quantitative Analysis by X-ray Fluorescence Method", Steel, Vol. 123, p. 88, Dec. 20, 1948.

(35) Gillam, E. and Heal T., "Some Problems in the Analysis of Steels by X-ray Fluorescence", Brit. J. of Appl. Phys., Vol. 3, p. 353, 1952.

(36) Gillam, E., "Quantitative Analysis by X-ray Fluorescence - Application to Alloy Systems", Metal Treatment and Drop Forging, Vol. 20, p. 99, 1953.

(37) Mortimore, D. M. and Romans, P. A., "X-ray Spectroscopy as a Control Method in the Production of Zirconium and Hafnium", J. Opt. Soc. Am., Vol. 42, p. 673, 1952.

(38) Campbell, W. J. and Carl, H. F., "The Fluorescent X-ray Spectrographic Analysis of Minerals", Symposium on Fluorescent X-ray Spectrographic Analysis, ASTM Special Technical Publication No. 157, p. 63, 1953.

(39) Birks, L. S. and Brooks, E. J., "Hafnium-Zirconium and Niobium-Tantalum Systems", Anal. Chem. Vol. 22, p. 1017, 1950.

(40) Despujols, J., "Application de la Spectrometrie des Rayons X au Dosage de Faibles Teneurs", J. Phys. Radium, Vol. 13 supplement to No. 2, p. 31A, 1952.

The third field of application of fluorescent analysis has been the determination of plating thickness.(41)

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(41) Beeghley, H. F., "An X-ray Method for Determining Coating Thickness on Steel", J. Electrochem. Soc., Vol. 97, p. 152, 1950.

The author was unable to find any articles dealing with the chemical analysis of coatings by x-ray fluorescent analysis.

In the present dissertation, an attempt is made to determine the composition of titanium coatings in various levels from the surface and to determine the thickness of the titanium coating by using a North American Philips x-ray fluorescent analysis unit.

H. Explanation Of The Operation Of The North American Philips Machine

The Philips machine is of the flat crystal reflection type. The primary tungsten continuous radiation strikes the specimen on a surface area of 5/8 inch by 5/8 inch and at an angle of 45°. The resulting emergent fluorescent x-rays are directed toward the analyzing crystal where they are diffracted according to Bragg's law. The diffraction is from the (100) plane of rock salt with an interplanar spacing of 2.8197Å. The (100) plane of rock salt will diffract wave lengths shorter than 2d or 5.6394Å and so is applicable to all the fluorescent wave lengths that might be produced in these experiments. After the fluorescent rays are diffracted, they are collimated before entering the Geiger tube. As may be seen from the accompanying diagram, the Geiger tube moves through an angle twice as great as the analyzing crystal so that the Geiger tube is in position as soon as the Bragg relation is satisfied. Because the K-alpha line of titanium occurs at 58.37° and the K-alpha line of iron occurs at 40.18°, when using the (100) plane of rock salt, there was no resolution problem involved in this work. The Geiger tube was filled with argon and chlorine was added as a quenching agent. Because argon almost completely absorbs the K spectrum rays of elements of atomic number less than 29, (42) it is very efficient for determining iron and titanium which have atomic numbers of 26 and 22 respectively. The function of the quenching gas is to neutralize the positive ions after they reach the cathode.

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(42) Friedman, H., Birks, L. S. and Brooks, E. J., "Basic Theory and Fundamentals of Fluorescent X-ray Spectrographic Analysis", Symposium on Fluorescent X-ray Spectrographic Analysis, ASTM Special Technical Publication No. 157, p. 15, 1953.

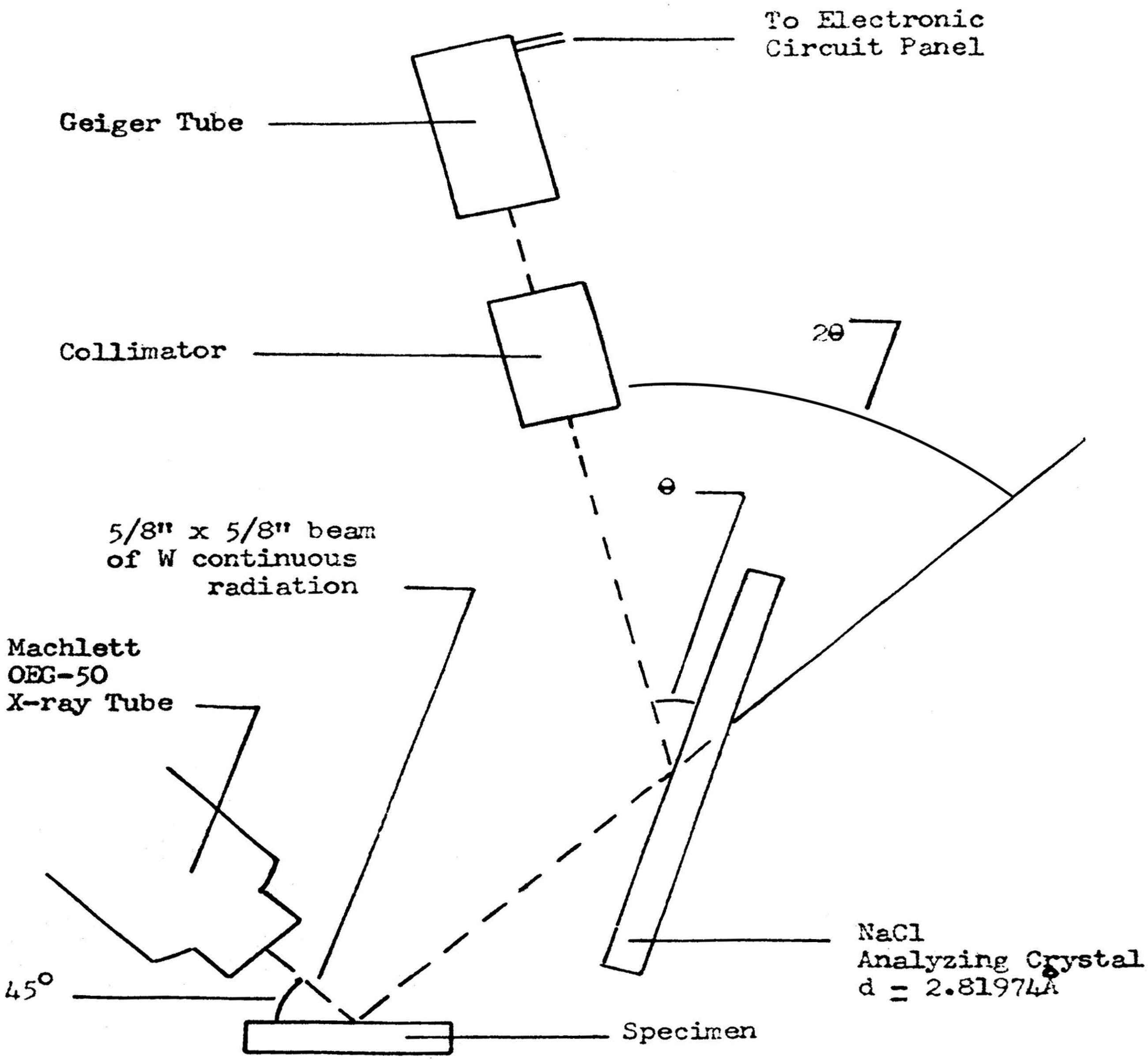

Fig. 3. Norelco Flat Crystal Reflection Method

EXPERIMENTAL WORK

A. Apparatus And Equipment

The following is a list of the apparatus and equipment used in this investigation:

1. Machlett OEG-50 X-ray Tube with a Tungsten Target - Used to provide a source of continuous x-rays.

2. North American Philips Spectrograph Attachment - Includes the goniometer and Geiger tube.

3. North American Philips Electronic Circuit Panel - Included in this panel are the input voltage stabilizer, scaler-rate meter, and interval timer. The voltage stabilizer guarantees a line fluctuation of less than ± 0.25 percent for any line load within the rated limits of the machine.

4. Geiger Tube - This tube contained argon at a pressure of 66 cm. of mercury plus chlorine as a quenching agent at a pressure of a few mm. of mercury. The potential applied to the Geiger tube was 1570 volts.

5. Analyzing Crystal - A single crystal of sodium chloride covered with a protective lacquer was used as the analyzing crystal.

6. Brown and Sharpe 1 inch Micrometer Caliper - This micrometer had a vernier capable of reading to one ten-thousandth of an inch. The micrometer was calibrated with Pratt and Whitney Hoke blocks.

7. Protective Metal Shield - Designed to protect the operator against stray x-radiation.

8. Protective Plastic Bag - Designed to protect the analyzing crystal from moisture and dirt in the air.

9. Aluminum Specimen Positioner - Designed to expose a constant sample area to the primary radiation.

10. Platinum Wound Resistance Furnace - Used in conjunction with a helium atmosphere to coat one of the samples.

11. Vacuum Retort Furnace - Four of the samples were coated under a helium atmosphere in this furnace.

12. Behr-Manning Belt Grinder - Used to prepare ingot iron specimens for coating and also used to remove surface layers from the coated samples, when the removal of relatively large layers was required.

13. Electromet Arc Melting Furnace - Used to melt the standard alloys. This work was done by the Electrometallurgical Company, a division of Union Carbide and Carbon Corporation.

B. Materials And Reagents

1. Remington-Rand titanium plate.
2. Armco ingot iron plate.
3. Behr-Manning No, 1 emery polishing paper.
4. 2/0 and 3/0 Fisher metallographic emery paper.
5. Iron powder.
6. Potassium chloride powder, U. S. P. granular ground down to -60 mesh.
7. No. 320 belt for Behr-Manning belt grinder.
8. No. 120 belt for Behr-Manning belt grinder.
9. Titanium sponge powder ground down to -200 mesh.
10. Iodide titanium sheet 0.062 - 0.063 mm. thick, prepared by the Foote Mineral Company.
11. 48 percent hydrofluoric acid.

C. Experimental Procedures

1. Preparation of Ingot Iron Samples

In all cases the material that was coated with titanium was ingot iron and was prepared from the same piece of plate. The plate was cut on a band saw and then ground on the belt grinder until a sample 7/8 in. by 11/8 in. was produced. The surface of the samples was smoothed on the belt grinder and also by hand on the No. 1 emery paper. The thickness of the finished ingot iron sample varied from about 1.7 mm. to about 1.8 mm.

2. Coating of Ingot Iron Samples

Five different samples were coated using three different methods. Samples No. 1, No. 2 and No. 3 were all coated at the same time and under the same conditions. The salt bath method was used with the bath consisting of 10 percent by weight of titanium sponge powder and 90 percent by weight of potassium chloride. Samples No. 1 and No. 2 were both coated in the same $3\frac{1}{2}$ in. casserole, while sample No. 3 was coated in a smaller 2 in. casserole. The casseroles were placed in the large vacuum retort furnace and heated for 4 hours at 1000° C. under a helium atmosphere. Although other samples in the same furnace were being concurrently coated by the iodide deposition method, it was thought that the molten salt solution would protect the samples in the casseroles from any effect caused by the presence of the iodide vapor.

Sample No. 4 was also coated by the salt bath method with the same bath composition as samples Nos. 1 to 3. The furnace temperature was again 1000° C., but the time was 6 hours and the furnace was a platinum wound resistance furnace. A helium atmosphere was used to coat sample No. 4.

Sample No. 5 was coated by the iodide deposition process in the large vacuum retort furnace under a helium atmosphere and again at a temperature of 1000° C. and for a time of 4 hours.

3. Dissolution of Adhering Potassium Chloride Particles

Samples Nos. 1 to 3 were scrubbed in water to remove any loosely adhering particles. It is thought that this scrubbing process also removed the soft outer layer of the coating, because the layer after scrubbing was relatively hard. No attempt was made to remove any loosely adhering layer from samples No. 4 and No. 5. When thickness measurements were made on samples No. 4 and No. 5, there was a tendency for the thickness to decrease with successive measurements even though no attempt was made to remove any of the surface layer. Finally, after a series of measurements were made, the thickness tended to become constant. It is assumed that the pressure of the micrometer slightly compressed the loose outer surface on the layer and gave a gradual decrease in thickness. Upon applying samples No. 4 and No. 5 to the emery paper, only a very few strokes were necessary to produce a large decrease in the thickness of the sample. These results would tend to indicate that a soft outer layer was completely removed from the first three samples. This soft outer layer was probably of higher titanium content than any other part of the coating.

4. Method of Removing Successive Layers from the Coating

Metallographic polishing paper was used to remove layers of about 0.002 to 0.003 mm. from the coated samples. Because of the hardness of the coating, No. 1 emery paper and 2/0 polishing paper were used to remove successive layers. The belt grinder was used for grinding away relatively thick surface layers in order to determine the limit of titanium diffusion in the iron. The belt grinder tended to produce an uneven surface on the specimen.

5. Measurement of the Amount of Layer Removed

A micrometer caliper, accurately calibrated and with a vernier reading to 0.0001 inch, was used to measure the sample thickness. Each thickness measurement was an average of nine readings taken at nine separate points on the surface of the coating. Details of the method used to obtain the nine measurements on each of the surfaces and the results of these measurements are in the appendix.

6. Calibration of Goniometer

When the spectrometer was moved from the diffraction unit to the Machlett external tube, it was necessary to recalibrate the goniometer. With a copper sample and a rock salt analyzing crystal, the maximum K-alpha intensity should occur at a 2θ value of 31.73°. Using a copper sample, the goniometer was adjusted until a maximum occurred at 31.73°. As an added check, it was also determined that the maximum K-alpha intensities for iron and titanium occurred at 40.18° and 58.37° respectively. These are the 2θ values which correspond with the maximum predicted by Bragg's law and were in good agreement with the tabulated data.

7. Determination of Operating Conditions

Friedman and Birks (25) state that the most effective voltage for exciting iron characteristic x-rays is about 35 kilovolts. However, for lighter elements, producing longer wave lengths, the optimum voltage decreases, as it is limited to a depth of penetration which will allow the secondary x-rays to penetrate to the surface. It was found that 30 kilovolts and 20 milliamperes produced an iron K-alpha line that gave the maximum permissible counting rate for the Geiger tube.

So 30 kilovolts and 20 milliamperes were the tube operating conditions used in all intensity determinations. The intensities were determined by the fixed count method which is considered to be more accurate than the fixed time method. In all cases, the intensity of the iron K-alpha line was determined by finding the time required to record 25600 counts on the electronic scaling circuit. Since the titanium K-alpha line is much weaker, 25600 counts would require too long a counting period, so the titanium intensities were determined over a shorter interval which varied with the amount of titanium present in the sample.

8. Determination of the Intensity Caused by the Background

The background intensity of fluorescent radiation is much lower than that of primary radiation, but still must be considered. To determine the background intensity, a sample of ingot iron was used and the spectrometer was set at a 2θ value of 58.37°, which corresponds to the K-alpha maximum for titanium. The resulting intensity was attributed entirely to the background. In the same manner, using a titanium sample, the background intensity was determined at a 2θ value of 40.18°, which corresponds to the K-alpha maximum for iron.

The experimental data used to calculate the average background intensity are recorded in Table I on the next page. This background intensity was subtracted from all subsequent intensity readings so as to give only absolute intensity values.

Table I

Determination of the Background Intensity

Area of sample: 7/8 in. x 7/8 in. or 4.94 sq. cm.

