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DEPOSITION OF METALLIC COATINGS FROM FUSED SALT BATHS

BY

ANDREW HESSLER LARSON

A

THESIS

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in partial fulfillment of the work required for the

Degree of

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1954

Approved by AW Schlechten
Professor and Chairman Department of
Metallurgical Engineering

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An expression of gratitude is hereby extended to Dr. Albert W. Schlechten, Chairman of the Department of Metallurgical Engineering, for his invaluable guidance and suggestions throughout the entire period of investigation.

The author also wishes to express his appreciation for the opportunity to work on the Electrodeposition of Titanium project conducted for the Air Force under Contract No. A F 33 (616) - 75.

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INTRODUCTION

This thesis is the result of an investigation undertaken to study some of the important factors affecting the deposition of metallic diffusion coatings on other metals immersed in a fused salt bath.

It is well known that metals differ from each other with respect to their corrosion resistance in various corrosive media. Since metal corrosion takes a severe toll of the common construction metals, especially ferrous metals, present day engineers are constantly confronted with the problem of protecting iron, steel, and other base metals with suitable resistant coatings or coverings.

Some of the present day modes of protecting metals from ordinary corrosion are: (a) to apply uniform metallic coatings of less or more noble metals, (b) to apply uniform nonmetallic coatings, or (c) to produce coatings of corrosion resistant alloys. With respect to the first method, it is known that some of the metals which possess excellent corrosion resistance are very difficultly coated on other metals by the usual methods of spraying, dipping, or electrodeposition. The last method describes best the results obtained when coatings are applied by diffusion. In this case the coating metal is caused to come in contact with the base metal and interdiffusion occurs to cause the formation of an alloy which varies in composition with depth.

The fact that diffusion coatings can be made of metals nót easily electroplated lends importance to the method.

There are many methods which have been devised to obtain diffusion coatings on various metals. One which is quite well known and used commercially is the process of "chromizing" which produces a diffusion layer of chromium on another metal. One method of "chromizing" consists of immersing the specimen to be coated in a mixed chloride fused bath containing chromium metal flakes. Another method consists of packing a low carbon steel in intimate contact with powdered chromium in the presence of hydrogen gas and heating to temperatures between 1200° and 1400° C. still another method, which was developed in Germany, consists of passing gaseous chromium chloride over steel to be chromized at temperatures between 900° and 1000° C. Typical high temperature applications of chromized steel includes heating and cooking appliances, heat treatment equipment, fixtures and jigs, etc.

A somewhat similar process has been developed at Missouri School of Mines for producing diffusion coatings of titanium on metals. This process consists of using either a plate of metallic titanium fixed adjacent to the metal to be coated and immersing the assemblage in an alkali salt mixture which has been fused, or packing the metal article in titanium powder and the salt mixture and then fusing the salt. The mechanism of deposition is not exactly known; however, it is presently thought that the deposition occurs from a "pyrosol" or metal fog.(1)

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(1) Alexander, J. Colloid Chemistry Theoretical and Applied. Vol. 1. Chemical Catalog Company, N.Y., 1926. pp. 681-706.

Since "chromizing" has been proved to be generally quite applicable to commercial processes and the formation of diffusion coatings of titanium appears to be also commercially applicable, especially where corrosion resistant coatings are desired, it was thought that an investigation of diffusion coatings of other metals, such as manganese, uranium, and zirconium would prove to be quite profitable. Zirconium diffusion coatings are of special interest since it is a highly corrosion resistant metal which seemingly is impossible to deposit by electrolytic methods from aqueous solutions.

A process similar to the one used for titanium was used to deposit manganese, uranium, and zirconium diffusion coatings. Chromium was also included to serve as a comparison with the other diffusion coatings, since these coatings have undergone extensive investigation and many data are in the literature. A metal plate was used as the source of the coating metal, thus minimizing the oxidation problem associated **with** the use of metal powders.

Review of Previous Literature

A. Metallic Coatings from Fused Salt Baths

A series of investigations concerning the deposition of metallic coatings from fused salt baths were conducted by H. R. Hogue.(2)

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(2) Hogue, H. R., Protective Metal Coatings from Molten Salts, Metal Progress, Vol. 52, pp. 819-823, Nov. 1947.

The purpose of these investigations was to develop a thin yet highly corrosion resistant coating for small, intricately shaped metal articles. It was found during World War II that the usual methods of protecting metals from corrosion, such as electroplating, metal spraying, and painting, were often inapplicable where fine dimensional tolerances must be kept.

As a result of these investigations by Hogue it was found that if a metal sample such as iron is dipped in a fused salt bath such as stannous chloride (sometimes with extra metallic tin dissolved in it) the surface metal of the sample will be replaced by the metal of the salt, provided the metal of the salt is in the correct position in the electromotive series, or that the cation has more affinity for the metal of the sample than it has for the anion. The thickness of coatings thus obtained averaged between 0.0001 in. and 0.0005 in.

Hogue found that the principal factors affecting the thickness of coating obtained were: (a) Time in salt bath,

(b) temperature of the bath, (c) initial temperature of the specimen, and (d) composition of the bath. It was found that, in general, no precleaning of the surface to be coated is necessary where molten salt baths are used for plating, although, the "cementation" process rate is somewhat decreased.

Campbell, Barth, Hoeckelman, and Gonser (3) have conducted a series of investigations dealing with salt bath chromizing. They have applied smooth, non-porous, deformable, nitric acid resistant coatings on a variety of ferrous materials. They chromized by immersing the ferrous specimens in fused salt baths at temperatures from 900 to 1200° C. The salt bath compositions investigated varied from 5 to 30 weight percent chromous chloride with varying amounts of barium chloride, sodium chloride, and chromium metal flakes. An argon atmosphere was provided to protect the bath against air attack.

These investigators found that, in general, the presence of air above the bath was deleterious to the coating process. They also found that it was not possible to chromize successfully in the absence of metallic chromium. They claim that salt bath chromizing, like all of the pack processes except those depending solely on the diffusion of metallic chromium, is a displacement process; wherein the chromous chloride

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(3) Campbell, I. E., Barth, V. D., Hoeckelman, R. F. and Gonser, B. W. Salt Bath Chromizing. Trans. of the Electrochem. Soc. Vol. 96, No. 4, 1949, pp. 262-263.

reacts with the iron to form a chromium-iron alloy and ferrous chloride. Consequently, chromium metal is added to react with the ferrous chloride to form more chromous chloride with the reduction of the ferrous chloride.

The two processes upon which they claim the rate of case formation to be dependent are: (a) the replacement reaction and (b) the interdiffusion of chromium and iron; the latter being the limiting process since the replacement reaction is assumed to be instantaneous.

B. Metallic Coatings not from Fused Salt Baths

1. Chromium Cementation

There have been many methods devised for the purpose of chromizing steels and alloys of steels. Kelly(4) developed a method which consisted of packing a low carbon steel in intimate contact with powdered chromium in the presence of hydrogen gas and heating to temperatures between 1200 and 1400° C. A more practical method has since been developed in Germany by Daeves, Becker, Dusseldorf, and Steinberg(5-10), and in Russia by Izgaryshev and Sarkisov(11). This process consists of passing gaseous

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(4) Kelley, F. C. U.S. Patent 1365494. Jan. 11, 1921.

(5) Daeves, Becker, Dusseldorf, and Steinberg. U.S. Patent 2219004. October 22, 1940.

(6) Daeves, Becker, Dusseldorf, and Steinberg. U.S. Patent 2255482. Sept. 9, 1941.

(7) Becker, Dusseldorf, and Steinberg. U.S. Patent 2257668. 1941.

(8) Daeves, Becker, and Steinberg. French Patent 840975.

(9) Becker and Steinberg. British Patent 492521.

(10) Hertel and Becker. British Patent 440641.

(11) Izgaryshev, I. and Sarkinsov, E. Comp. rend. Acad. U.S.S.R. Vol. 18, 1938, pp. 437-440.

chromium chloride over the steel to be chromized at temperatures of 900 to 1000° C. or packing them in a porous ceramic carrier material that previously had been charged with chromium chloride to give a more uniform and adherent layer. Chromized layers up to 0.0004 in thick were obtained by this chromium chloride method. Lauenstein and Ulmer (12) packed iron castings in ferrochromium and common salt, and heated for approximately three hours at temperatures of 900 to 1000° C.

Many investigators have discovered the difficulty involved in chromizing high carbon content steels. Daeves (13) experienced difficulty in chromizing steels containing more than 0.10 percent carbon. Kelley (14-15) found that high carbon steels are difficult to chromize unless their surfaces are previously decarburized by heating in hydrogen. Kramer and Häfner (16) chromized steel by the chromium chloride method. They discovered that in order to

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(12) Lauenstein, C. and Ulmer, P. Process of Treating Metal U.S. Patent 20466380. July 7, 1936.

(13) Daeves, U.S. Patent 2255482. Sept. 9, 1941.

(14) Kelley, F. C. American Electrochemical Society. Trans. Vol. 43, 1923, p. 551.

(15) Kelley, F. C. U.S. Patent 1365499.

(16) Kramer, I. R. and Hafner, R. H. A.I.M.E. Trans. Vol. 154, Iron and Steel Division, 1943, pp. 415-422.

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chromize steels successfully the carbon must be combined with strong carbide forming elements which decrease the diffusion rate of carbon. If this carbon combination is not accomplished, the carbon will diffuse from the interior of the steel faster than the chromium can diffuse inward, thus forming a carbide layer which is almost impassable to more chromium atoms. Laissus(17) also discovered the deleterious effect of carbon in chromizing high carbon content steels with ferrochromium.