Operating conditions: 30 kilovolts
20 milliamperes

A. Iron Sample at a Goniometer Setting of $2\theta = 58.37^\circ$

Time in seconds to record 1600 counts	Background intensity in counts per second
888.8	1.8
991.6	1.6
1022.0	1.6
1004.0	1.6
Average	1.6

B. Titanium Sample at a Goniometer Setting of $2\theta = 40.18^\circ$

Time in seconds to record 1600 counts	Background intensity in counts per second
972.4	1.6
1006.2	1.6
945.2	1.7
976.8	1.6
Average	1.6

9. Reproduction of Results

It was found that a variation in the positioning of the analyzing crystal caused an appreciable variation in the intensities of the various characteristic x-ray lines. Experiments were made to determine the position of the analyzing crystal that corresponded to the maximum intensity values and the crystal was then left permanently in that position. A plastic bag was placed around the crystal and the ends of the slit system to protect the crystal from the effects of moisture and dirt in the air. From a consideration of the work of Koh and Caugherty,(32) it was decided that the effect of grain size and previous mechanical treatment would be negligible. An aluminum positioner was prepared in order to expose a constant sample area of 7/8 in. by 7/8 in. to the primary 5/8 in. by 5/8 in. x-ray beam. When the aforementioned precautions were taken, it was found that reproducible results could be obtained.

10. Determination of Fluorescent Line Intensities

After each set of polishing and thickness measurements, the intensities of the K-alpha lines for titanium and iron were determined under the previously mentioned operating conditions. Alternate removal of layers and intensity measurements were taken until the intensity of the iron K-alpha line became constant and the intensity of the titanium K-alpha line became indistinguishable from the background. This point was assumed to be the limit of diffusion of titanium into the iron base. Each of the readings was corrected for background intensity to give an absolute intensity which, after proper modifications, was taken to be a measure of the amount of the element present in the layer.

11. Preparation of Standards

The composition of an element in an alloy is not expected to vary linearly with the intensity of the characteristic K-alpha line for that element because of the effects of the factors known as mutual fluorescence and differential absorption.

If the absorption of the characteristic x-ray of an element in an alloy is greater in the other elements of the alloy than in the element itself, the resulting intensity of the characteristic x-ray line is decreased. This effect is known as differential absorption. The mass absorption coefficient of iron K-alpha in titanium is 377, while the mass absorption coefficient of iron in itself is only 73. Therefore, because of the differential absorption effect, the intensity of the iron K-alpha is decreased in the presence of titanium. In a similar manner, titanium K-alpha is more highly absorbed in iron than in itself; so the intensity of titanium K-alpha is also decreased.

If the wave length of the fluorescent x-rays of one element in the specimen is less than the wave length at the absorption edge of another element in the specimen, the fluorescent x-rays will be absorbed by the second element and produce fluorescent rays of the second element in addition to those formed by the absorption of the primary rays. This effect is known as mutual fluorescence. von Hevesy (26) has stated that the effect of mutual fluorescence is noticeable only if the wave length of the K-alpha line of the element causing the mutual fluorescence is within 0.2Å of the wave length at the K-absorption edge of the element being determined. Although the wave length of iron K-alpha, 1.94Å, is less than that at the K-absorption edge of titanium, 2.49Å, the difference is greater than 0.2Å and the mutual fluorescence effect is not observable. Because the wave length of titanium K-alpha, 2.75Å, is greater than the K-absorption edge of iron, 1.74Å, the iron K-alpha intensities will not be affected by mutual fluorescence.

From a consideration of these effects on the intensities of iron-titanium alloys, it is supposed that the intensities of both the iron and titanium K-alpha lines will be less than that predicted from the linear relationship for any given composition of the alloy. As this absorption effect is greater for the iron K-alpha than for the titanium K-alpha, it follows that there will be a greater variation from the linear relationship for the iron intensities than for the titanium intensities, if these are plotted against the composition of the iron-titanium alloys.

It was thought that the variation of iron K-alpha intensity with the thickness of the titanium layer might be determined by gluing titanium foil on an ingot iron base and then determining iron K-alpha intensities after removing successive layers of titanium. A procedure could not be developed in which the resulting base and glued layer were of uniform thickness. Also it was found that the layer of glue caused an appreciable reduction in the intensity of the iron K-alpha line. So any further experiments with glued layers were abandoned.

Attempts were then made to prepare actual standards by mixing together known amounts of titanium and iron powders and then compacting the mixtures. A circular die, one inch in diameter, was used in conjunction with a pressure of 70 tons per square inch to prepare the compacts. Intensity determinations on the resulting compacts showed too much segregation to allow the compacts to be of any use. The procedure was repeated and greater care taken to avoid segregation, but the compacts still exhibited too much segregation to be useful.

The Electrometallurgical Company, a division of Union Carbide and Carbon Corporation, was kind enough to arc melt the compacts under an inert atmosphere. Two of the five samples were ruined during the arc melting process. The other three samples were ground on a grinding wheel until a smooth surface was produced. Two samples were also made from iron and titanium plate. In Table II, the intensities of the titanium and iron K-alpha lines for both pure samples and alloys are tabulated. The sample area of the Electromet alloys was limited by the smaller size of these samples. However, as the primary beam is only 5/8 in. by 5/8 in., the smaller size of the Electromet samples had no effect because the same positioning technique was used in all cases. Reference to Table II shows that the titanium K-alpha intensity of the smaller Electromet sample was just as great as the titanium K-alpha intensity of the larger plate. The average intensities listed in Table II include the average background correction. The ratio of the average intensity of titanium K-alpha from pure titanium to the average intensity of iron K-alpha from pure iron was 0.068. This compares favorably with the value of 0.071 recorded by Koh and Caugherty.(32)

The ratio of the titanium K-alpha intensity from each of the Electromet alloys to the intensity of the K-alpha line of pure titanium was plotted in figure No. 4 against the atomic percent of titanium in each of the Electromet alloys. The theoretical linear relationship which ignores the effects of mutual fluorescence and differential absorption is also plotted as a dashed line in figure No. 4. Figure No. 5 on the page following figure No. 4 is a similar graph for iron. Figures No. 4 and No. 5 may be used as standard curves to convert intensities into atomic percentages.

Table II

Intensity Determinations of Standard Samples

A. Intensity Determinations of Iron and Titanium Plate

sample area: 7/8 in. x 7/8 in. or 4.94 sq. cm.

operating conditions: 30 kilovolts
20 milliamperes

1. Intensity of Ti K-Alpha from Ti plate

Time in sec. to record 25600 counts	Counts per sec.
579.0	44.2
558.8	45.8
548.0	46.7
564.4	45.4
550.2	46.5
576.0	44.4
566.8	45.2
566.4	45.2
Average	45.4
Aver. with background correc.	43.8

2. Intensity of Fe K-Alpha from ingot iron plate

Time in sec. to record 25600 counts	Counts per sec.
38.0	673.7
38.2	670.2
37.8	677.3
38.2	670.2
38.4	666.7
38.2	670.2
38.6	663.2
38.2	670.2
Average	670.2
Aver. with background correc.	668.6

B. Intensity Determinations of Electromet Samples

sample area: 7/8 in. x 7/8 in. or 3.52 sq. cm.

operating conditions: 30 kilovolts
20 milliamperes

1. Intensity of Ti K-Alpha from 50% (wt.) Ti alloy

Time in sec. to record 12800 counts	Counts per sec.
600.8	21.3
612.0	20.9
606.2	21.1
604.0	21.2
Average	21.1
Average with background corr.	19.5

2. Intensity of Ti K-Alpha from 20% (wt.) Ti alloy

Time in sec. to record 6400 counts	Counts per sec.
638.4	10.0
634.0	10.1
643.2	9.9
636.4	10.1
Average	10.0
Average with background corr.	8.4

Table II (Cont'd.)

3. Intensity of Fe K-Alpha from 50% (wt.) Fe alloy

Time in sec. to record 25600 counts	Counts per sec.
108.0	237.0
110.8	231.1
106.0	241.5
107.2	237.9
Average	237.0
Aver. with background correc.	235.4

4. Intensity of Fe K-Alpha from 80% (wt.) Fe alloy

Time in sec. to record 25600 counts	Counts per sec.
54.8	467.2
55.6	460.4
54.8	467.2
54.0	474.1
Average	467.2
Aver. with background correc.	465.6

5. Intensity of Ti K-Alpha from 100% (wt.) Ti

Time in sec. to record 25600 counts	Counts per sec.
564.4	45.4
558.8	45.8
563.0	45.5
Average	45.5
Aver. with background correc.	43.9

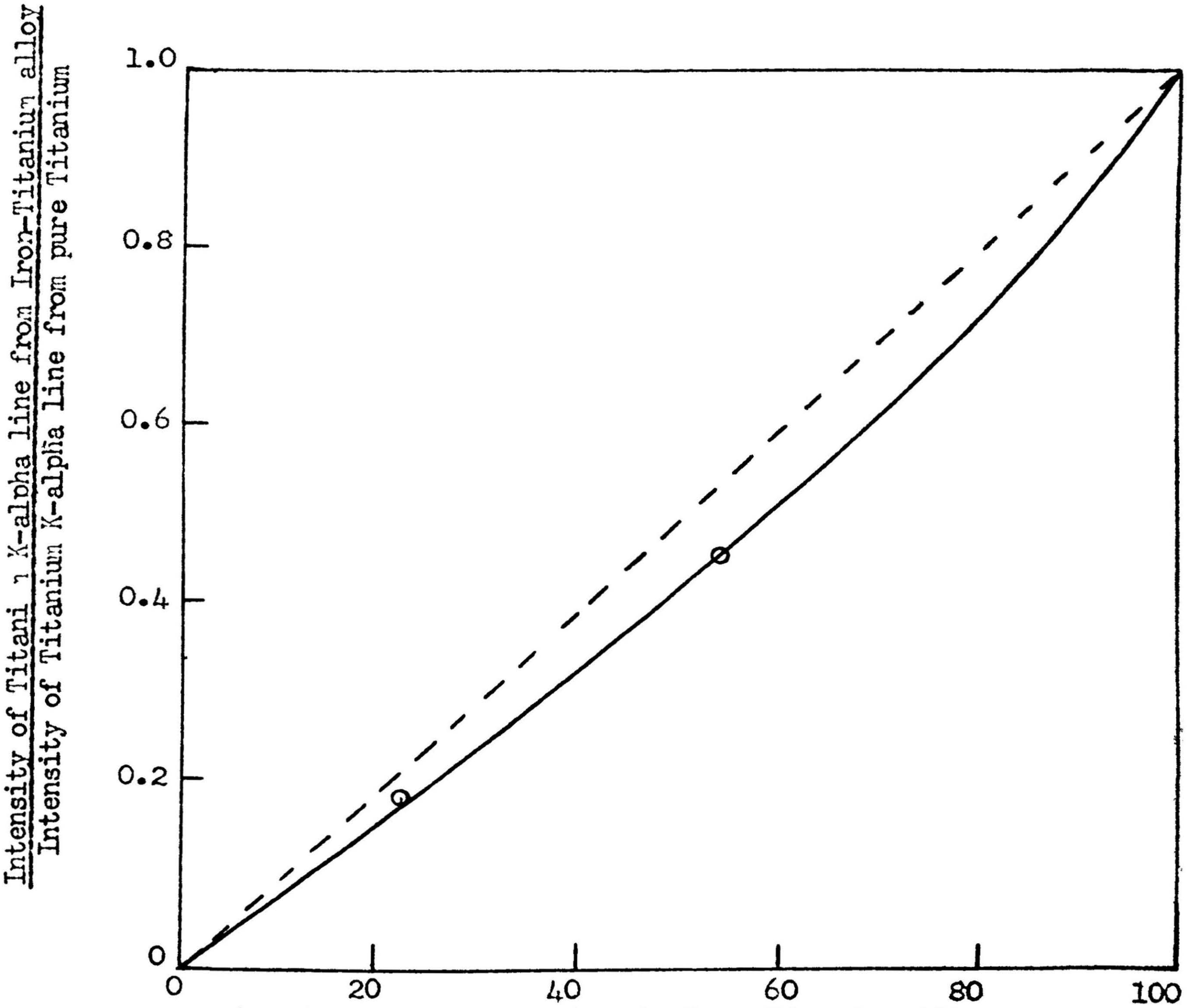

Fig. 4. Correction Curve for Differential Absorption and Mutual Fluorescence of Titanium in Iron-Titanium Alloys.

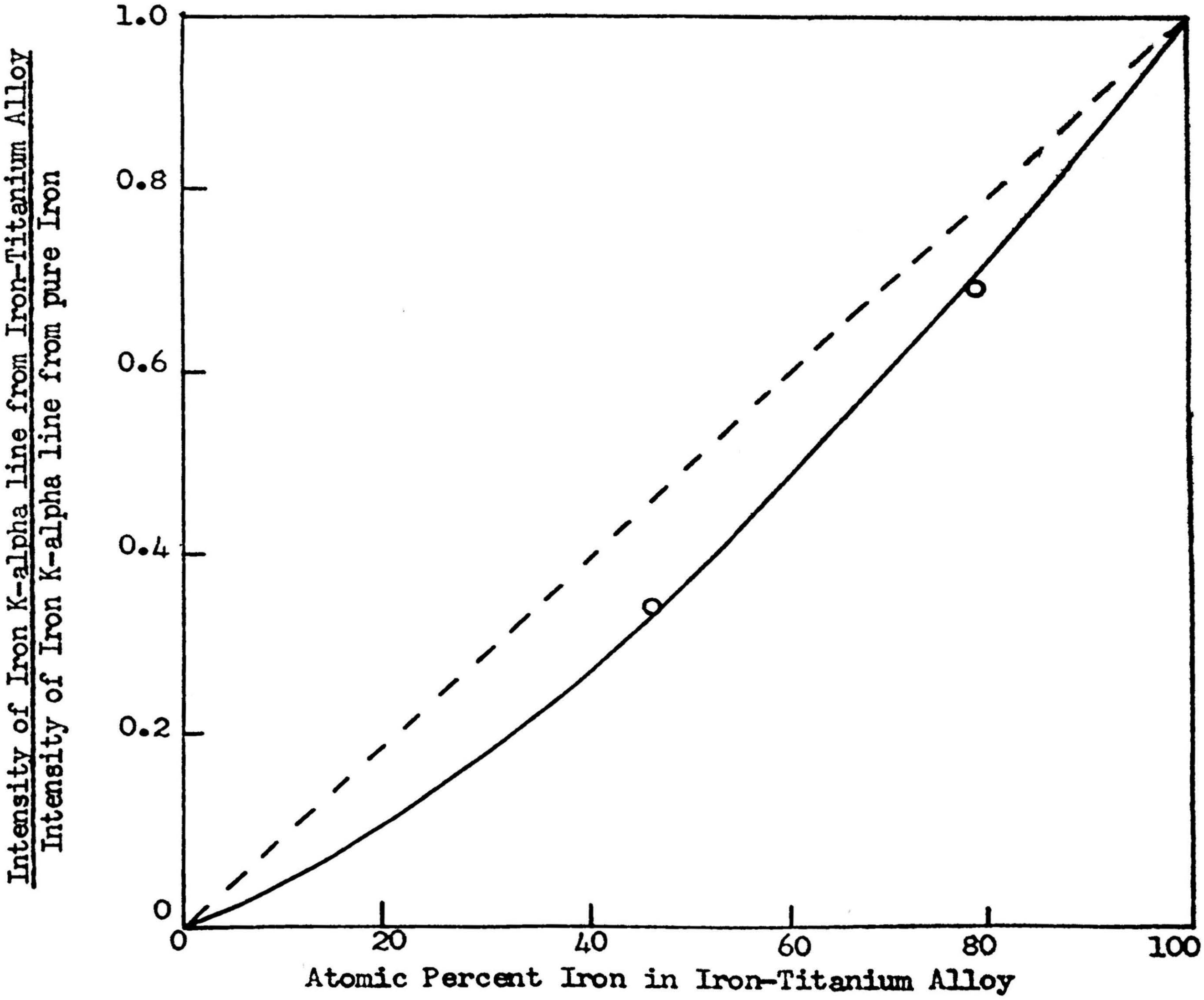

Fig. 5. Correction Curve for Differential Absorption and Mutual Fluorescence of Iron in Iron-Titanium Alloys.