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(17) Laissus, J. Sur La Diffusion Intersolide Des Produits. Metallurgiques. Chimie et Industrie, French. Vol. 29, No. 3, 1933, pp. 515-526.

2. Manganese Cementation

Some investigations have been conducted for the purpose of determining the possibilities of cementing manganese on various metals. Kase(18) investigated the diffusion of pulverized commercial manganese into iron, nickel, and

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(18) Kase, Tsutomu. Metallic Cementation by Means of Manganese Powder. Kinzoku on Kenkyu. Vol. 12, Oct. 1935, pp 478-483.

copper at temperatures between 600° and 1000° C. for times between one and five hours using a pack method. He found that, in general, manganese diffusion increases appreciably with temperature above 600° C., while in the particular case of iron, manganese diffusion increases very rapidly above the A_3 temperature. The cemented coatings which were obtained were readily attacked by concentrated acids.

Lauenstein and Ulmer (19) packed iron castings in pulverized manganese metal and sodium chloride and then heated

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(19) Lauenstein, C. and Ulmer, P. U.S. Patent 2, 102, 539. Dec. 14, 1937.

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the constituents at a temperature of 950 to 1000° C. for three hours. They obtained a high manganese-iron alloy coating on the castings.

Laissus (20) obtained manganese diffusion coatings by packing steel specimens in ferro-manganese and heating to temperatures between 900° and 1050° C.

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(20) Laissus, J. op. cit., pp 515-526.

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3. Zirconium Cementation

Some research has been conducted to determine the possibilities of cementing zirconium on various metals. Schlechton, Kroll, and Carmody (21) passed zirconium chloride gas

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(21) Schlechten, A. W., Kroll, W. J. and Carmody, W. R. High Temperature Experiments with Zirconium and Zirconium Compounds. Bureau of Mines Report of Investigations 4915. U.S. Department of Interior. Nov. 1952, pp 16-17.

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over iron, copper, and nickel sheet at a temperature of 1000° C. Iron and nickel reacted with the zirconium chloride, but copper was not affected. The cemented layers were not very uniform and were readily attacked by dilute nitric acid. It was also found by these investigators that zirconium bromide gas reacted with iron more rapidly than the chloride.

Laissus (22) obtained zirconium diffusion coatings by packing steel specimens in ferro-zirconium and heating to a temperature of approximately 900° C.

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(22) Laissus, J. <u>op. cit.</u>, pp. 515-526.

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4. Uranium Cementation

Laissus (23) obtained uranium diffusion coatings by packing steel specimens in ferro-uranium and heating to temperature between 800° and 1100° C.

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(23) Laissus, J. <u>ibid.</u>, pp. 515-526.

Experimental Work

A. Apparatus and Equipment

1. Thermal Apparatus

The furnace used forthe experiments was a Hayes "Globar" Electric Furnace; Type A-3, 10 KW, 104 V., 9.0 amp., Single Phase. The furnace temperature was controlled by a Bristol Pyrometer Controller, Model 478. The crucibles used were glazed porcelain crucibles, size #2 (Coors).

2. Specimen Mounting Apparatus

The specimens were mounted in lucite plastic using a press.

3. Specimen Grinding and Polishing Apparatus

The specimens were initially ground on belt grinders and then were polished on "Microcloth" covered lapping wheels.

4. Metallographic Apparatus

The metallographic inspections were made on a Bausch and Lomb Metallograph which is illustrated in Figure 1.

B. Materials and Reagents

The lapping compound known as "Dymo" diamond compound, was obtained from the Elgin Watch Co., Elgin, Illinois, the grades were 8, 3, and 1µ.

The metals which were used are as follows:

1/32 in. dia. low carbon steel wire
1/32 in. diam. copper wire (electrolytic)

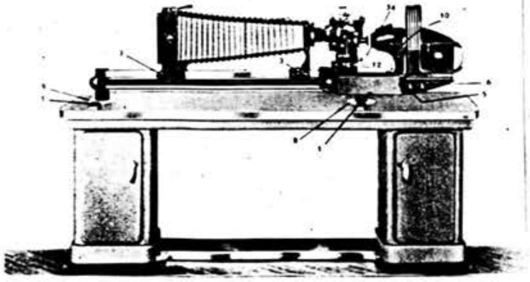

Figure 1

Bausch and Lomb Metallograph

5/8 in. diam. 0.18% plain carbon steel rod
5/8 in. diam. ingot iron rod (commercially pure)
1/16 in. X 3/4 in. diam. copper slugs
1/8 in. zirconium sheet (Kroll process)
1/4 in. diam. uranium rod
1/16 in. manganese sheet (electrolytic)
1/16 in. chromium sheet (electrolytic)

The salt used was chemically pure sodium chloride.

C. Experimental Procedure

1. Placement of Specimen Before Fusion of Salt Bath
    - a. An iron specimen to be coated was made by cutting a 3/16 in. slug from 5/8 in. dia. rod stock (ingot iron and 0.18 percent plain carbon steel); a copper penny was used as the copper specimen.
    - b. A plate approximately one inch square to supply the coating metal was cut from either the Mn, Cr, or Zr plate; a slug approximately 1/4 in. thick was cut from 3/8 in. diam. uranium rod stock.
    - c. The above pieces were wired together, with 1/32 in. diam. spacer wires separating them as shown in Figure 2.
    - d. A porcelain crucible was partially filled with sodium chloride; the above specimen was placed within the crucible with the plane of the coating metal plate and base metal slug parallel with the bottom of the crucible, and with the iron base metal slug (or copper penny) on the bottom; the crucible was then completely filled with salt, level with the top of the crucible.
    - e. The above filled crucible was then placed within the furnace which was at temperature (950° C. for iron base metal slug, 850° C for copper base metal penny); the time in the furnace (6 hours) was meas-

ured from the time of complete fusion of the salt bath.

f. The crucible was removed from the furnace at the end of the heating period and the molten salt poured off; subsequently, the crucible with the contained specimen was allowed to air cool.

2. Placement of Specimen After Fusion of Salt Bath

Everything was similar to procedure 1 except that instead of positioning the wired assemblage in the salt bath before the salt was fused, the assemblage was positioned in the salt bath after the salt was fused. A piece of iron wire was attached to the assemblage (on the back side of the coating metal plate) so it could be easily positioned in the fused salt filled crucibles while they were in the furnace.

D. Specimen Examination Procedure

1. The base metal slug was washed in hot water to remove the adhering solidified salt.

2. The slug was mounted in lucite with a piece of steel conduit tubing (pressed into an elliptical shape) surrounding the slug the purpose of which was to act as a bearing surface during polishing and grinding as shown in Figure 2.

3. The mounted slug was then sectioned diametrically with a hack saw as shown in Figure 4. This method of cutting was utilized so there would be a minimum impairment of the coating.

4. The sectionedslug was then initially ground on a belt

grinder, then it was ground on emery papers 0, 1-0, 2-0, 3-0, 4-0, respectively. The method of grinding and polishing with minimum edge rounding is shown in Figure 3.

5. The ground sectioned slug was then polished on lapping wheels with 8μ, 3μ, and 1μ diamond compound; the 1μ compound was not used in all cases since some edge rounding was obtained with this abrasive.

6. The slug was then etched with an appropriate etchant (5% Nital for iron; 30% NH_4OH, 70% of a 3% H_2O_2 solution for copper).