12. Determination of Minimum Effective Thickness

Although the approximate composition of a surface layer may be roughly determined from the respective intensities by reading directly from graphs, such as figures No. 4 and No. 5, which compensate for the effect of mutual fluorescence and differential absorption, the resulting compositions are not that of the surface layer but really an average composition of a finite thickness of the surface layer. The question arose as to just what thickness of the inner layer was contributing to the surface intensities.

The following method was used to determine from what depths of the specimen the secondary x-rays may escape to the surface and contribute measurably to the recorded surface intensity.

For any metallic element there exists a thickness which just produces the maximum fluorescent yield by that element under the specified operating conditions. This thickness which varies with the material is known as the minimum effective thickness. With a constant primary intensity any thickness under the minimum effective thickness produces a decrease in the intensity of the characteristic radiation, but any greater thickness produces no greater intensity. The assumption was made that any fluorescent radiation excited at a depth greater than the minimum effective thickness of the sample will be absorbed to such extent that the surface intensities will be unaffected. Therefore, from the values obtained for the minimum effective thickness, the depth from which fluorescent x-rays emerge, that is, the thickness of the layer which contributes to the surface intensities, may be estimated.

The minimum effective thickness of titanium was determined experimentally. Iodide titanium foil, 0.062 mm. thick, produced by the

Foote Mineral Company was immersed in hydrofluoric acid to decrease the thickness of the foil. After each immersion, the thickness of the foil was measured with a micrometer and the intensity of the titanium K-alpha line recorded. The resulting data are recorded in Table III. In figure No. 6 the thickness of the titanium foil is plotted against the intensity of the K-alpha line from the foil. The x-ray tube was operated under the constant conditions of 30 kilovolts and 20 milliamperes. From figure No. 6, the minimum effective thickness of titanium was estimated to be slightly greater than 0.04 mm.

Attempts were made to determine the minimum effective thickness of iron in a similar manner. The first attempt was unsuccessful because nothing was done to eliminate the effect of hydrogen embrittlement in the iron. During the second experiment, the iron sample was placed in boiling water each time it was removed from the hydrochloric acid in order to dissolve the absorbed hydrogen. The specimen was considerably less brittle, but it still tended to "shred" at small thicknesses. The acid appeared to attack the specimen unevenly, so that holes appeared in the surface before the region of minimum effective thickness could be reached.

Koh and Caugherty (32) have determined the minimum effective thickness of iron, chromium, and nickel by building up successive layers of each metal on a piece of aluminum by electrolytic plating. The thickness was determined by weighing a known surface area. By this method, the minimum effective thicknesses of iron, chromium, and nickel were found to be 0.02, 0.03 and 0.02 mm. respectively. Generally the minimum effective thickness increases with a decrease in density, as the secondary x-rays may penetrate through a greater thickness of a less dense element than a heavier one.

Table III

Determination of Minumum Effective Thickness of Titanium

Operating conditions: 30 kilovolts
20 milliamperes

$2\theta = 58.37^\circ$

Material: iodide titanium foil

Thickness decreased by etching in HF (48%) 10 ml. to 90 ml. of water

Average thickness in millimeters	Time in seconds to record 6400 counts	Ti K-Alpha intensity in counts/second including background correction
.0666	144.0	42.8
.0536	144.0	42.8
.0440	148.6	41.5
.0310	156.2	39.4
.0217	158.4	38.8
.0141	191.4	31.8
.0104	275.6	21.6

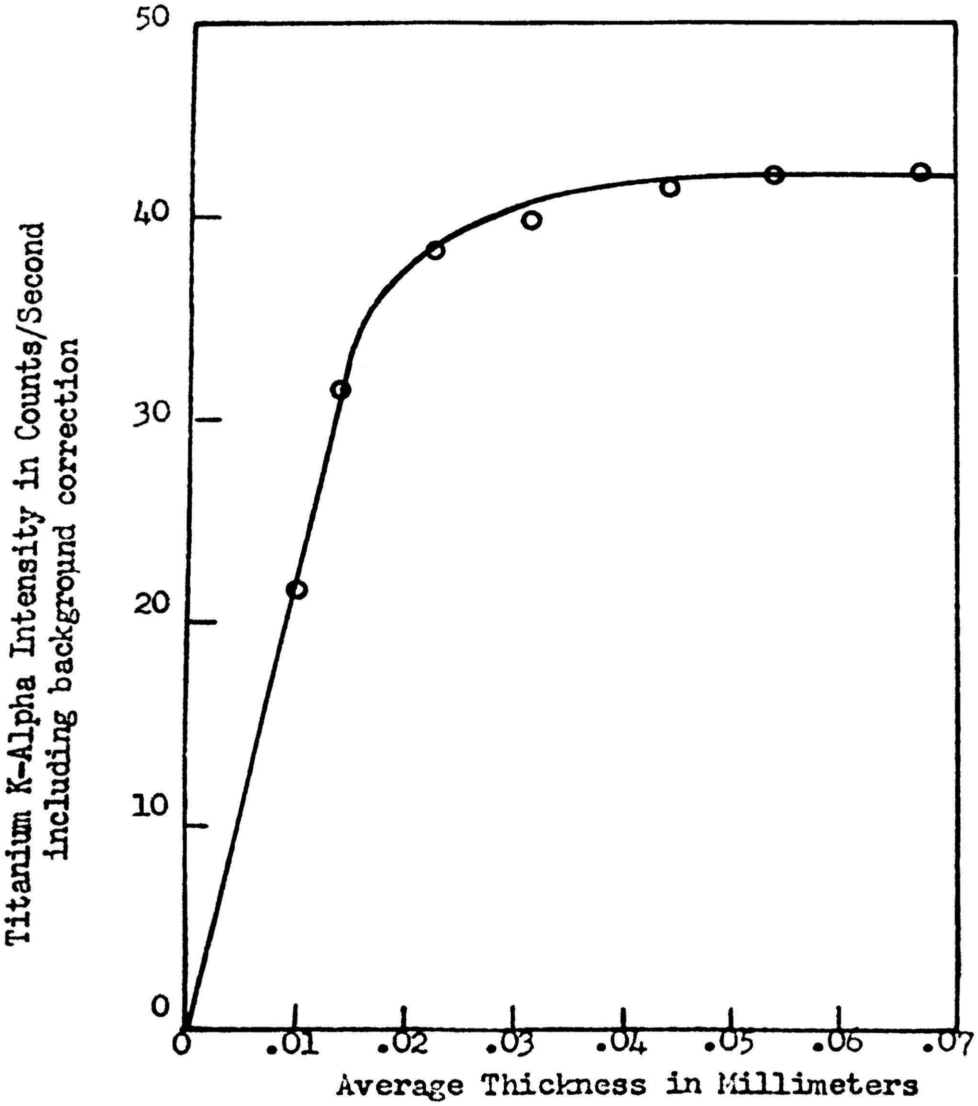

Fig. 6. Average thickness of titanium vs. intensity of titanium K-alpha.

The samples whose surface intensities were determined in this work were actually composed of layers of various iron-titanium alloys. Therefore, it was necessary to determine the minimum effective thickness of various iron-titanium alloys in order to find the thickness of the alloy layer which contributed to the recorded surface intensities. The recorded surface intensities were then taken as the average composition of the finite layer of the surface which contributed to the surface intensities.

As the values of the mass absorption coefficients of x-rays of various wave lengths in titanium and iron are necessary for subsequent calculations, this information was plotted in figure No. 7. Figure No. 7 shows the variation of the mass absorption coefficients of iron and titanium from wave lengths of 0.4 to 2.8Å for the absorbed radiation. The data for this plot were obtained from pp. 577 to 578 of the Internationale Tabellen zur Bestimmung von Kristallstrukturen (43) and from pp. 2031 to 2036 of the Handbook of Chemistry and Physics. (44)

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(43) Internationale Tabellen zur Bestimmung von Kristallstrukturen, Gebrüder Borntraeger, Berlin, Vol. 2, pp. 577 to 578, 1935.

(44) Hodgman, C. D., Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, Ohio, 31st ed., pp. 2031 to 2036, 1949.

The absorption of iron K-alpha in iron and titanium has been determined experimentally; however, the mass absorption coefficients of titanium K-alpha in iron and titanium have not been determined experimentally. Therefore, it was necessary to obtain these values from an extrapolation of the curves in figure No. 7.

The values obtained for the mass absorption coefficients of iron

K-alpha and titanium K-alpha in both iron and titanium are recorded in Table IV.

Table IV

Values of Mass Absorption Coefficients of Titanium K-Alpha and Iron K-Alpha in Titanium and Iron

Titanium K-alpha in Iron	190
Iron K-alpha in Iron	73
Iron K-alpha in Titanium	377
Titanium K-alpha in Titanium	110

It was assumed that the value of I/I_o, as obtained from Lambert's law, should be constant for the minimum effective thickness of any material.

The Lambert law relationship, $I/I_o = e^{-\mu \rho x}$

where: $I =$ the intensity of the emergent beam,

$I_o =$ the intensity of the incident beam,

$\rho =$ the density of the absorbing material,

$\mu =$ the mass absorption coefficient of the incident beam in the absorbing material,

$x =$ the thickness of the absorbing material,

was used, therefore, to determine the value of I/I_o at the minimum effective thickness of iron, titanium, nickel and chromium.

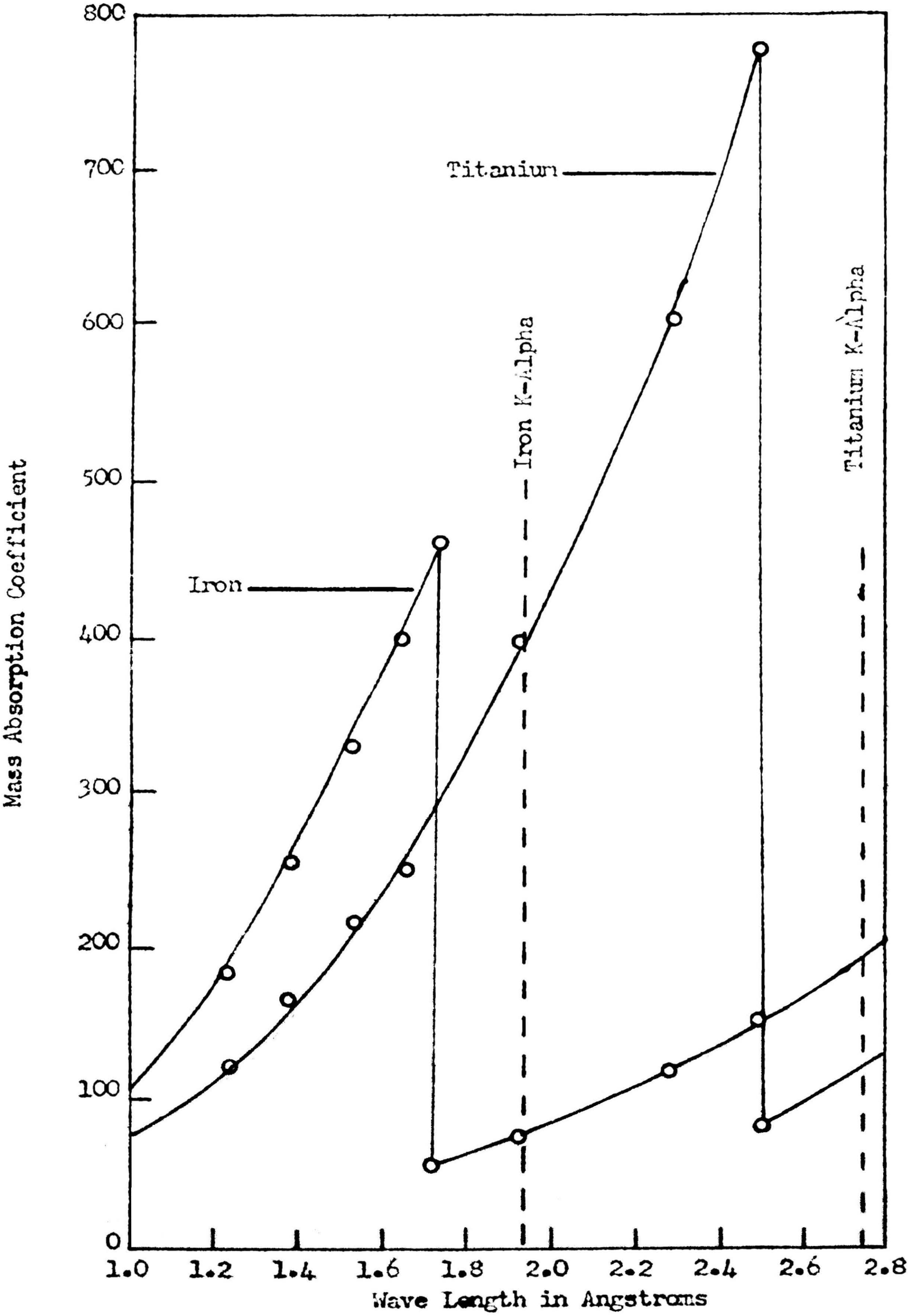

Fig. 7. Mass absorption coefficient of iron and titanium vs. wave length of absorbed radiation.

The results of the calculations are tabulated below in Table V.

Table V

Minimum Effective Thicknesses of Various Materials

	Density in gm/cm^3	Mass abs. coeff.	Experimental min. eff. thick. in cm.	Calculated value of I/I_o
Iron	7.87	73	.002	.316
Titanium	4.54	110	.004	.135
Nickel	8.90	61	.002	.336
Chromium	7.19	90	.003	.144

Table V shows that the values of I/I_o calculated from the experimentally determined minimum effective thicknesses ranged from 0.14 to 0.34. It was assumed that this variation was caused by experimental error. As the average value of I/I_o was about 0.20, this value was arbitrarily chosen as the value for which the Lambert equation might be solved to determine the minimum effective thickness of a substance. It was thus assumed that the minimum effective thickness of an element was equivalent to the thickness which would absorb 80 percent of the K-alpha radiation of that element as the K-alpha radiation passed through it.