7. The slug was then examined with the metallograph.

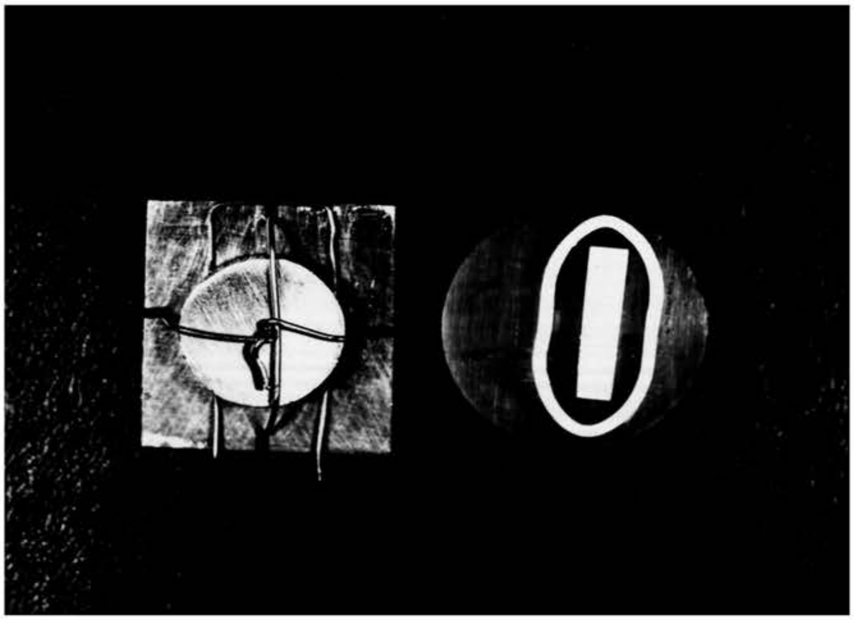

Figure 2

Salt Bath Specimen and

Specimen Mounting Arrangement

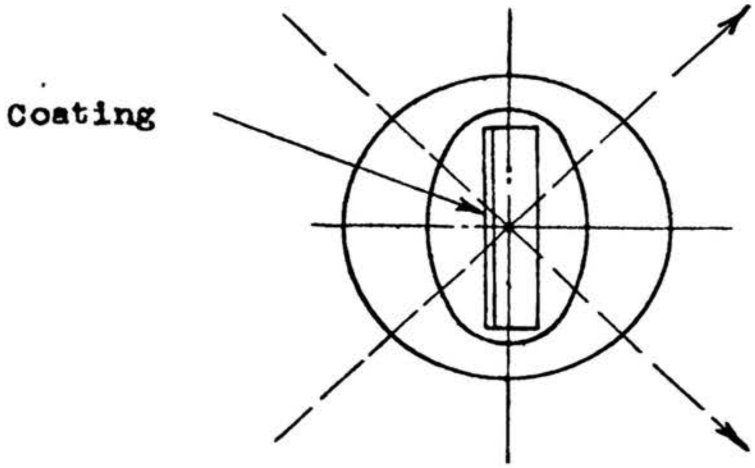

Figure 3 Direction of Movement of Specimen During Grinding and Polishing

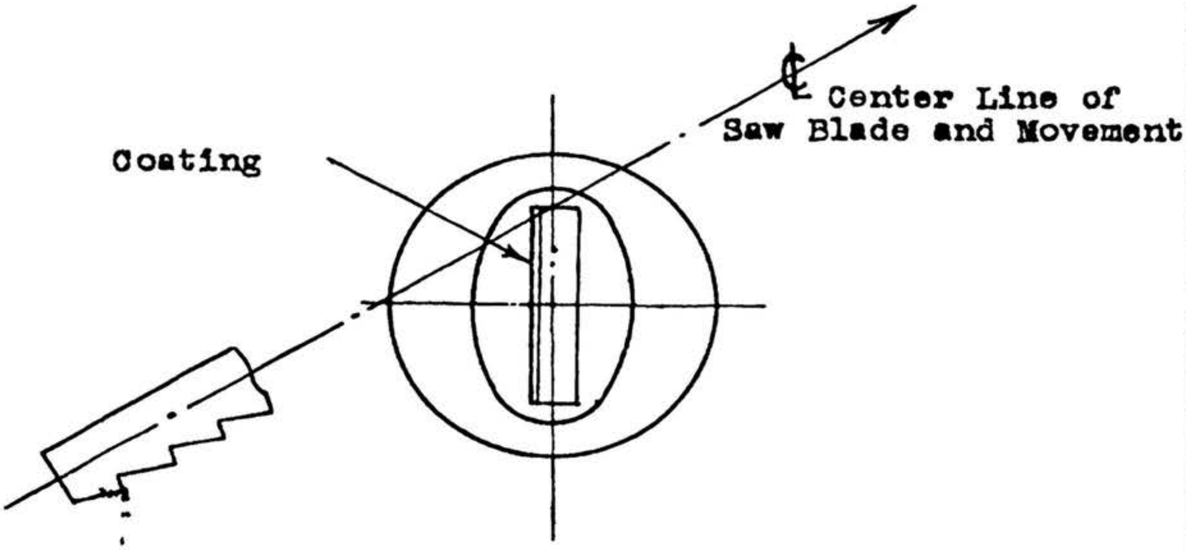

Figure 4 Direction of Saw Movement During Sectioning of Sample

D. Data

1. Chromium Diffusion Coatings

The diffusion coatings obtained on both ingot iron and steel by both procedures were rather uniform in thickness, as can be seen from Figures 5, 7, 8, 13 and 14. The coating obtained by procedure 2 (Figures 13 and 14) was a very good uniform coating which yielded a good luster when buffed with a fine wire brush.

2. Manganese Diffusion Coatings

The diffusion coatings obtained on both ingot iron and steel by procedure 1 were fairly uniform. The coating obtained on ingot iron by procedure 2 was quite thick; however, small cracks perpendicular to the surface were observed, as can be seen from Figures 15 and 16.

3. Uranium Diffusion Coatings

The diffusion coatings obtained on both ingot iron and steel by procedure 1 (Figures 6, 9, and 10) were fairly uniform; however, the ingot iron slug was slightly deformed around the periphery manifesting possible liquid formation. The coating obtained on ingot iron by procedure 2 was very uneven and the iron slug was badly deformed.

4. Zirconium Diffusion Coatings

The diffusion coating obtained on steel by procedure 1 was not uniform and, in general, very poor, The coating obtained on ingot iron by procedure 1 was fairly uniform as can be seen from Figures 11 and 12. The diffusion coating obtained on ingot iron by procedure 2 (Figures 17 and 18) was uniform and, in general, good.

The coating obtained on copper by procedure 2 was very uniform as can be seen from Figure 19; furthermore, half of the slug which was not used for metallographic examination was bent into a U-shape without rupturing the coating. There was no coating of zirconium obtained on the copper slug by procedure 1; furthermore, the copper slug was very badly corroded.

A hard crust (approximately 1/32" thick) apparently composed of solidified salt with dispersed metallic particles enveloped the iron slugs in the experiments dealing with chromium, manganese, and zirconium coatings on ingot iron by procedure 2.

The results of the above described diffusion coatings are summarized in Table 1.

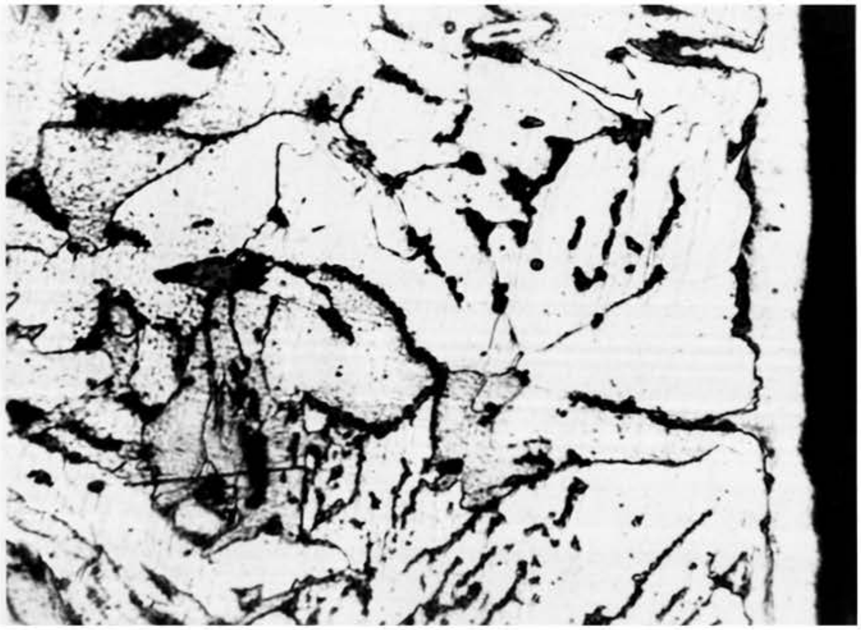

Figure 5

Chromium Diffusion Coating on Steel

Procedure I

5% Nital Etch

Magnification: 500X

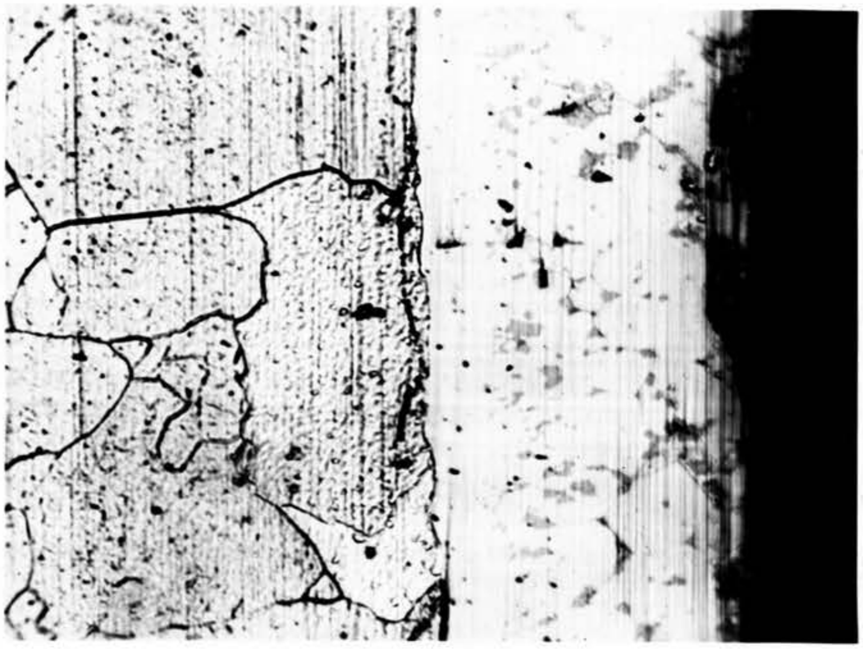

Figure 6

Uranium Diffusion Coating on Steel

Procedure 1

5% Nital Etch

Magnification: 500X

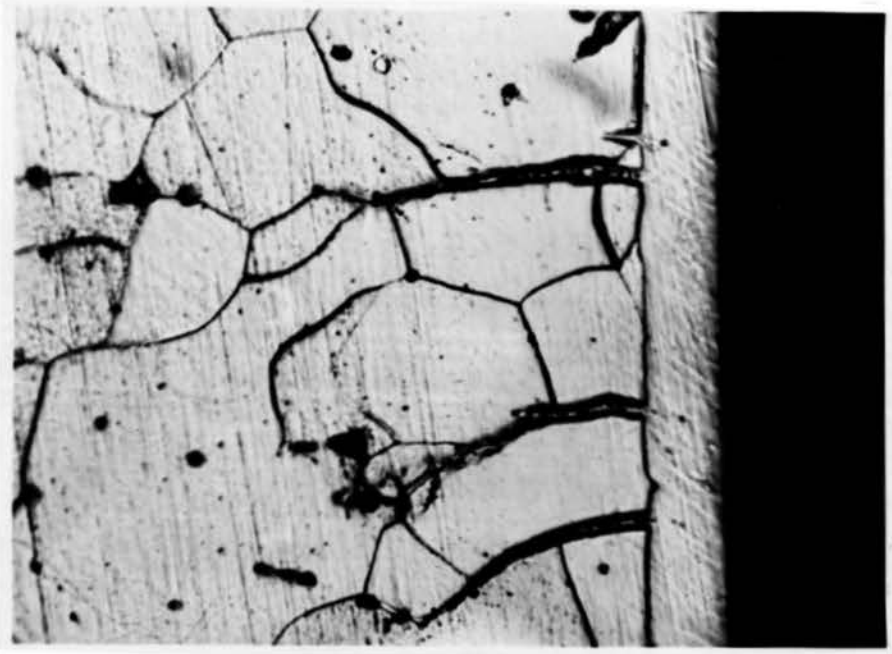

Figure 7

Chromium Diffusion Coating on Iron

Procedure 1

5% Nital Etch

Magnification: 500X

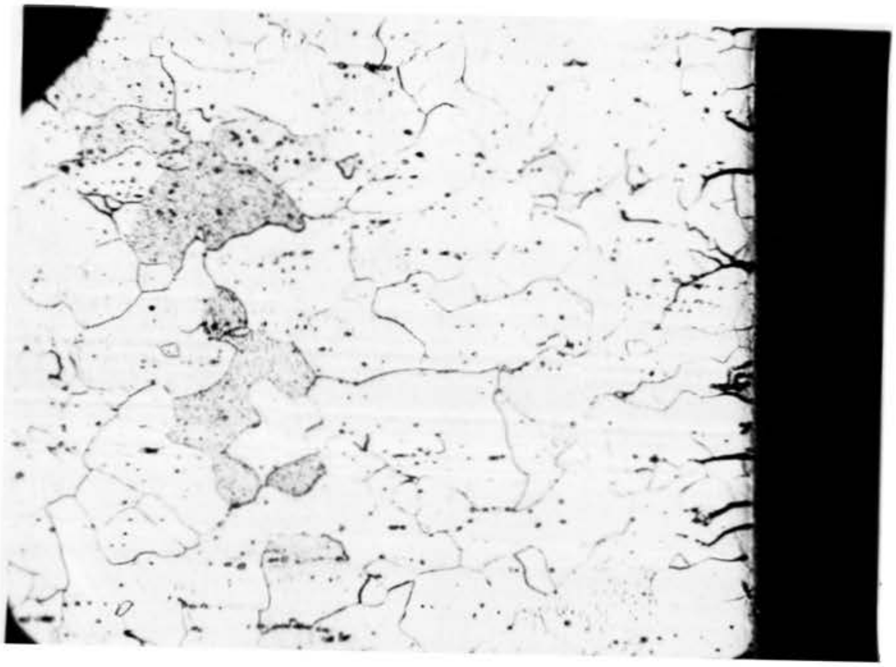

Figure 8

Chromium Diffusion Coating on Iron

Procedure 1

5% Nital Etch

Magnification: 100 X

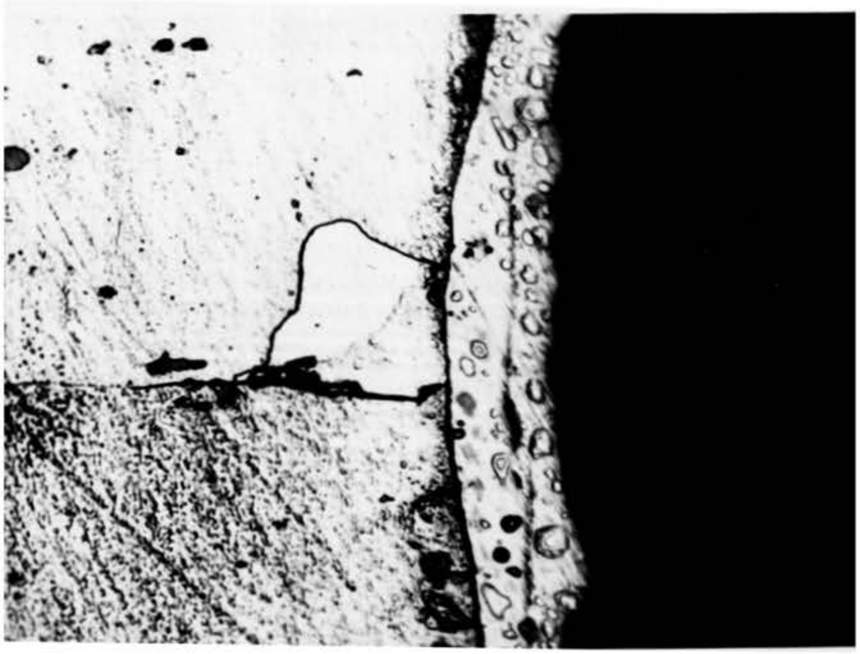

Figure 9

Uranium Diffusion Coating on Iron

Procedure 1

5% Nital Etch

Magnification: 500 X

Figure 10

Uranium Diffusion Coating on Iron

Procedure 1

5% Nital Etch

Magnification: 100 X

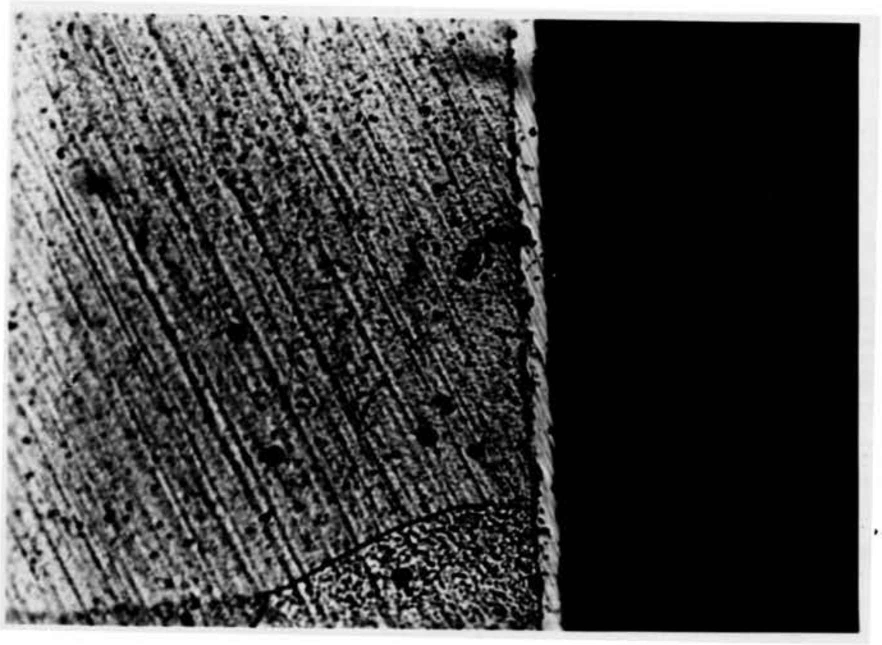

Figure 11

Zirconium Diffusion Coating on Iron

Procedure 1

5% Nital Etch

Magnification: 500 X

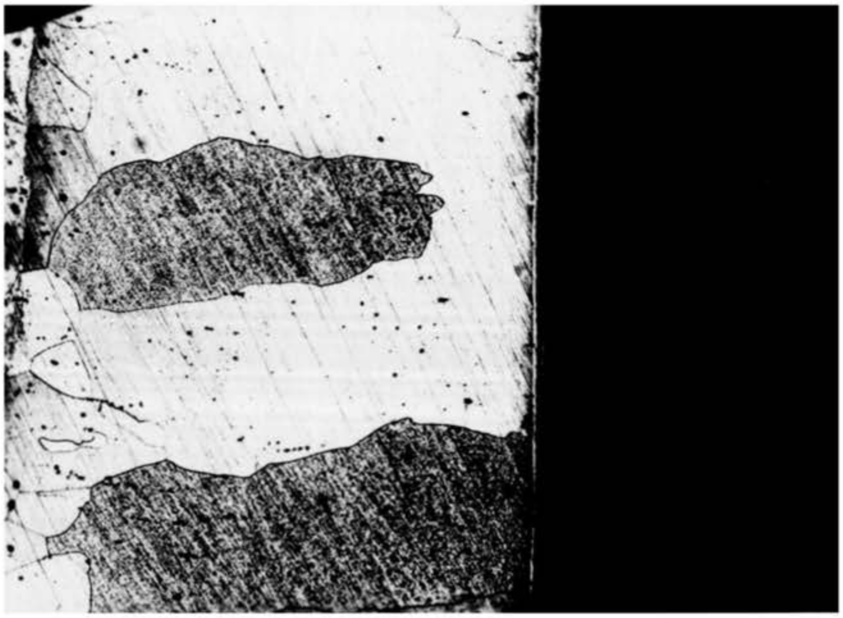

Figure 12

Zirconium Diffusion Coating on Iron

Procedure 1

5% Nital Etch

Magnification: 100 X

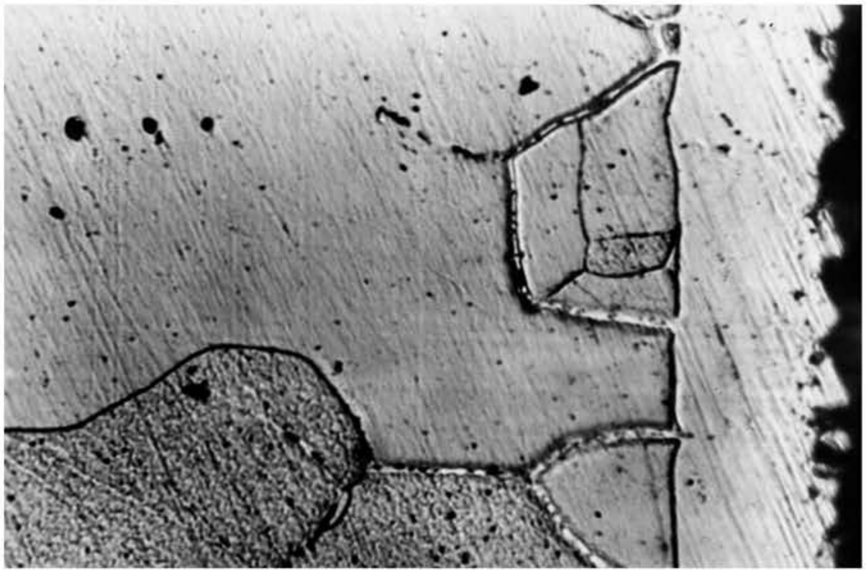

Figure 13

Chromium Diffusion Coating on Iron

Procedure 2

5% Nital Etch

Magnification: 500 X

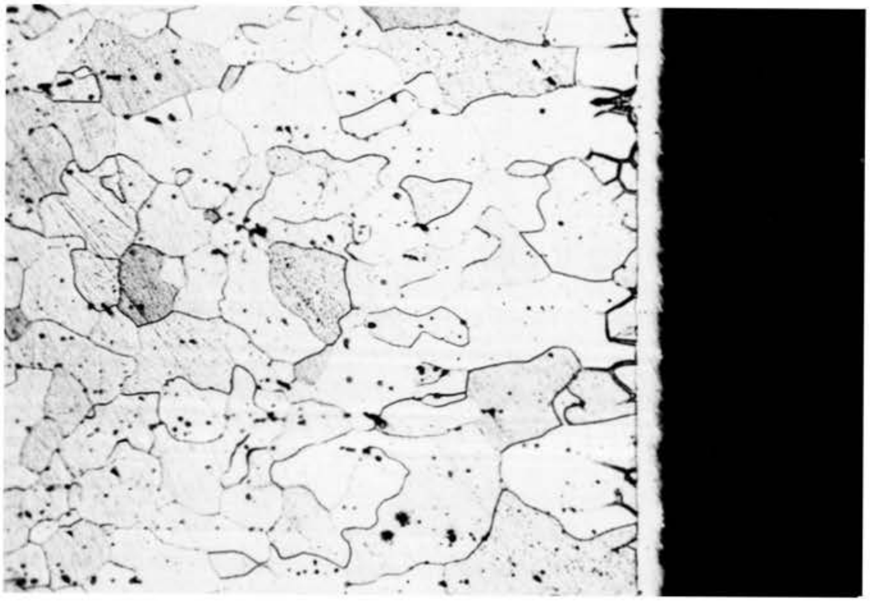

Figure 14

Chromium Diffusion Coating on Iron

Procedure 2

5% Nital Etch

Magnification: 100 X

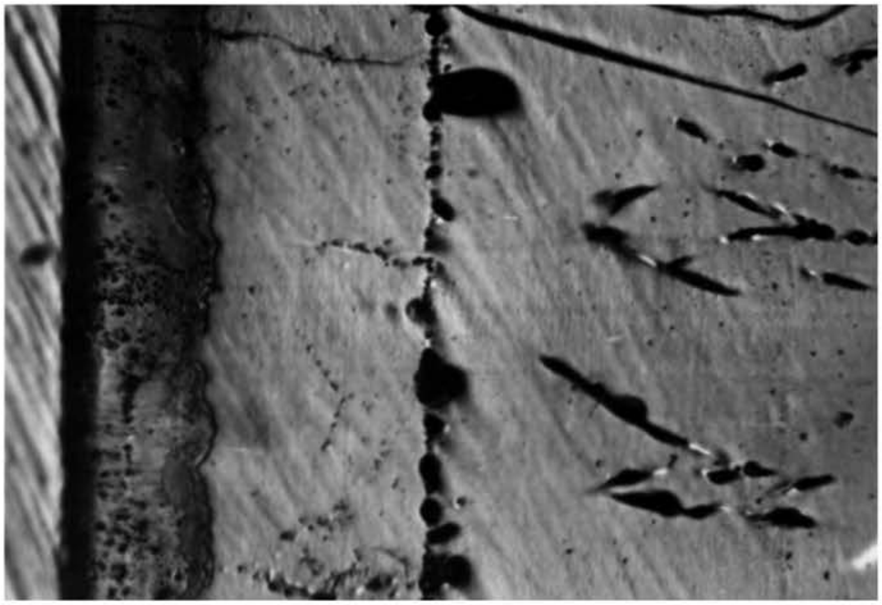

Figure 15

Manganese Diffusion Coating on Iron

Procedure 2

5% Nital Etch

Magnification: 500 X

Figure 16

Manganese Diffusion Coating on Iron

Procedure 2