In figure No. 8, the plot of ln I/I_o against the thickness of various iron-titanium alloy layers is shown. In this case, I is the intensity of the titanium K-alpha line transmitted through the alloy and I_o is the intensity of thetitanium K-alpha line incident upon

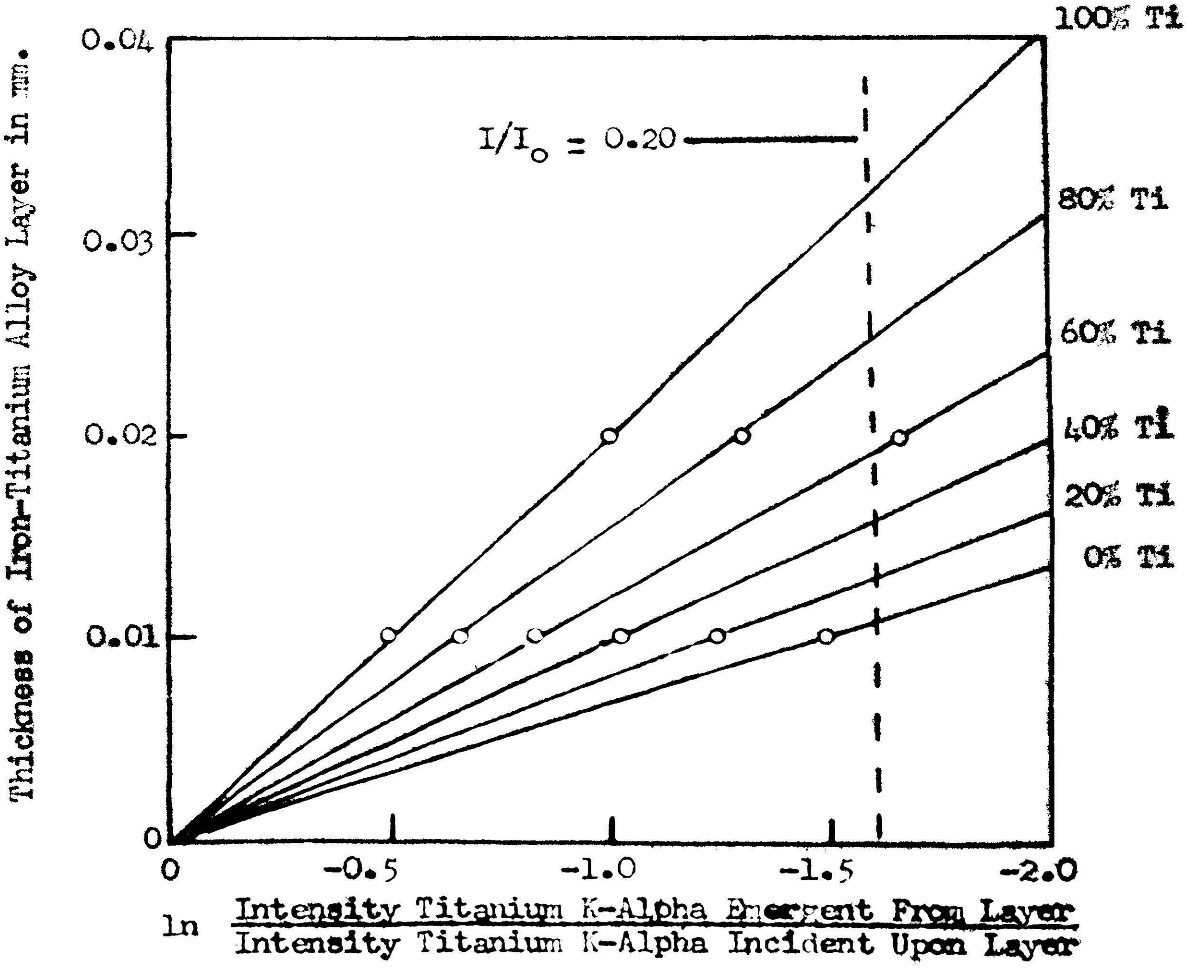

Fig. 8. ln I/I_o for titanium K-alpha vs. thickness of iron-titanium alloy layer in mm.

the other side of the alloy layer. The minimum effective thickness of any alloy layer for titanium K-alpha radiation is assumed to occur at the point where the ln 0.20 intersects the line representative of the composition of the alloy layer concerned. Because the ln 0.20 is equal to -1.61, this line has been drawn on figure No. 8.

Figure No. 9 is a similar plot of ln I/I_o against the thickness of various iron-titanium alloy layers, except that in this case I is the intensity of the iron K-alpha line transmitted through the alloy and I_o is the intensity of the iron K-alpha line incident upon the other side of the alloy layer.

The data used to plot ln I/I_o against thickness in figures No. 8 and No. 9 is tabulated in Table VI. For iron-titanium alloys of various compositions, the densities were determined by averaging the densities of the pure metals, according to the amount of each of the elements present in the alloy. The mass absorption coefficient of iron K-alpha and titanium K-alpha in the various alloys was also determined in this manner. Knowing the values of μ and ρ , Lambert's equation becomes: $\ln I/I_o = -kx$
where k is the product of μ and ρ .
As may be seen from figures No. 8 and No. 9, all the resulting plots were straight lines.

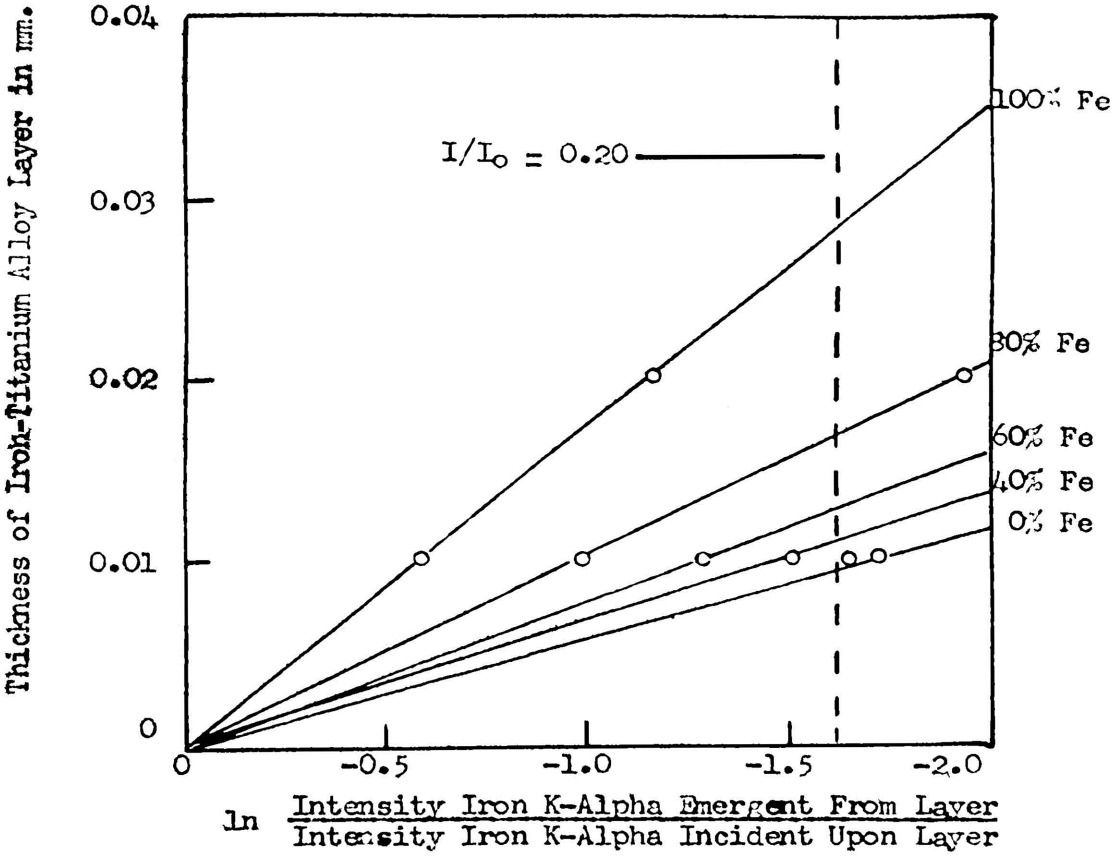

Fig. 9. ln I/I_0 for iron K-alpha vs. thickness of iron-titanium alloy layer in mm.

Table VI

Mass Absorption Coefficients and Densities of Various Iron - Titanium Alloys

Percent Fe		for Fe K-Alpha	for Fe K-Alpha	for Ti K-Alpha	for Ti K-Alpha
100	7.87	73	575	190	1495
90	7.54	104	784	182	1372
80	7.20	134	965	174	1253
70	6.87	164	1127	166	1140
60	6.54	195	1275	158	1033
50	6.20	225	1395	150	930
40	5.87	255	1497	142	834
30	5.54	286	1584	134	742
20	5.21	316	1646	126	657
10	4.87	347	1690	118	575
0	4.54	377	1712	110	500

D. Experimental Data

The experimental data are listed in Table VII. These are the data determined by using the previously mentioned procedures for determining sample thickness, grinding down the surface layer, recording fluorescent line intensities and correcting for the background intensity. These procedures are described in detail beginning on page 21 of this manuscript. The values upon which each average thickness of the layer removed by grinding is based are listed in Table IX in the appendix. The average thicknesses were originally measured using a micrometer with an inch scale and then converted to millimeters. The time required to record 25600 counts was the method used to determine all the iron K-alpha intensities in counts per second. 25600 counts is the maximum number that can be recorded on the count register for one setting. The statistical probable error involved in the recording of 25600 counts by the Geiger tube is 0.4 percent. As the titanium K-alpha intensities were much smaller, shorter counting times were used for titanium K-alpha. The statistical probable error for the recording of 800, 1600, and 3200 counts is 2.4, 1.6, and 1.2 percent respectively.

A constant factor of 1.6 counts per second was subtracted from all the intensities calculated from the experimental data in order to correct for the background intensity. The intensities recorded in Table VII include this background correction.

Table VII

Experimental Data

Sample #1

Aver. thick. in Mm.	Amt. removed in Mm.	Time in sec. for 25600 Fe K-Alpha counts	Fe K-Alpha intensity in c/s corr. for background	No. of counts	Time in sec.	Ti K-Alpha intensity in c/s corr. for background
1.8288	0	130.0	195.3	12800	562.6	21.2
		129.2	196.5			
1.8257	0.0031	144.6	175.5	12800	550.4	21.7
		145.2	174.7	12800	530.4	22.5
1.8229	0.0059	141.4	179.4	12800	602.6	19.6
		144.2	175.9	12800	593.4	20.0
1.8206	0.0082	115.0	221.0	12800	698.0	16.7
		113.0	224.9	12800	624.0	18.9
1.8192	0.0096	104.8	242.7	12800	638.4	18.4
		117.0	217.2	12800	641.0	18.4
1.8164	0.0124	90.2	282.2	12800	779.0	14.8
		91.0	279.7	12800	768.6	15.1
1.8133	0.0155	82.4	309.1			
1.8110	0.0178	66.0	386.3	12800	1222.	8.9
		64.4	396.0	12800	1226.	8.8
1.8085	0.0203	53.6	476.0	3200	471.2	5.2
		54.4	469.0	1600	235.0	5.2
1.8037	0.0251	46.2	552.5	1600	368.4	2.7
		44.4	575.0	1600	357.0	2.9
1.8014	0.0276	45.6	559.8	800	196.2	2.5
		45.2	564.7	800	206.0	2.3
1.7966	0.0324	48.0	531.7	800	195.6	2.5
		47.4	538.4	800	200.4	2.4
1.7537	0.0751	41.6	613.8	6400	2210.	1.3
		42.0	607.9			
1.7503	0.0785	40.4	631.7	200	83.0	0.8
				200	88.4	0.6

Table VII' (Cont'd.)

Sample #1 (Cont'd.)

Aver. thick. in Mm.	Amt. removed in Mm.	Time in sec. for 25600 Fe K-Alpha counts	Fe K-Alpha intensity in c/s corr. for background	No. of counts	Time in sec.	Ti K-Alpha intensity in c/s corr. for background
1.6990	0.1298	38.8	658.2	400	199.2	0.4
		39.0	654.8			
1.6820	0.1468	38.4	665.1	400	253.8	0
		38.2	668.6			

Sample #2

1.7182	0	129.2	196.5	6400	312.8	18.9
		131.0	193.8	6400	314.4	18.8
1.7125	0.0057	128.0	198.4	6400	322.8	18.2
		128.0	198.4	6400	316.6	18.6
1.7105	0.0077	126.6	200.6	6400	323.0	18.2
		126.2	201.3	6400	322.0	18.3
1.7083	0.0099	120.2	211.4	6400	347.2	16.8
		119.0	213.5	6400	349.8	16.7
1.7069	0.0133	109.0	233.3	3200	184.2	15.8
		108.0	235.4	3200	189.0	15.3
1.7041	0.0141	88.8	286.7	3200	196.0	14.7
		87.6	290.6	3200	193.0	15.0
1.7024	0.0158	78.0	326.6	3200	221.0	12.9
		77.4	329.1	3200	220.2	12.9
1.6998	0.0184	61.2	416.7	3200	298.0	9.1
		61.2	416.7	1600	146.2	9.3
1.6959	0.0223	58.8	433.8	1600	174.4	7.6
		59.0	432.3	1600	174.8	7.6
1.6891	0.0291	51.0	500.4	1600	259.0	4.6
		51.4	496.5	800	126.4	4.7

Table VII (Cont'd.)

Sample #2 (Cont'd.)

Aver. thick. in Mm.	Amt. removed in Mm.	Time in sec. for 25600 Fe K-Alpha counts	Fe K-Alpha intensity in c/s corr. for background	No. of counts	Time in sec.	Ti K-Alpha intensity in c/s corr. for background
1.6583	0.0599	42.6 43.0	599.3 593.7	200	69.4	1.3
1.6572	0.610	41.0	622.2	200	80.0	0.9

Sample #3

Aver. thick. in Mm.	Amt. removed in Mm.	Time in sec. for 25600 Fe K-Alpha counts	Fe K-Alpha intensity in c/s corr. for background	No. of counts	Time in sec.	Ti K-Alpha intensity in c/s corr. for background
1.7884	0	109.8 108.6	231.6 234.1	3200 3200	169.4 166.0	17.3 17.7
1.7859	0.0025	106.0 105.8	239.9 240.4	3200 3200	166.2 167.0	17.7 17.6
1.7834	0.0050	104.4 105.0	243.6 242.2	3200 3200	172.2 168.4	17.0 17.4
1.7808	0.0076	89.6 89.8	284.1 283.5	3200 3200	188.0 184.2	15.4 15.8
1.7777	0.0107	63.8 63.4	399.7 402.2	3200 3200	238.2 241.0	11.8 11.7
1.7740	0.0144	50.4 50.0	506.3 510.4	1600 1600	189.4 191.4	6.8 6.8
1.7582	0.0302	44.8 44.2	569.8 577.6	200 400	99.6 218.8	0.4 0.3
1.7438	0.0344	41.6 41.2	613.8 619.8	200	127.8	0
1.7433	0.0451	41.6 41.8	613.8 610.8	200 200	134.2 121.0	0 0.1
1.6900	0.0984	38.0	672.1	400	266.0	0
1.6733	0.1151	38.0 38.2	672.1 668.5	400	248.8	0

Table VII (Cont'd.)