5% Nital Etch

Magnification: 100 X

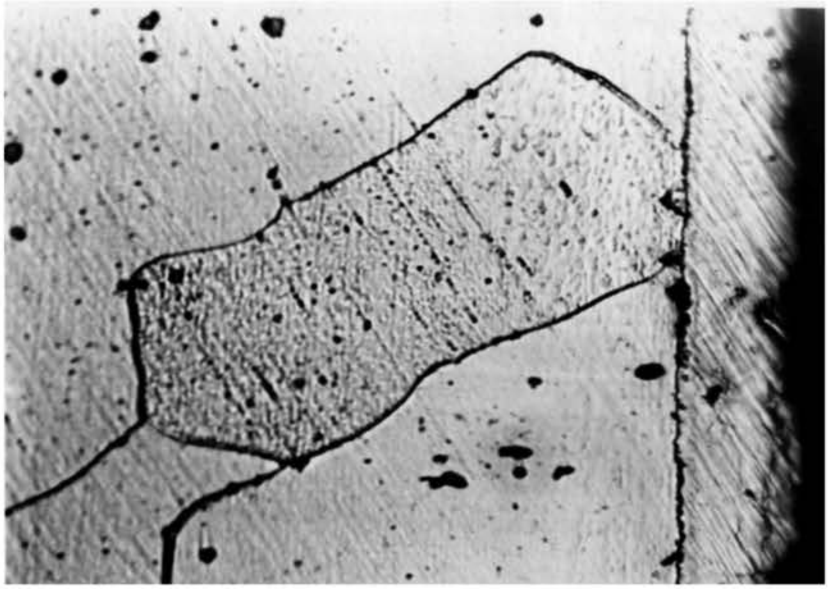

Figure 17

Zirconium Diffusion Coating on Iron

Procedure 2

5% Nital Etch

Magnification: 500 X

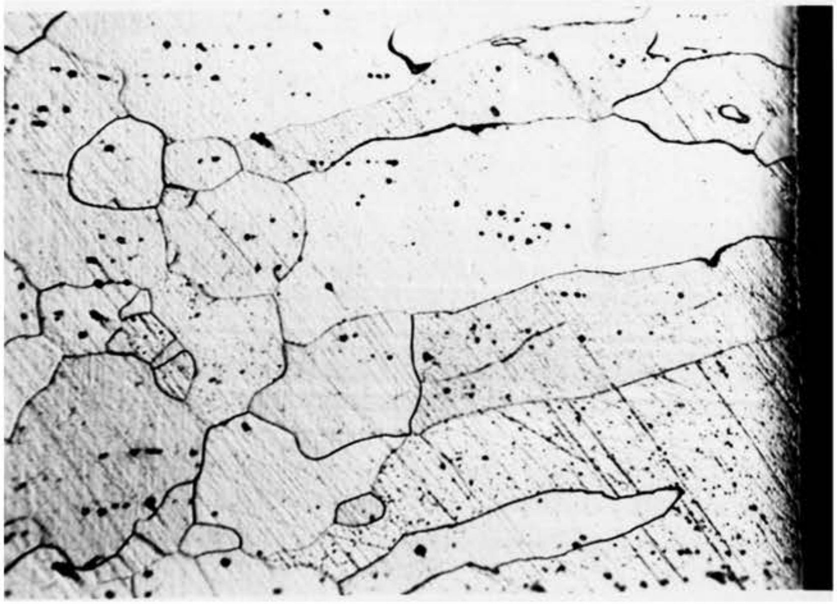

Figure 18

Zirconium Diffusion Coating on Iron

Procedure 2

5% Nital Etch

Magnification 100 X

Figure 19

Zirconium Diffusion Coating on Copper

Procedure 2

30% NH_4OH, 70% of 3% H_2O_2 Solution Etch

Magnification: 500 X

DISCUSSION

A. Theory

1. General

The deposition of metallic coatings from fused salt baths probably involves two processes: (a) a replacement process, wherein the coating metal ions are reduced and replace the base metal atoms which are oxidized and (b) a deposition of "pyrosol" particles on the base metal from the fused salt bath. The first process would involve the dissolution of the coating metal as a metal chloride; and when this coating metal chloride concentration becomes appreciable in the area immediately adjacent to the base metal surface, the coating metal chloride will react with the surface metal forming a coating metal-base metal alloy and a chloride of the base metal. This latter reaction will be a function of the activity of the metals and metal chlorides involved. The second process would involve the dispersion of the coating metal as colloidal particles (pyrosol) and the subsequent migration or movement to the base metal surface where they deposit. The deposition probably being a function of the collision probability and the electrokinetic properties of the pyrosol formed.