Sample #4

Aver. thick. in Mm.	Amt. removed in Mm.	Time in sec. for 25600 Fe K-Alpha counts	Fe K-Alpha intensity in c/s corr. for background	No. of counts	Time in sec.	Ti K-Alpha intensity in c/s corr. for background
1.7752	0	131.0	193.8	6400	285.8	20.8
		132.0	192.3	6400	274.0	21.8
1.7594	0.0158	109.0	233.3	6400	284.0	20.9
		108.8	233.7	6400	293.0	20.2
1.7582	0.0170	105.0	242.2	6400	295.0	20.1
		104.4	243.6	6400	280.4	21.2
1.7557	0.0195	92.0	276.7	3200	153.6	19.2
		92.6	274.9	3200	155.0	19.0
1.7529	0.0223	90.4	281.6	3200	189.2	15.3
		91.2	278.5	3200	198.0	14.9
1.7503	0.0249	64.8	393.5	3200	225.8	12.6
		64.8	393.5	3200	241.0	11.7
1.7478	0.0274	66.6	382.8	1600	136.2	10.1
		66.4	383.9	1600	133.0	10.4
1.7453	0.0299	59.2	430.8	1600	151.0	9.0
		60.2	423.6	1600	151.0	9.0
1.7388	0.0364	44.4	575.0	1600	244.0	5.0
		44.8	569.8	1600	247.0	4.9
1.7331	0.0421	42.4	602.2	800	161.8	3.3
		42.4	602.2	800	152.2	3.7
1.7292	0.0460	45.6	559.8	800	212.6	2.2
		45.2	564.8			
1.7255	0.0497	41.2	619.8			
		41.8	610.8			
1.7190	0.0562	40.8	625.8	400	123.2	1.6
		41.4	616.8	400	133.8	1.4
1.6719	0.1033	38.8	658.2	400	193.0	0.5
		39.0	654.8			

Table VII (Cont'd.)

Sample #4 (Cont'd.)

Aver. thick. in Mm.	Amt. removed in Mm.	Time in sec. for 25600 Fe K-Alpha counts	Fe K-Alpha intensity in c/s corr. for background	No. of counts	Time in sec.	Ti K-Alpha intensity in c/s corr. for background
1.6504	0.1248	38.0 38.0	672.1 672.1	400	253.4	0

Sample #5

Aver. thick. in Mm.	Amt. removed in Mm.	Time in sec. for 25600 Fe K-Alpha counts	Fe K-Alpha intensity in c/s corr. for background	No. of counts	Time in sec.	Ti K-Alpha intensity in c/s corr. for background
1.8206	0	172.0 174.4	147.3 145.2	1600 1600	65.6 68.0	22.8 21.9
1.8026	0.0180	181.0 180.0	139.8 140.6	1600 1600	67.0 71.4	22.3 20.8
1.7978	0.0228	161.4 162.0	157.0 156.4	1600 1600	69.2 69.2	21.5 21.5
1.7935	0.0271	140.0 142.4	181.3 178.2	1600 1600	73.4 73.8	20.2 21.1
1.7896	0.0310	133.0 132.0	190.9 192.3	1600 1600	77.0 77.0	19.2 19.2
1.7876	0.0330	98.6 98.0	258.0 259.6	1600 1600	79.6 79.6	18.5 18.5
1.7836	0.0370	90.6 90.4	281.0 281.6	1600 1600	84.0 86.4	17.4 16.9
1.7797	0.0409	83.6 83.2	304.6 306.1	1600 1600	104.8 102.0	13.7 14.1
1.7755	0.0451	63.6 64.6	400.9 394.7	1600 1600	138.0 142.6	10.0 9.6
1.7718	0.0488	54.2 54.4	470.7 469.0	1600 1600	188.4 181.0	6.9 7.2
1.7673	0.0533	47.8 48.2	534.0 529.5	800 800	160.2 149.2	3.4 3.8

Table VII (Cont'd.)

Sample #5 (Cont'd.)

Aver. thick. in Mm.	Amt. removed in Mm.	Time in sec. for 25600 Fe K-Alpha counts	Fe K-Alpha intensity in c/s corr. for background	No. of counts	Time in sec.	Ti K-Alpha intensity in c/s corr. for background
1.7577	0.0629	43.2	591.0	800	186.4	2.7
		42.8	596.5	800	191.0	2.6
1.7486	0.0720	41.4	616.7	400	98.0	2.5
		41.6	613.8	400	94.6	2.6
1.6592	0.1614	40.0	638.4	400	141.0	1.2
		39.8	641.6			
1.6420	0.1786	38.4	665.1	400	158.6	0.9
		38.4	665.1			
1.6044	0.2162	38.4	665.1	400	199.8	0.4
		38.6	661.6			
1.5706	0.2500	38.4	665.1	400	240.6	0.1

E. Sample Calculation

To clear away possible confusion concerning this method, a sample calculation is given here. The data are from the intensities at the surface of specimen No. 1 before any of the coating was removed.

The maximum intensity of the iron K-alpha line at this original surface was recorded as 195.3 and 196.5 counts per second, while the maximum intensity of the titanium K-alpha at this surface was recorded as 21.2 counts per second. These intensities include the background correction and were taken from the experimental data in Table VII. In Table VIII, the ratio of the surface intensity of iron K-alpha to the iron K-alpha intensity of a pure sample is listed as 0.29, while the corresponding ratio for titanium is 0.48. The corrected compositions may be read directly from figures No. 4 and No. 5. Figure No. 4 shows that a ratio of 0.48 is equivalent to 58 atomic percent titanium in the iron-titanium surface layer. Figure No. 5 shows that a ratio of 0.29 is equivalent to 39 atomic percent iron in the surface layer.

The method of minimum effective thicknesses is then employed to determine the thickness of the layer which contributes to the recorded surface intensities. From figure No. 8, the minimum effective thickness for titanium K-alpha x-rays from a layer containing 58 atomic percent titanium is about 0.019 mm. Therefore, it is assumed that 58 atomic percent is the average titanium composition for a layer from the surface down to a depth of 0.019 mm. For the plot of distance from the original surface versus atomic percent titanium, in figure No. 10, 58 atomic percent titanium is assumed to be the titanium composition at a point equal to half the minimum effective thickness or 0.0095 mm. In a similar manner, from figure No. 9, the minimum effective thickness for iron K-alpha x-rays from a layer of iron-titanium alloy containing 39 atomic percent iron is about 0.011 mm. Therefore, it is assumed that 39 atomic percent is the average iron composition from the surface to a depth of 0.011 mm. For the plot of distance from the original surface versus atomic percent iron, in figure No. 10, 39 atomic percent iron is assumed to be the iron composition at a point equal to half the minimum effective thickness or 0.0055 mm.

The original surface was then ground down, the new thickness measured and intensities of the new surface determined. For example, an average thickness of 0.0031 mm. was removed from sample No. 1. The surface intensities were corrected as before with figures No. 4 and No. 5 to give an average composition of 60 atomic percent titanium and 35 atomic percent iron. From figure No. 8, the minimum effective thickness for titanium K-alpha x-rays from a layer containing 60 atomic percent titanium is about 0.0195 mm. For the plot of distance from the original surface layer versus atomic percent titanium in figure No. 10, 60 atomic percent titanium is assumed to be the titanium composition at a point equal to half the minimum effective thickness of the new surface layer plus the thickness ground from the original surface. In this case, the distance is taken as 0.013 mm., because $\frac{0.0195}{2} + 0.0031 = 0.013$ mm. The minimum effective thickness for an alloy layer containing 35 percent iron is 0.011 mm., and so the distance from the original surface for the iron curve in figure No. 10 is $\frac{0.011}{2} + 0.0031 = 0.0085$ mm.

F. Final Results

The final results, as obtained from all the intensities of all the layers which were sectioned, are tabulated in Table VIII for each sample. The ratios of the surface intensities to the intensities of the pure elements are listed. The values of the atomic percentages of iron and titanium obtained in figures No. 4 and No. 5 from these ratios are also listed. Half of the minimum effective thickness of each surface layer was determined and assumed to be the point at which the composition was actually that given by the surface intensities after correction for differential absorption and mutual fluorescence. The distance of each of these points from the original surface was determined and listed in Table VIII. From the data in Table VIII, figures No. 10 to No. 14 were plotted. These graphs show the variation of composition with distance from the original surface. By extrapolation of the curves to a zero layer thickness, the composition at the original surface of the titanium coating was estimated. The thickness of the titanium coating can also be estimated from these curves.

Figure No. 15 is included in order to compare the compositions at various depths determined by the method of minimum effective thickness with the results obtained when only the surface layer itself is assumed to contribute to the surface intensity. Figure No. 15 is a plot of the results obtained from sample No. 4 and should be compared with figure No. 13 which is also a plot of the results obtained from sample No. 4. However, in figure No. 13, a finite thickness of the coating is assumed to contribute to the surface intensity.

Table VIII

Analysis of Coating Layers

Sample #1

Aver. dist. of layer from orig. surf. in Mm.	Fe K-Alpha Int. from alloy layer / Fe K-Alpha Int. from pure Fe	Atomic Percent Fe	Ti K-Alpha Int. from alloy layer / Ti K-Alpha Int. from pure Ti	Atomic Percent Ti
.0055	.292 - .294	39 - 40		
.0085	.261 - .262	35		
.0095			.484	58
.0120	.263 - .268	35 - 36		
.0130			.495 - .514	59 - 61
.0135	.331 - .336	44 - 45		
.0150	.325 - .363	43 - 47	.447 - .457	54 - 55
.0170			.381 - .431	46 - 52
.0180			.420	51
.0185	.418 - .422	53		
.0205			.338 - .345	41 - 42
.0215	.462	57		
.0250	.578 - .592	68 - 69	.201 - .203	24
.0265			.119	15
.0290	.701 - .712	78 - 79		
.0315			.062 - .066	7 - 8
.0330			.053 - .057	6 - 7
.0350	.826 - .860	88 - 90		
.0380	.837 - .845	89	.055 - .057	6 - 7
.0430	.795 - .805	85 - 86		
.0805			.029	3 - 4
.0840			.014 - .018	2
.0870	.909 - .918	94 - 95		
.0915	.945	96 - 97		
.1300			.009	1
.1435	.979 - .984	99		
.1520			0	0
.1570	.995 - 1.000	100		

Table VIII (Cont'd.)

Sample #2

Aver. dist. of layer from orig. surf. in Mm.	$\frac{\text{Fe K-Alpha Int. from alloy layer}}{\text{Fe K-Alpha Int. from pure Fe}}$	Atomic Percent Fe	$\frac{\text{Ti K-Alpha Int. from alloy layer}}{\text{Ti K-Alpha Int. from pure Ti}}$	Atomic Percent Ti
.0050	.290 - .294	39 - 40		
.0090			.429 - .431	52
.0110	.297	40		
.0130	.300 - .301	40		
.0140			.416 - .425	50 - 51
.0155	.316 - .319	42 - 43		
.0160			.416 - .418	50
.0170	.349 - .352	46		
.0185			.381 - .384	46
.0190			.349 - .361	42 - 43
.0200	.429 - .435	54 - 55		
.0220	.488 - .492	59 - 60	.336 - .342	40 - 41
.0235			.295	35
.0250			.208 - .212	25
.0260	.623	71 - 72		
.0285			.174	20
.0305	.647 - .649	74		
.0350			.105 - .107	13
.0375	.743 - .748	81 - 82		
.0655			.029	4
.0660			.021	2
.0710	.888 - .896	92 - 93		
.0735	.931	95		

Table VIII (Cont'd.)

Sample #3

Aver. dist. of layer from orig. surf. in Mm.	Fe K-Alpha Int. from alloy layer / Fe K-Alpha Int. from pure Fe	Atomic Percent Fe	Ti K-Alpha Int. from alloy layer / Ti K-Alpha Int. from pure Ti	Atomic Percent Ti
.0055	.346 - .350	45 - 46		
.0080	.359 - .360	47		
.0085			.395 - .404	47 - 49
.0105	.362 - .364	47 - 48		
.0110			.402 - .404	48 - 49
.0135	.424 - .425	53 - 54	.388 - .397	47 - 48
.0155			.352 - .361	42 - 43
.0180	.598 - .602	70	.267 - .269	32
.0210			.155	19
.0225	.757 - .763	82 - 83		
.0350			.007 - .009	1
.0395			0 - .001	0
.0405	.852 - .864	90 - 91		
.0470	.918 - .927	95		
.0500			0	0
.0575	.914 - .918	94 - 95		
.1035			0	0
.1145	1.000	100		

Table VIII (Cont'd.)

Sample #4

Aver. dist. of layer from orig. surf. in Mm.	$\frac{\text{Fe K-Alpha Int. from alloy layer}}{\text{Fe K-Alpha Int. from pure Fe}}$	Atomic Percent Fe	$\frac{\text{Ti K-Alpha Int. from alloy layer}}{\text{Ti K-Alpha Int. from pure Ti}}$	Atomic Percent Ti
.0050	.288 - .290	39		
.0095			.475 - .498	57 - 60
.0210	.349 - .350	46		
.0225	.362 - .364	47 - 48		
.0250			.461 - .477	55 - 57
.0255	.411 - .414	52		
.0260			.459 - .484	55 - 58
.0280	.417 - .421	53	.434 - .438	52
.0295			.340 - .349	41 - 42
.0320	.589	69	.267 - .288	32 - 35
.0340	.573 - .574	67	.231 - .237	28 - 29
.0365			.205	25
.0390	.634 - .644	73 - 74		
.0425			.112 - .114	14
.0460	.852 - .860	90		
.0475			.075 - .084	9 - 10
.0515			.050	6
.0540	.901	93		
.0560	.837 - .845	89 - 90		
.0610			.032 - .037	4
.0620	.914 - .927	94 - 95		
.0690	.923 - .936	95 - 96		
.1080			.014	1
.1170	.979 - .984	99		
.1350			0	0
.1390	1.000	100		

Table VIII (Cont'd.)

Sample #5

Aver. dist. of layer from orig. surf. in Mm.	Fe K-Alpha Int. from alloy layer / Fe K-Alpha Int. from pure Fe	Atomic Percent Fe	Ti K-Alpha Int. from alloy layer / Ti K-Alpha Int. from pure Ti	Atomic Percent Ti
.0050	.212 - .220	30		
.0095			.500 - .521	60 - 62
.0230	.209 - .210	29		
.0275			.475 - .509	57 - 61
.0280	.234 - .235	32		
.0320	.267 - .271	36 - 37		
.0325			.491	59
.0360	.286 - .288	38 - 39	.461 - .482	55 - 58
.0385	.386 - .388	50		
.0400			.438	53
.0415			.422	51
.0430	.420 - .421	53		
.0455			.386 - .397	46 - 48
.0470	.456 - .458	56 - 57		
.0485			.313 - .322	37 - 39
.0515			.219 - .228	26 - 28
.0520	.590 - .600	69 - 70		
.0555			.158 - .164	19 - 20
.0570	.701 - .704	78		
.0585			.078 - .087	9 - 11
.0625	.792 - .799	85 - 86		
.0680			.059 - .062	7
.0745	.884 - .892	92 - 93		
.0770			.057 - .059	7
.0845	.918 - .922	95		
.1660			.027	3 - 4
.1750	.955 - .960	97		
.1835			.011	1
.1940	.990 - .995	99 - 100		
.2150			.002	0

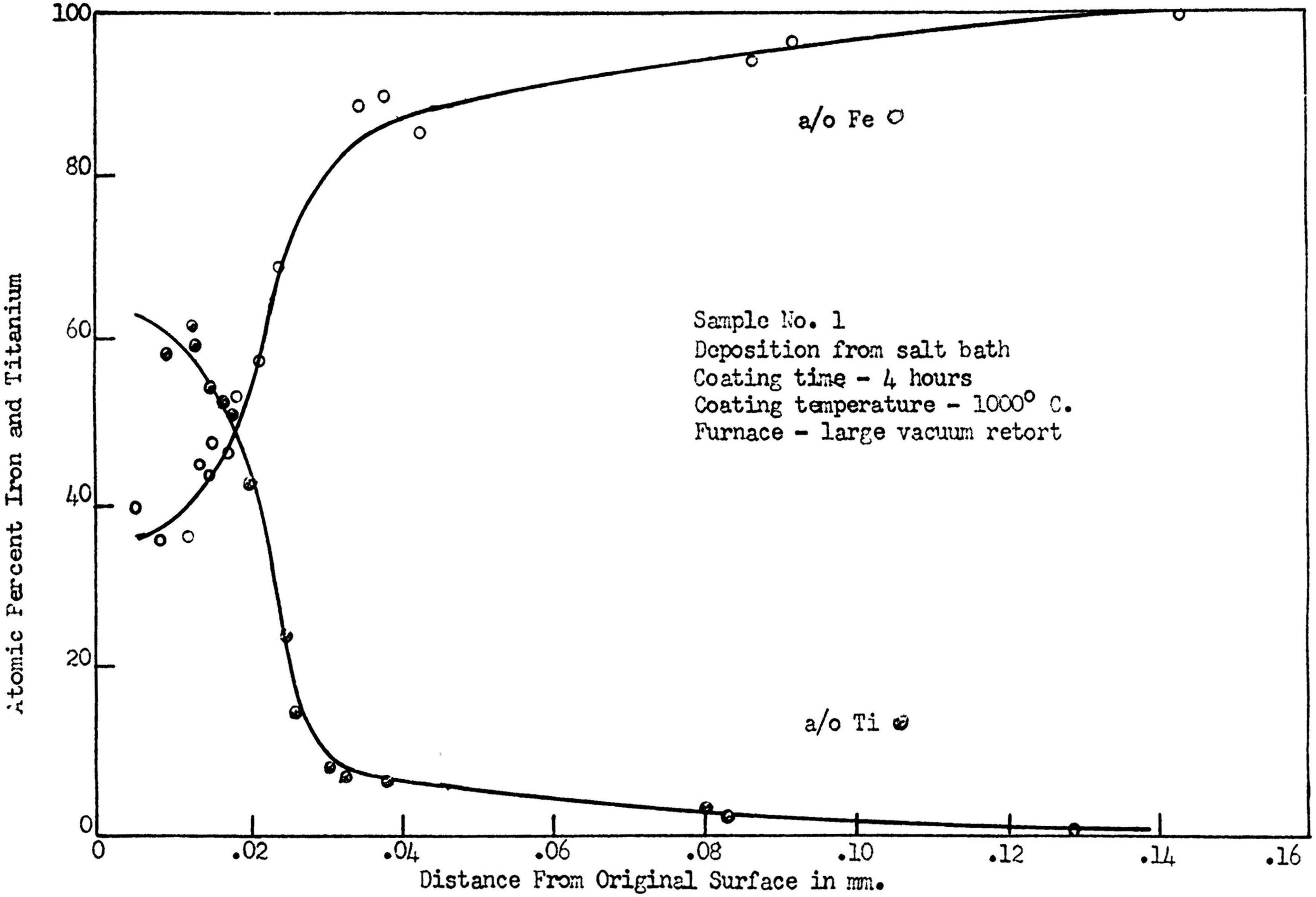

Fig. 10. Distance of layer from original surface vs. composition for sample No. 1

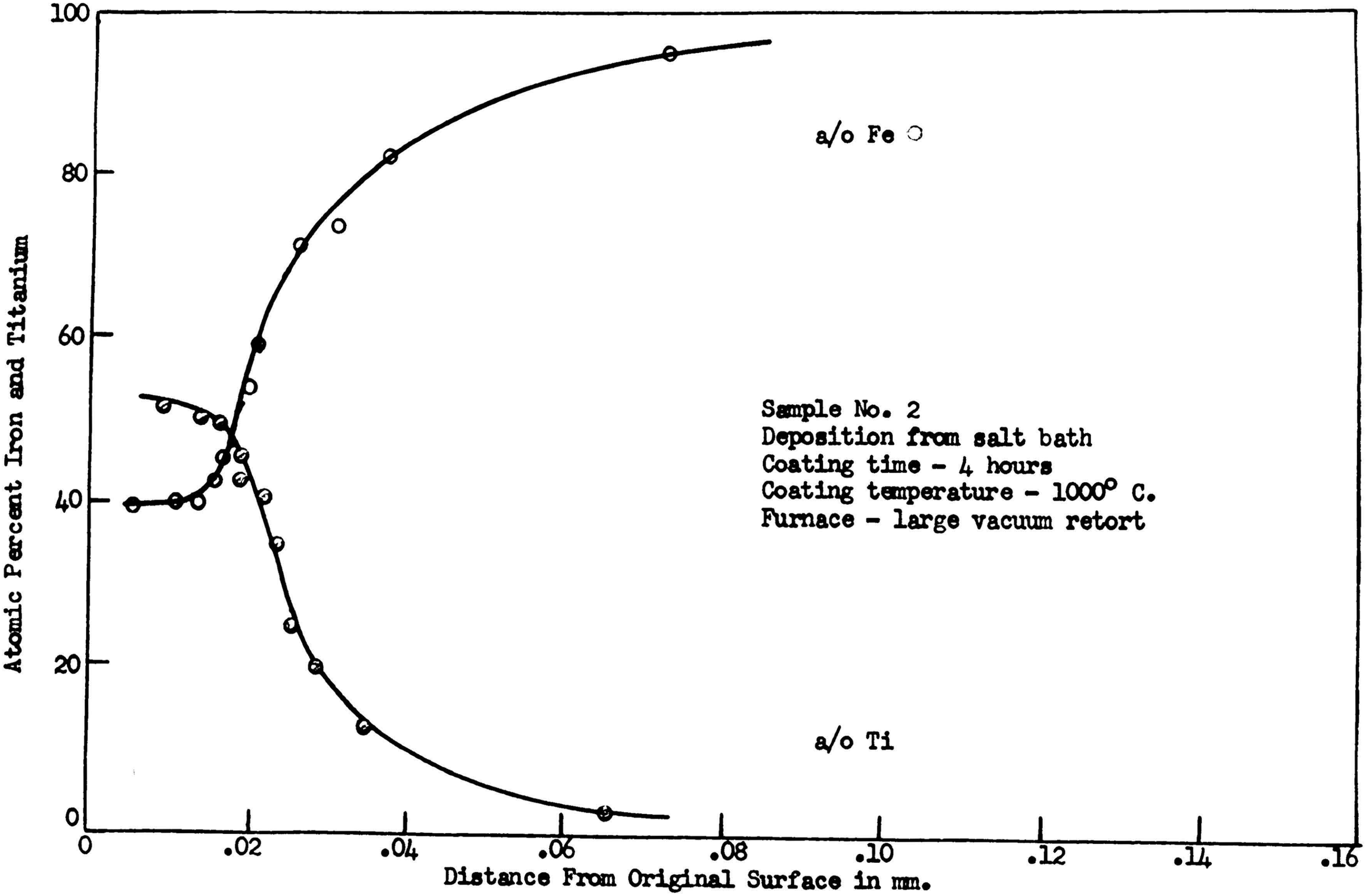

Fig. 11. Distance of layer from original surface vs. composition for sample No. 2

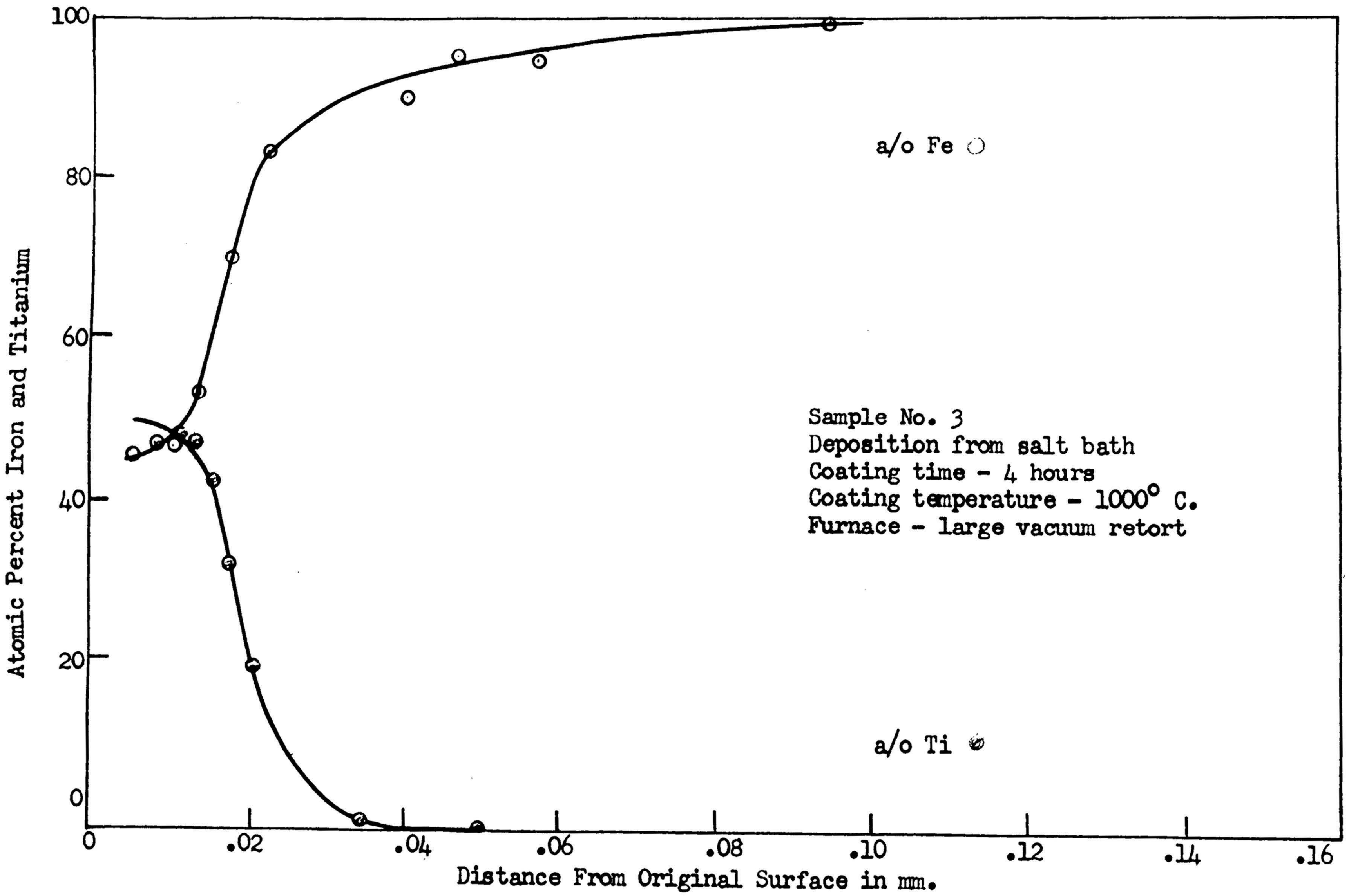

Fig. 12. Distance of layer from original surface vs. composition for sample No. 3

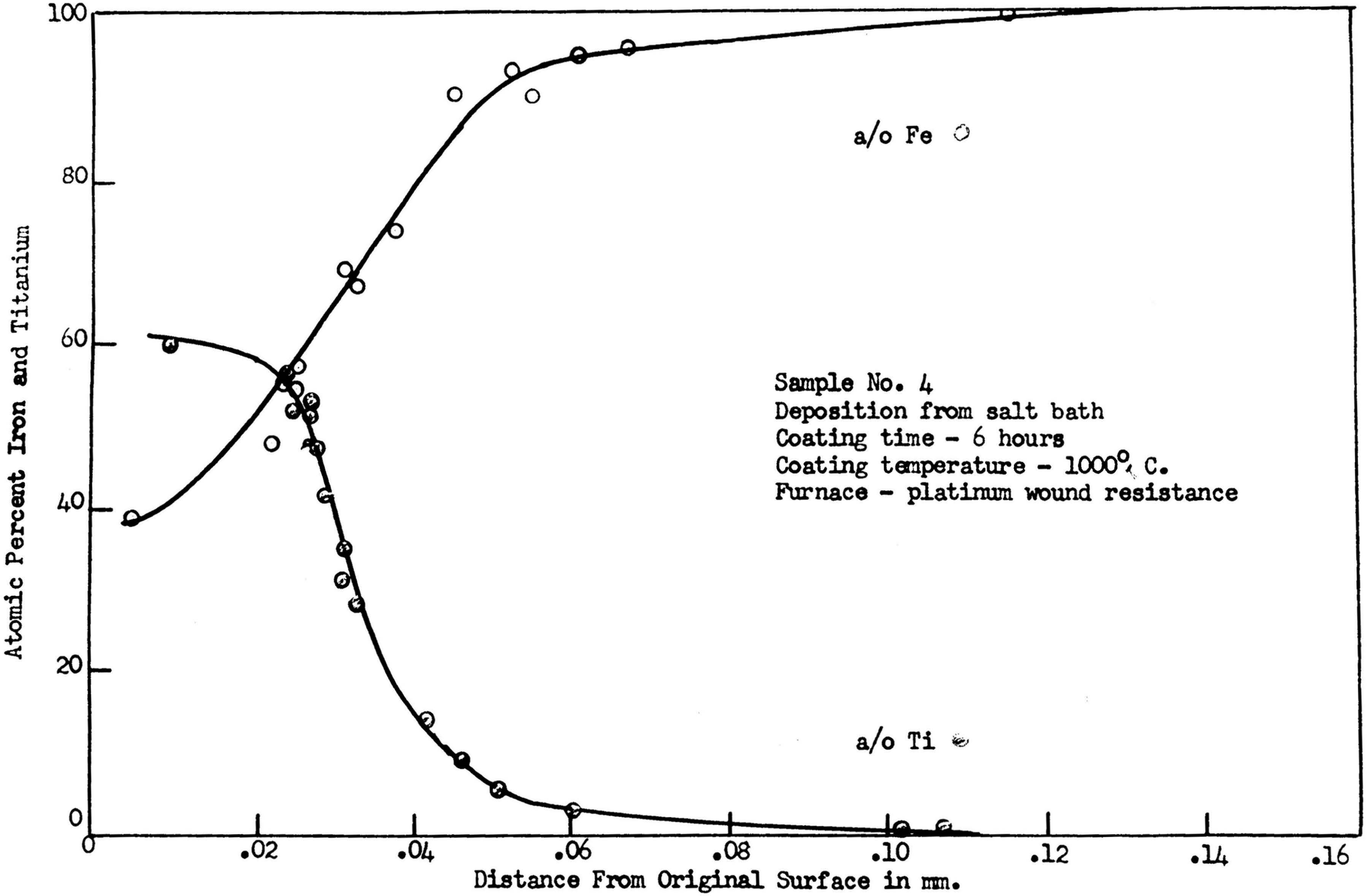

Fig. 13. Distance of layer from original surface vs. composition for sample No. 4