The thickness of the diffusion layer thus obtained by the deposition of the coating metal will be dependent upon two processes: (a) the rate of diffusion of the coating metal atoms into the base metal lattice, and (b) the rate of deposition of the coating metal from the salt bath immediately adjacent to the surface of the diffusion layer.

In binary systems, when diffusion occurs at a substantially constant temperature and pressure, the layers formed correspond, in kind and in order of their occurrence, to the single phase regions in the phase diagram at the temperature and pressure of diffusion; no two phase layers appear. In general, the layers formed by the isothermal and isobaric diffusion of metals across an interface correspond in kind and in 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 (two or more degrees of freedom in the conventional temperature - concentration section where pressure is disregarded).(24)

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(24) Rhines, N. F. Surface Treatment of Metals. A. S. M. 1941. Edward Brothers Inc. pp. 123 - 124.

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2. Chromium Diffusion Coatings

The interpretation of a diffusion coating formed by the diffusion of chromium into an iron surface at 950 C. can be approximated from the iron-chromium equilibrium phase diagram (Figure 20).(25) As the chromium deposits on the surface of the

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(25) Metals Handbook. American Society for Metals. 1948 Ed., p. 1194.

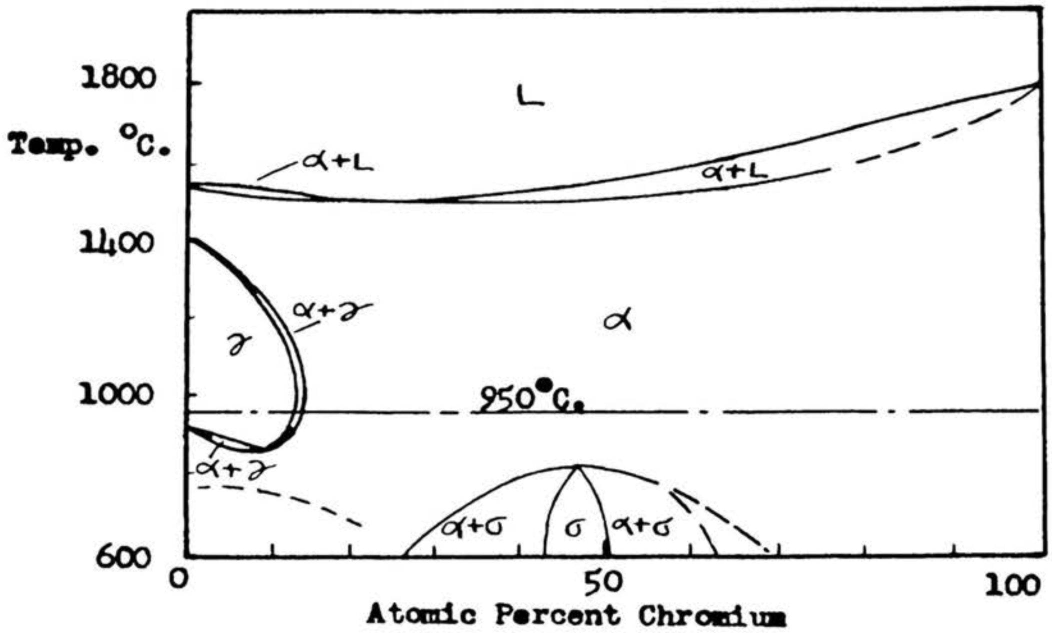

Figure 20 Iron- Chromium Equilibrium Diagram

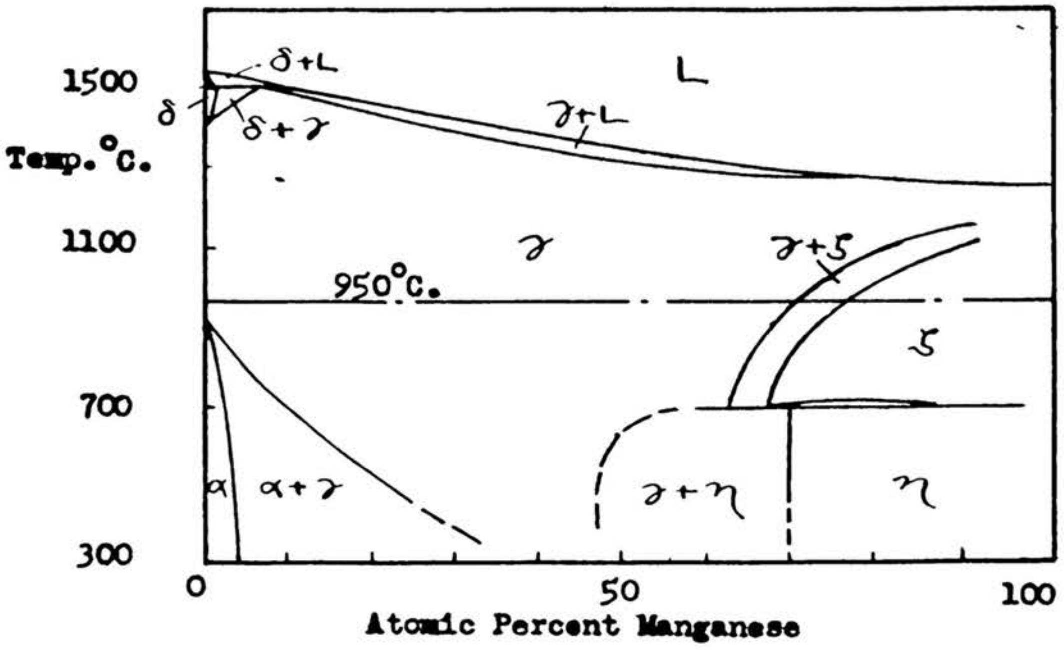

Figure 21 Iron- Manganese Equilibrium Diagram

iron the chromium will diffuse into the γ iron and form a γ phase. The diffusion layer thus formed will consist of the γ phase until the composition of the original interface reaches approximately 12 atomic percent, chromium. Then α phase will commence to form with a concentration jump between the γ and α phases. (12 to 13 atomic percent chromium). As further deposition and diffusion occur the thickness and chromium content of the α phase layer will increase.

The diffusion layer at this stage of the diffusion process will probably consist of a layer of chromium rich γ-iron or γ phase, and a layer of α phase. If the specimen is cooled to room temperature, the diffusion layer will probably consist of a layer of α phase on α-iron, a region of $\alpha+\sigma$ on σ, a thin layer of σ, a region of $\alpha+\sigma$ on, σ and a layer of α phase on the $\alpha+\sigma$ region.

3. Manganese Diffusion Coatings

The interpretation of a diffusion coating formed by the diffusion of manganese into an iron surface at 950 C. can be approximated from the iron-manganese equilibrium phase diagram (Figure 21).(26) When the manganese diffuses into the iron at a temperature of 950 C., the manganese will go into solid solution with the γ-iron to form the γ phase. As

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(26) Metals Handbook. <u>op. cit.</u>, p. 1210