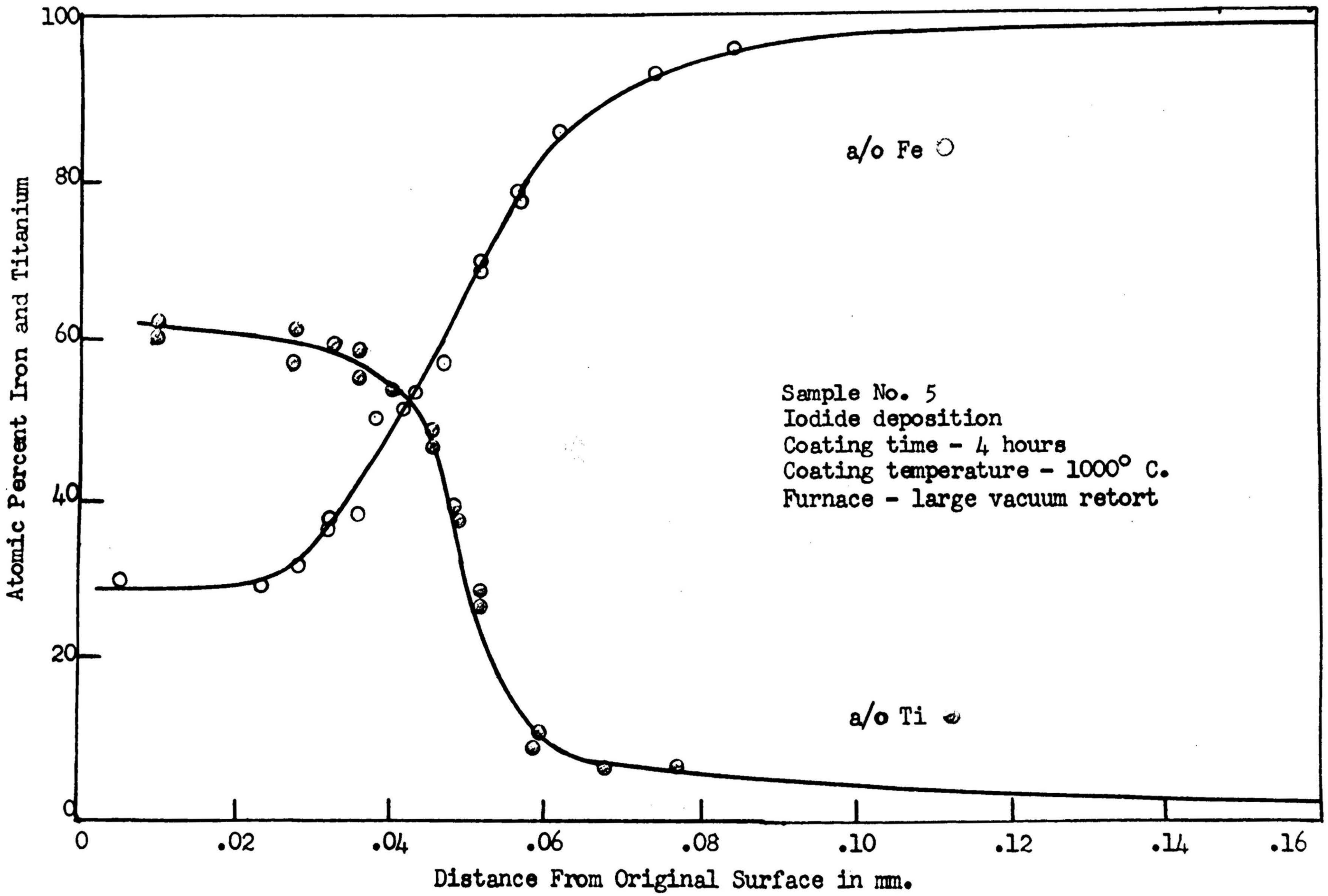

Fig. 14. Distance of layer from original surface vs. composition for sample No. 5.

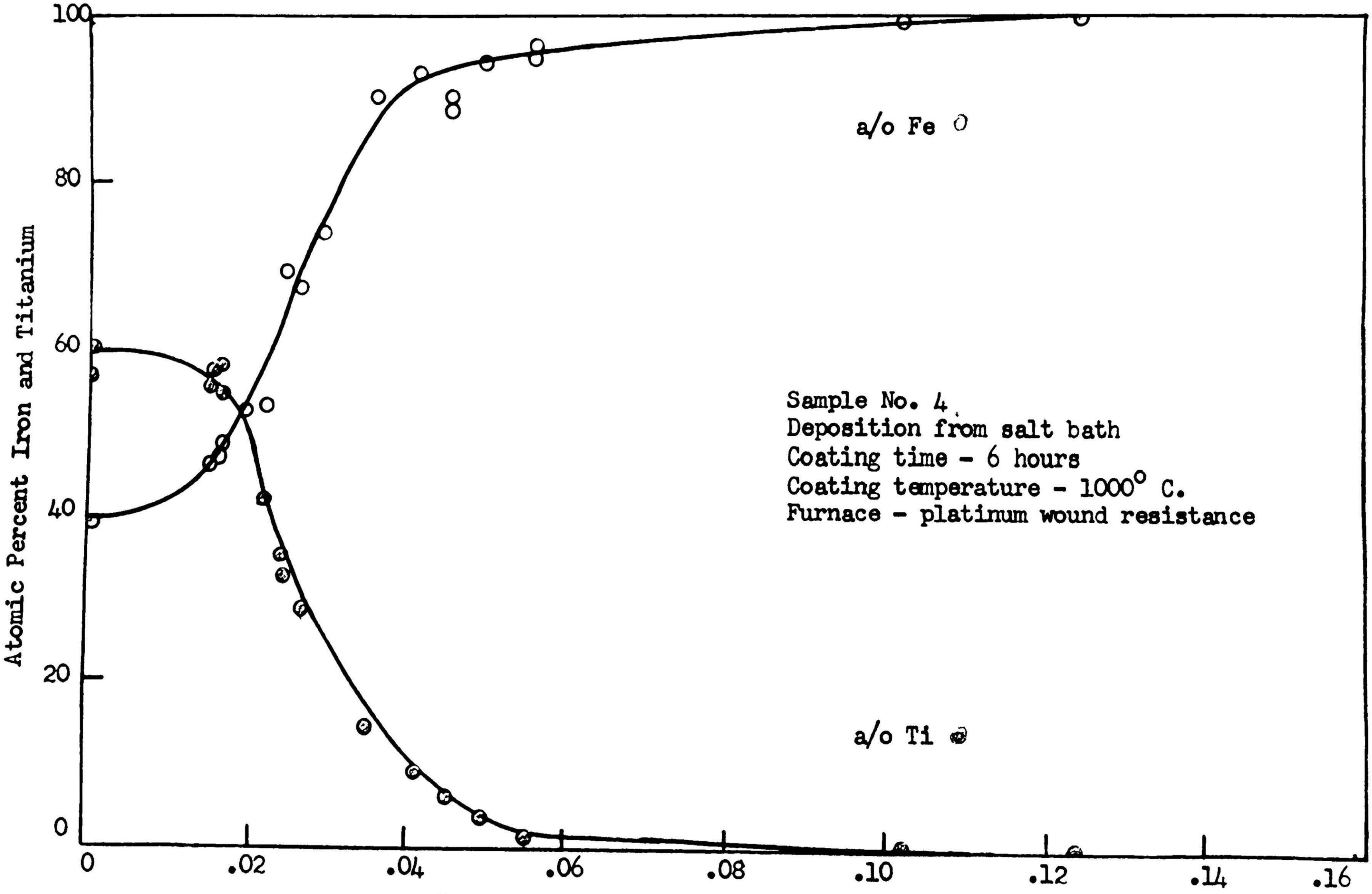

Fig. 15. Uncorrected distance of layer from original surface vs. composition for sample No. 4.

DISCUSSION

A. Errors And Deficiencies Of The Investigation

The errors in this investigation were of two main types. One class of errors was attributable to the experimental error associated with the method employed and the other group of errors evolved from the assumptions which were required in order to evaluate the experimental data.

The following is a list of the errors attributable to the experimental procedure:

1. The statistical error involved in the recording of events in the Geiger tube. This was minimized by using a large number of counts over a long counting period to determine the characteristic line intensities.
2. Unequal pressure when removing coating layers by abrasion with emery paper could cause the removal of unequal amounts at different places on the sample surface.
3. Variation in the background intensity, which was assumed to remain constant.
4. Removal of the soft outer layer of samples No. 1, No. 2 and No. 3 by scrubbing the samples in water to remove the adherent potassium chloride. Although it was speculated that this outer coating had the highest titanium composition, this part of the coating was not adherent enough to be of any practical significance.
5. As there was considerable variation in hardness throughout the coating, it was not possible to remove a constant amount of the coating by polishing on the emery paper with a constant number of strokes

between each intensity determination. Consequently, the tendency was to remove too much of the softer part of the coating between intensity measurements. In samples No. 4 and No. 5 there has been too great a thickness of coating removed after the first and before the second intensity determination.

The following is a list of the errors caused by the assumptions required to evaluate the data:

1. The calibration curves of figure No. 4 and figure No. 5 were determined from a plot of only three points. In order to prepare a more accurate calibration curve on each figure, a larger number of standard samples should have been prepared and analyzed.
2. Because there were no values given in the literature for the mass absorption coefficient of titanium K-alpha in iron or titanium, it was necessary to obtain these values by an extrapolation of the curves in figure No. 7.
3. In order to obtain the minimum effective thickness of various iron-titanium alloy layers, it was assumed, without being proven, that the minimum effective thickness occurred when the I/I_o ratio was 0.20. However, because of the logarithmic relation between the minimum effective thickness and the ratio of I/I_o, a large variation in the I/I_o ratio will only have a small effect on the minimum effective thickness.
4. The assumption that the surface intensity gives the composition of the layer at a point equivalent to half the minimum effective thickness is probably slightly erroneous, because the atoms nearer the surface contribute a disproportionate amount to the surface intensity.

B. Conclusions

An analysis of the results showed that the composition of the coatings produced by the salt bath deposition method contained from 50 to 65 atomic percent titanium and from 45 to 30 atomic percent iron at the surface of the coating. The coating produced by the iodide deposition method contained about 65 atomic percent titanium and about 30 atomic percent iron at the surface of the coating. Although the iodide deposition coating was much thicker than the salt bath coatings, the titanium content at the surface of the coating was only slightly increased. In all cases, there seemed to be a fairly constant tendency for the composition of the iron and the titanium on and near the surface to total less than 100 percent. An analysis of the titanium powder used in this investigation showed the powder contained only about 97 percent titanium. It was thought that the remaining part of the powder was oxygen. Therefore, it was assumed that some oxygen diffusion also occurred at the surface of the sample being coated.

It was observed that the sum of iron and titanium more nearly approached 100 percent for the sample coated in the platinum wound resistance furnace than for the other samples which were coated in the large vacuum retort furnace. The vacuum retort furnace was only pumped down to a pressure of about 300 microns of mercury before being filled with helium. Hence, with a furnace of this size, there seemed to be a greater chance for leaks than with the smaller platinum wound resistance furnace which was operated at a much lower pressure.

Samples No. 1 and No. 2 were prepared by the salt bath deposition method under the same conditions and gave nearly equivalent results. The results obtained from samples No. 1 and No. 2 agree to within

5 percent, hence the error attributable to variation in the experimental procedures is less than 5 percent. The anomalous behavior of sample No. 3, which was also prepared by the salt bath deposition method under the same conditions as samples No. 1 and No. 2, can only be explained in terms of the smaller casserole that was used during the coating operation. It was assumed that this smaller casserole could not hold enough titanium powder to coat the specimen with a coating of thickness comparable to those obtained on samples No. 1 and No. 2. It is possible that some unknown effect sharply limited the diffusion of titanium into sample No. 3.

Sample No. 4 was coated for 6 hours, while the previous samples had only been coated for 4 hours. The results obtained from sample No. 4 show that a thicker coating may be obtained by increasing the coating time. Although the coating on sample No. 4 was thicker, the titanium content of the surface layer appeared to be no higher than the results obtained for the previous samples. Even though the thickness of the coating was greater, the distance of titanium diffusion into the base metal was no greater than in previous samples. However, the layer of relatively high titanium content extended to a greater depth in sample No. 4.

The coating obtained by iodide deposition on sample No. 5 was thicker than the salt bath coatings, but the titanium composition at the surface of this coating was only slightly greater. The layer of relatively high titanium content extended to a much greater depth than on any of the previously discussed samples.

A detectable amount of titanium was observed at a maximum depth of 0.14 mm., 0.05 mm., 0.10 mm., and 0.19 mm. respectively for samples

No. 1, No. 3, No. 4 and No. 5. The intensity of the iron K-alpha line reached its maximum at a depth of 0.14 mm., 0.09 mm., 0.13 mm. and 0.19 mm. respectively for samples No. 1, No. 3, No. 4 and No. 5. In the case of sample No. 2, these determinations were not made. An analysis of this data shows that the point at which there was no longer any trace of titanium present and the point at which the iron K-alpha intensity became equivalent to the intensity of pure iron did not usually coincide for any particular sample. A small variation in the time required to record a fixed number of counts would cause a much greater variation in the intensity of the iron K-alpha than in the titanium K-alpha. Hence, a 5 percent variation in the intensity of the iron K-alpha line would case a considerable variation in the point at which the intensity of the iron K-alpha line from the coating coincided with the intensity of pure iron. A conclusion was not reached as to why the titanium penetration was not greater in sample No. 4 than in sample No. 1. Recent work, done at the Missouri School of Mines by P. Chao, shows that the distance of titanium diffusion in a sample coated for 6 hours was 0.13 mm. Chao used a cumulative electrolytic stain etching method in conjunction with a microscope to determine the depth of titanium penetration. The coating temperature of 1000° C. and the bath composition of 10 percent oxygen-containing powder and 90 percent KCl were the same conditions as were used in this investigation. It may be seen that Chao's results are in good agreement with the results obtained for samples No. 1 and No. 4 of this investigation.

The surface layers of all coatings were rather soft and were followed by a very hard intermediate layer. At a greater depth in the coating, the layer once again became soft. Reference to the existing 1000° C. isothermal section of the iron-titanium-oxygen phase diagram (45) and the iron-titanium phase diagram (46)(47) shows that with an oxygen content of less than 2 percent, the same phases are present as are in the iron-titanium binary phase diagram. The outer layer of the coating was probably a two phase area consisting of the intermetallic compound, FeTi, and the solid solution of iron and oxygen in titanium. Immediately following this surface layer, the compound FeTi appeared in the coating. The next layer should be a two phase area consisting of the solid solution of titanium and oxygen in iron plus FeTi. The innermost region of the coating was assumed to be the solid solution of titanium and oxygen in iron.

Rhines (48) has stated that the layers formed by the isothermal and isobaric diffusion of metals across an interface correspond in kind and in the order of their occurrence to all regions in the phase diagram lying between the concentrations of the original bodies and having three or more degrees of freedom according to the phase rule. By the application of this principle, it is seen that, at the diffusion

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(45) Rostoker, W., "Selected Isothermal Sections in the Ti-Rich Corners of the Systems Ti-Fe-O, Ti-Cr-O, and Ti-Ni-O", J. of Metals, Trans. Sect., Vol. 7, No. 1, p. 113, 1955.

(46) Worner, H. W., "The Constitution of Titanium-Rich Alloys of Iron and Titanium", J. Inst. Met., Vol. 79, p. 173, 1951.