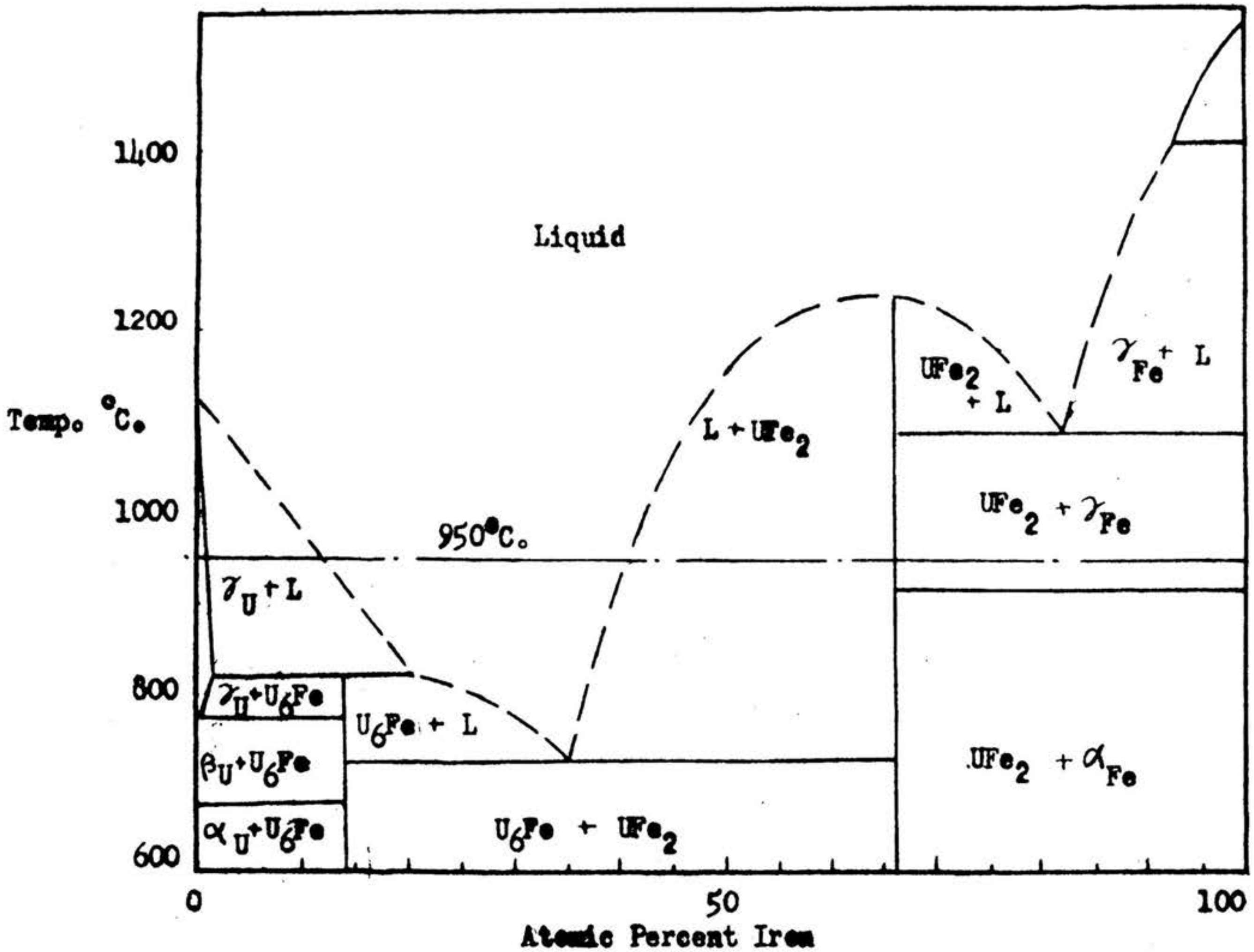

Figure 22 Uranium - Iron Equilibrium Diagram

the manganese continues to deposit on the surface of the iron, the manganese content of the original interface will continue to increase, but the total diffusion layer will remain as the γ phase until the composition of the outer layer reaches approximately 69 atomic percent manganese. Then the ξ phase will commence to form in the outer layer with a concentration jump between the γ and ξ phases (69 to 76 atomic percent manganese). As more diffusion of manganese occurs the thickness and manganese content of this ξ phase layer will increase.

The diffusion layer at this stage of the diffusion proces will probably consist of a layer of γ phase, and a layer of ξ phase. If the specimen is cooled to room temperature, the total diffusion layer will probably consist of a region of $\alpha+\gamma$ on the α phase, a layer of γ phase on the $\alpha+\gamma$ region, a layer of $\gamma+\eta$ on the γ phase, and a layer of η on the region $\gamma+\eta$.

4. Uranium Diffusion Coatings

The interpretation of a diffusion coating formed by the diffusion of uranium into an iron surface at 950° C. can be approximated from the iron - uranium equilibrium phase diagram (Figure 22).(27) As the uranium deposits on the surface the iron will commence to diffuse into it. The uranium will

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(27) Gordon, P. and Kaufmann, Uranium - Aluminum and Uranium Iron. Transactions A. I. M. E. Vol. 188, 1950. p. 189

not diffuse into the iron to any appreciable extent initially since there is no single phase solid solution formed. When the composition of the iron in the uranium reaches a certain value (approximately 1 atomic percent) a liquid phase will commence to form, into which the iron will diffuse more rapidly than it did into the γ_U. This liquid will then probably spread over the surface of the specimen, dissolving the γ_U and deposited uranium at the expense of the iron.

At room temperature the coating will probably consist of a layer of $U_6Fe + UFe_2$,

5. Zirconium Diffusion Coatings

The interpretation of a diffusion coating formed by the diffusion of zirconium into an iron surface at 950° C. can be approximated from the iron - zirconium equilibrium phase diagram (Figure 24).(28) As zirconium deposits on the γ-iron surface it will diffuse into the iron to form the γ phase solid solution. When the composition of the original interface reaches approximately one atomic percent zirconium, the θ phase will commence to form with a large concentration jump between the γ and θ phases (1 to 84 atomic percent zirconium). As further deposition and diffusion occur the θ phase layer will increase in thickness composition of the θ phase reaches approximately 88 atomic percent zirconium,

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(28) Metals Handbook. *op. cit.*, p. 1221.

at which concentration there will be a concentration jump up to 95 atomic percent zirconium and the η phase will commence to form. As further deposition and diffusion occur the phase η will increase in zirconium content and thickness.

If the specimen is cooled to room temperature the total diffusion layer will probably consist of an α phase on α iron, a region of $\alpha + \epsilon$, a thin layer of ϵ, a region $\theta + \epsilon$, and a layer of θ phase.

The interpretation of a diffusion coating formed by the diffusion of zirconium into copper at 850° C. cannot be done completely from the copper - zirconium equilibrium phase diagram since it is only partially established (Figure 23).(29)

As zirconium deposits and diffuses into the copper an α phase will be formed. The phenomena which occur after this formation cannot be prognosticated.

If the specimen is cooled to room temperature, the first two layers on the copper should be α and $\alpha + \beta$.

B. Interpretation of Data

From a comparison of the results tabulated in Table 1 for the coating thicknesses obtained on ingot iron by the two different procedures, one can observe that the coatings obtained by procedure 1 were in general thinner and of poorer quality than the coatings obtained by procedure 2. This difference can

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(29) Metals Handbook. *op. cit.*, p. 1207.

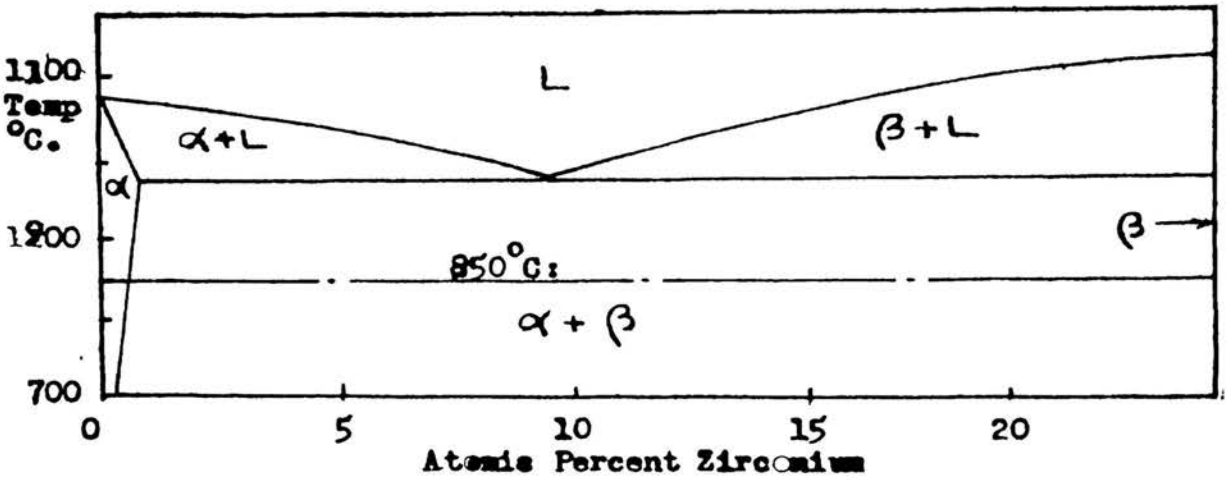

Figure 23 Copper- Zirconium Equilibrium Diagram

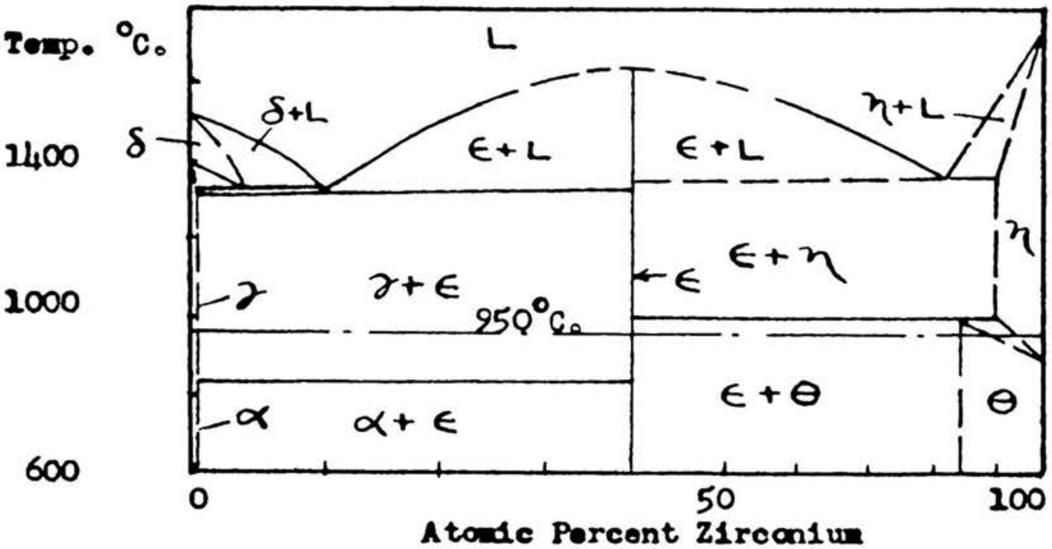

Figure 24 Iron- Zirconium Equilibrium Diagram

probably be explained by the fact that in procedure 1 more oxidation of the coating metals occurred, since they were exposed to the furnace atmosphere at 950°C. until the salt fused. This oxidation probably caused an oxide layer to form on the surface of the coating metals (and base metals) and thus impeded their dissolution and dispersion into the salt bath when fused. Consequently, less metal was supplied to the iron surface, with a corresponding decreased coating thickness.

From a comparison of the results tabulated in Table 1 for the coating thicknesses obtained on steel and ingot iron by procedure 1, one can observe that the coatings were thicker (except for uranium) on ingot iron than on steel. This phenomenon might be explained by the fact that since the coating metals used are strong carbide formers, the carbon in the steel matrix probably diffused to the diffusion layer and impeded the diffusion process.(30) This phenomenon is substantiated by inspection of Figure 5.

In the case of uranium the interpretation of the diffusion coating is complicated since, as can be seen from Figure 22, a liquid phase forms upon diffusion. The explanation for the thicker coating of uranium obtained on the steel than the ingot iron by procedure 1 can probably be made on the basis that

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(30) Kramer and Hafner. op. cit., p. 416.

Procedure	Base Metal	Approximate Coating Thickness (in.)			
		Cr.	Mn.	U.	Zr.
1.	0.18% C. Steel	0.00050	0.0004	0.002	0.0001
	Ingot Iron	0.00075	0.0007	0.001	0.00025
	Copper				Copper Badly Corroded -None-
2.	Ingot Iron	0.00150	0.0070	Liquid Formation Distortion	0.0010
	Copper				0.0020

TABLE 1

SUMMARIZATION of COATING THICKNESSES

the carbon in the steel impeded the diffusion of uranium into the iron, since uranium is a strong carbide former.(31) Consequently, the composition of the coating probably was such that not very much liquid formed (see Figure 22) and the liquid solution remained in situ. Whereas, in the case of ingot iron, the diffusion was rapid enough to allow enough liquid to form so that the liquid solution flowed over the edge of the periphery of the iron slug, thus decreasing the thickness of the layer on top. So much liquid was formed by procedure 2 (reaction with spacer wire and slug) that the iron slug was badly deformed.

The definite layers manifested by the manganese in Figure 15 where there is a distinct line of demarcation followed by a dark region followed by a region terminated by what appears to be a line of etch pits, which in turn is followed by the outer layer can be explained by the phase diagram interpretation. The inner dark region to the left of the definite line of demarcation is probably $\alpha + \gamma$, followed by a region of γ, followed by an outer region of $\gamma + \eta$. The region to the left of the definite line of demarcation is probably α. The cracks in the coating are probably due to the rapid air cooling following the removal of the specimen from the furnace.

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(31) Bullens, D. K. Steel and Its Heat Greatment. Vol II. John Wiley and Sons, Ltd., 1939. p. 458.

When the diffusion process results in the formation of a new phase, this layer is usually composed of columnar crystals with their long axis lying parallel to the direction of growth.(32) This phenomenon was manifested in most of the diffusion coatings investigated (Figures 8, 10, 12, 14, 16 and 18).

Preferential diffusion along grain boundries and in certain crystallographic directions usually occurs when the temperatures of melting and diffusion are widely separated.(33)

This phenomenon was most pronounced in the diffusion of chromium into iron (Figures 5, 7, 8, 13 and 14), but was not quite so evident in the case of the diffusion of zirconium into iron (Figure 17).

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(32) Rhines, F. N. op. cit., p. 134.

(33) Rhines, F. N. ibid., p. 134.

C. Errors

The main errors that were encountered in the experimental work of this investigation were: (a) the temperature of the furnace was cortrolled within 20° C. limits; a temperature control within 5($^{\circ}$ C. limits would be much more desirable from the point of predicting the composition of the diffusion coatings from the phase diagrams, and (b) the moisture variation of the atmosphere was not taken into account.

D. Suggested Further Study

The main aspects of this study which should be investigated are: (a) the corrosion resistance of the diffusion coatings, (b) the mechanical properties of the diffusion coatings, (c) the chemical composition of the diffusion coatings (X-Ray study), (d) the variation of the thickness of the diffusion coatings with time and temperature, to obtain diffusion coefficients, (e) the effect of different bath compositions, (f) the measurement, if possible, of the size of the coating m metal particles dispersed in the salt bath, (g) the investigation of the electrokinetic properties of the pyrosols, (h) the effect of varying the distance between the coating metal plate and the base metal, (i) the effect of an inert atmosphere during the diffusion process, (j) the development of etchants to selectively etch the diffusion coatings obtained so the various phases can be identified and correlated with the equilibrium phases of the phase diagram, and (k) the effect of alloying elements in the base metal on the rate of diffusion.

CONCLUSIONS

The process of forming diffusion coatings of chromium on other metals, known commercially as "chromizing" has proved to be quite useful for the protection of low carbon and alloy steel objects. It was found in this investigation that zirconium and manganese diffusion coatings can be produced in a comparable manner. Diffusion coatings of these metals could possibly also be quite useful for varied commercial applications, especially zirconium coatings since it is impossible to electrodeposit this metal from aqueous solutions and very difficult to deposit it from fused salts by electrolytic methods. Zirconium is of special interest since it possesses the property of very good corrosion resistance to most corrosive media. Uranium diffusion coatings, however, do not appear to be too promising because of the liquid solution formation at elevated temperatures.

An interpretation of the composition of diffusion coatings of chromium, manganese, zirconium, and uranium on iron or low carbon steels can be approximated from a consideration of the respective equilibrium phase diagrams. The number of phase present at the temperature of diffusion will be governed by the phase rule. Thus, for a binary system at isothermal and isobaric conditions, there can be no two phase regions present; consequently, there is necessarily a composition jump between the single phase solid solution layers formed.

It appears from the results of this investigation that diffusion coatings of strong carbide forming elements such as chromium, manganese, and zirconium on high carbon steel will be limited in thickness because of the carbide layer formation in the zone of diffusion (Figure 5); however, low carbon steels, steels in which the carbon has been stabilized, or steels which have been surface decarburized can be successfully treated.to obtain a relatively thick coating.

The high temperature requirement for the formation of diffusion coatings is not necessarily a deleterious aspect. When one considers the facility and uniformity of formation of these coatings, coupled with the fact that many metals such as zirconium cannot be electro-deposited successfully, the usefulness and applicability of diffusion coatings can be greatly appreciated.

SUMMARY

The deposition of metal for the formation of chromium, manganese, uranium and zirconium diffusion coatings from fused chloride salt baths is probably accomplished by two different processes: (a) a replacement process, and (b) a pyrosol deposition process. The thickness and composition of these coatings are apparently dependent upon the rate of diffusion of the coating metal into the base metal lattice, and the rate of deposition of the coating metal from the fused salt bath.

The formation of diffusion coatings on metals is not an equilibrium process; however, the composition of these coatings can be approximated from the respective equilibrium phase diagrams, with consideration of the phase rule.

The diffusion coatings of chromium, manganese, uranium, and zirconium on iron, and zirconium on copper in this investigation were produced by two different procedures. The first procedure was to take an ingot iron, low carbon steel, or copper slug and wire a small square plate of the coating metal to it with two parallel spacer wires between them (arrangement shown in figure 2). The assemblage was then placed in a small porcelain crucible and packed in pure sodium chloride. The crucible was then placed in a furnace and the salt fused. The second procedure was similar except that instead of packing the assemblage in the salt before it was fused, the salt was first fused in the crucible and then the assemblage was immersed in in the molten bath.

The diffusion coatings formed on ingot iron by procedure 1 were in general much thinner than those produced by procedure 2, probably due to an oxide formation on the metals which impeded the dissolution and dispersion of the coating metal in the bath when it was fused.

The diffusion coatings formed on the low carbon steel by procedure 1 were not uniform in thickness and, in general, very poor. The poor quality of these coatings is probably due to the formation of carbide layers in the diffusion zone which thus impeded diffusion.

The thicknesses of the diffusion coatings obtained on ingot iron by chromium, manganese and zirconium by procedure 2 are 0.0015", 0.0070", and 0.0010", respectively. The ingot iron slug which was coated by uranium was badly distorted as a result of a liquid solution formation at the temperature of diffusion.

The diffusion coating of zirconium on ingot iron withstood attack by 30 percent nitric acid for a testing period of 24 hours. The zirconium coating on copper by procedure 2 was approximately 0.002" thick; furthermore, it possessed rather good physical properties.

The diffusion coatings obtained on the ingot iron and copper slugs in this investigation seem to indicate the possible commercial application of diffusion coatings from fused halide salt baths by immersion. This fact has already been proven in the case of chromium, and is espe ially interesting in the case of zirconium since it is seemingly not possible to deposit zirconium by electrolytic methods from aqueous solutions.

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VITA

Andrew Hessler Larson was born in Peru, Illinois on September 14, 1931. After receiving his secondary education in LaSalle, Illinois, he attended LaSalle-Perú-Oglesby Junior College in LaSalle from September, 1949 to June, 1951. During the summer of 1951, he attended the Illinois Institute of Technology in Chicago. In September, 1951 he entered the Missouri School of Mines and Metallurgy and received the Bachelor of Science degree in Metallurgical Engineering in August 1953. During the summer of 1953, he attended the Colorado School of Mines. In September 1953, he was appointed a Research Fellowship in Metallurgical Engineering for a period of one school year.