(47) Comstock, G. F. and Southard, J. C., "Constitution of Binary Alloys - Iron-Titanium", Metals Handbook, American Society of Metals, Cleveland, Ohio, p. 1219, 1948.

(48) Rhines, F. N., "Diffusion Coatings on Metals", ASM, The Surface Treatment of Metals, p. 123, 1941.

temperature of 1000° C., the first layer to form is that of the solid solution of titanium and oxygen in iron. This layer will continue to form until the titanium at the original interface reaches about 4 percent titanium. At this point, a concentration jump to 47 percent titanium should occur with the resulting formation of the FeTi phase. Further deposition and diffusion of titanium should continue until the original interface reaches a composition of 50 percent titanium. At this point, another concentration jump to 78 percent titanium should occur with the resulting formation of the solid solution of iron and oxygen in titanium. Upon slowly cooling the bath from the diffusion temperature down to room temperature, the two phase regions which occur on the iron-titanium phase diagram should begin to appear between the one phase regions in the coatings.

From the experimental results, it was verified that the two phase regions do actually appear in the coating. The occurrence of an abrupt concentration jump could not be determined in any of the sample coatings. Generally, the jump in concentration from 20 to 40 percent titanium was very sharp; whereas, the concentration change in the region of the intermetallic compound, FeTi, and the solid solution of titanium and oxygen in iron was much more gradual.

The sections of the coating which possessed considerable hardness corresponded with the composition of the hard intermetallic compound, FeTi. The softer regions corresponded to compositions representative of the softer solid solutions.

C. Suggested Future Investigations

1. The development of curves to correlate observed intensity with composition on a theoretical basis rather than by empirical means is suggested. Noakes (48) has produced curves for nickel in iron by applying theoretical concepts that are in agreement with the curves for nickel in iron obtained experimentally.

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(48) Noakes, G. E., "An Absolute Method of X-ray Fluorescence Analysis Applied to Stainless Steels," Symposium on Fluorescent X-ray Spectrographic Analysis, ASTM, Spec. Tech. Publ. No. 157, p. 57 1953.

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2. The accurate determination of the minimum effective thickness of iron and titanium would be a useful contribution toward more accurate analysis of titanium diffusion coatings.

3. An experiment to determine the corrosion resistance of various iron-titanium alloys might show very interesting results. From such an experiment, the minimum titanium content that is required to insure corrosion resistance could be determined. After determining the minimum titanium content for corrosion resistance, experiments might be made to determine the coating thickness required to protect the base metal properly.

4. For a constant coating time and temperature, the iodide deposition process produced a much thicker coating than the salt bath process. However, the iodide deposition coating appeared to be more porous than the coatings produced in the salt baths. An investigation would be worthwhile to determine if the iodide deposition coating was more corrosion resistant or if the increased thickness was over balanced by the increase in porosity in the iodide deposition coating.

5. The methods used in this investigation might be applied to a similar investigation of the composition of titanium coatings on a copper base.

SUMMARY

X-ray fluorescent analysis was used to determine the composition at various depths of a titanium diffusion coating on iron. Calibration curves were established to convert intensities of iron and titanium K-alpha lines directly to atomic percent of iron and titanium. A method was developed to take into effect the finite depth from which secondary x-rays penetrate and which contribute to the experimentally determined surface intensities. The depth from which iron and titanium K-alpha x-rays penetrate through a titanium-iron layer to contribute to the surface intensities was found to vary from 0.1 to 0.3 mm., depending on the composition of the alloy layer.

There seemed to be no appreciable difference between the surface composition of coating produced by either the iodide deposition or the salt bath deposition methods. The extrapolated composition of the surface layer of the titanium coatings was found to vary from 50 to 65 atomic percent titanium and from 45 to 30 atomic percent titanium. It was suspected that there was also some oxygen present near the surface of the titanium coatings.

The iodide deposition method produced a thicker coating than the salt bath deposition method. The diffusion of titanium into the iron was greater in the case of the iodide deposition method.

The coatings were composed of a relatively soft outer layer, which was followed by a hard intermediate layer. The inner layer was also relatively soft. It was assumed that the soft outer layer consisted of the solid solution of iron and oxygen in titanium plus the intermetallic compound, FeTi. The hard middle layer was thought to be FeTi, while the soft inner layer was a solid solution of titanium and oxygen in iron.

APPENDIX

Nine thickness measurements were made at nine particular positions on the 5/8 in. by 5/8 in. sample area after each layer was removed by grinding. The average thickness of the sample was taken as the arithmetic average of the nine thickness measurements. A small mark was made on each sample to insure the proper orientation of the sample for each of the thickness measurements.

Figure No. 16 shows the positions at which the thickness measurements were made and lists the numbers which are used in Table IX to refer to these positions.

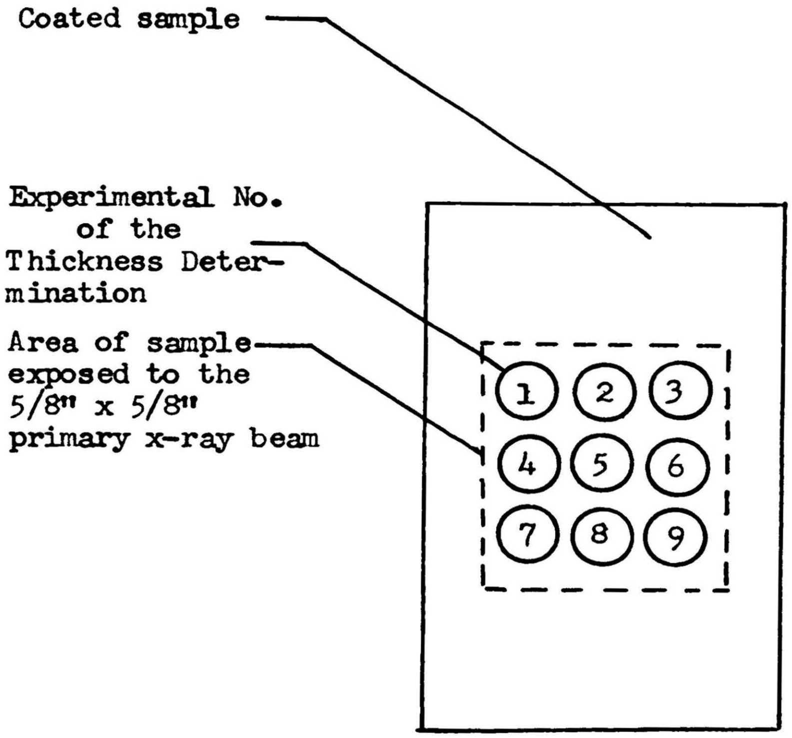

Fig. 16. Orientation of sample for thickness measurements.

Table IX

Determination of Average Thickness In Inches

1	2	3	4	5	6	7	8	9	Average Thickness In Inches	Average Thickness In Millimeters
Sample #1										
.0720	.0722	.0720	.0720	.0720	.0720	.0719	.0720	.0719	.0720	1.8288
.0720	.0720	.0718	.0719	.0719	.0718	.0719	.0718	.0718	.0718 7/9	1.8257
.0719	.0719	.0718	.0717	.0718	.0717	.0717	.0717	.0717	.0717 6/9	1.8229
.0717	.0718	.0717	.0718	.0718	.0716	.0716	.0717	.0715	.0716 7/9	1.8206
.0716	.0717	.0716	.0717	.0717	.0716	.0716	.0716	.0715	.0716 2/9	1.8192
.0715	.0716	.0715	.0716	.0716	.0715	.0715	.0715	.0713	.0715 1/9	1.8164
.0714	.0716	.0715	.0716	.0716	.0715	.0715	.0715	.0713	.0713 8/9	1.8133
.0713	.0713	.0713	.0712	.0713	.0713	.0713	.0714	.0713	.0713	1.8110
.0712	.0712	.0712	.0711	.0712	.0712	.0712	.0713	.0712	.0712	1.8085
.0708	.0710	.0711	.0707	.0711	.0712	.0711	.0711	.0710	.0710 1/9	1.8037
.0708	.0709	.0710	.0706	.0710	.0711	.0709	.0710	.0710	.0709 2/9	1.8014
.0707	.0707	.0708	.0705	.0707	.0708	.0706	.0709	.0709	.0707 3/9	1.7966
.0689	.0692	.0691	.0686	.0693	.0692	.0685	.0693	.0693	.0690 4/9	1.7537
.0686	.0691	.0691	.0682	.0692	.0692	.0683	.0692	.0693	.0689 1/9	1.7503
.0670	.0670	.0667	.0666	.0669	.0670	.0665	.0670	.0673	.0668 8/9	1.6990
.0662	.0665	.0662	.0659	.0662	.0662	.0657	.0664	.0667	.0662 2/9	1.6820

Table IX (Cont'd.)

Sample #2

.0675	.0676	.0675	.0676	.0677	.0676	.0675	.0676	.0673	.0675 4/9	1.7182
.0673	.0674	.0674	.0674	.0676	.0675	.0674	.0675	.0673	.0674 2/9	1.7125
.0672	.0674	.0674	.0674	.0675	.0674	.0673	.0674	.0671	.0673 4/9	1.7105
.0671	.0673	.0673	.0673	.0674	.0673	.0672	.0673	.0671	.0672 5/9	1.7083
.0671	.0673	.0672	.0672	.0673	.0672	.0672	.0672	.0671	.0672	1.7069
.0670	.0671	.0671	.0671	.0672	.0671	.0671	.0671	.0670	.0670 8/9	1.7041
.0670	.0671	.0670	.0670	.0671	.0670	.0670	.0670	.0670	.0670 2/9	1.7024
.0669	.0671	.0670	.0669	.0670	.0668	.0668	.0669	.0668	.0669 2/9	1.6998
.0668	.0669	.0668	.0668	.0668	.0667	.0667	.0667	.0667	.0667 6/9	1.6959
.0666	.0668	.0665	.0665	.0666	.0663	.0664	.0663	.0664	.0665	1.6891
.0651	.0654	.0653	.0653	.0656	.0653	.0652	.0653	.0651	.0652 8/9	1.6583
.0651	.0653	.0653	.0652	.0654	.0653	.0652	.0653	.0651	.0652 4/9	1.6572

Sample #3

.0704	.0704	.0705	.0704	.0705	.0703	.0704	.0705	.0703	.0704 1/9	1.7884
.0703	.0703	.0703	.0704	.0704	.0702	.0703	.0704	.0702	.0703 1/9	1.7859
.0703	.0702	.0702	.0702	.0703	.0701	.0702	.0703	.0701	.0702 1/9	1.7834
.0702	.0701	.0701	.0701	.0701	.0701	.0701	.0702	.0700	.0701 1/9	1.7808
.0701	.0700	.0700	.0699	.0700	.0700	.0700	.0699	.0700	.0699 8/9	1.7777
.0700	.0698	.0699	.0698	.0698	.0700	.0698	.0697	.0698	.0698 4/9	1.7740
.0693	.0693	.0692	.0693	.0692	.0692	.0692	.0692	.0691	.0692 2/9	1.7582
.0686	.0687	.0686	.0686	.0687	.0687	.0687	.0686	.0687	.0685 5/9	1.7438
.0687	.0687	.0684	.0687	.0687	.0685	.0689	.0688	.0683	.0686 3/9	1.7433
.0668	.0670	.0671	.0663	.0667	.0668	.0656	.0663	.0661	.0665 2/9	1.6900
.0664	.0663	.0661	.0659	.0662	.0662	.0651	.0655	.0652	.0658 7/9	1.6733

Table IX (Cont'd.)

Sample #4

.0697	.0700	.0698	.0702	.0700	.0696	.0701	.0699	.0697	.0698 8/9	1.7752
.0691	.0693	.0693	.0693	.0694	.0693	.0692	.0693	.0692	.0692 6/9	1.7594
.0690	.0693	.0693	.0692	.0693	.0692	.0692	.0693	.0692	.0692 2/9	1.7582
.0690	.0692	.0691	.0692	.0692	.0690	.0692	.0692	.0690	.0691 2/9	1.7557
.0690	.0690	.0690	.0691	.0691	.0690	.0690	.0690	.0689	.0690 1/9	1.7529
.0689	.0690	.0689	.0690	.0690	.0689	.0688	.0689	.0688	.0689 1/9	1.7503
.0687	.0689	.0688	.0689	.0688	.0688	.0687	.0688	.0689	.0688 1/9	1.7478
.0687	.0688	.0688	.0688	.0687	.0688	.0686	.0685	.0687	.0687 1/9	1.7453
.0685	.0684	.0686	.0685	.0685	.0686	.0682	.0683	.0685	.0684 5/9	1.7388
.0681	.0682	.0685	.0683	.0683	.0685	.0680	.0680	.0682	.0682 3/9	1.7331
.0680	.0681	.0683	.0681	.0680	.0683	.0678	.0679	.0682	.0680 7/9	1.7292
.0679	.0680	.0680	.0680	.0680	.0680	.0677	.0679	.0679	.0679 3/9	1.7255
.0677	.0677	.0676	.0679	.0679	.0678	.0673	.0677	.0675	.0676 7/9	1.7190
.0657	.0659	.0659	.0658	.0660	.0660	.0656	.0658	.0657	.0658 2/9	1.6719
.0646	.0651	.0652	.0646	.0651	.0653	.0652	.0648	.0649	.0649 7/9	1.6504

Table IX (Cont'd.)

Sample #5

.0712	.0710	.0713	.0712	.0725	.0719	.0719	.0721	.0720	.0716 7/9	1.8206
.0702	.0707	.0704	.0707	.0717	.0717	.0705	.0715	.0713	.0709 6/9	1.8026
.0700	.0706	.0702	.0706	.0714	.0712	.0704	.0714	.0712	.0707 7/9	1.7978
.0699	.0703	.0701	.0706	.0711	.0710	.0704	.0712	.0709	.0706 1/9	1.7935
.0697	.0702	.0700	.0704	.0710	.0709	.0702	.0710	.0707	.0704 5/9	1.7896
.0697	.0701	.0700	.0703	.0709	.0708	.0701	.0709	.0706	.0703 7/9	1.7876
.0695	.0700	.0699	.0701	.0707	.0706	.0699	.0708	.0705	.0702 2/9	1.7836
.0694	.0698	.0697	.0699	.0705	.0703	.0699	.0707	.0704	.0700 6/9	1.7797
.0693	.0698	.0695	.0699	.0704	.0701	.0697	.0704	.0700	.0699	1.7755
.0693	.0696	.0694	.0698	.0701	.0700	.0696	.0701	.0699	.0697 5/9	1.7718
.0692	.0696	.0692	.0697	.0699	.0697	.0695	.0699	.0695	.0695 7/9	1.7673
.0689	.0691	.0689	.0692	.0696	.0691	.0693	.0695	.0692	.0692	1.7577
.0686	.0687	.0685	.0689	.0692	.0685	.0689	.0693	.0690	.0688 4/9	1.7486
.0641	.0654	.0655	.0649	.0657	.0661	.0648	.0656	.0658	.0653 2/9	1.6592
.0642	.0647	.0650	.0639	.0650	.0652	.0640	.0648	.0650	.0646 4/9	1.6420
.0626	.0633	.0634	.0627	.0636	.0636	.0626	.0634	.0633	.0631 6/9	1.6044
.0607	.0619	.0620	.0616	.0623	.0624	.0614	.0620	.0622	.0618 3/9	1.5706

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