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Michael R. Writt

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A STUDY OF THE DIFFUSION OF ELECTROPLATED COATINGS IN THE SOLID STATE

by

Michael R. Writt

A Thesis Submitted to the Department of Metallurgy in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science in Metallurgical Engineering

Montana School of Mines
Butte, Montana
May, 1948
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INTRODUCTION

Definition. The term diffusion means an equalization or homogenization of diverse materials. Specifically applied to metals, diffusion is the interchange of atoms. It is, in effect, an invasion of one crystal lattice by the atoms of one or more other crystal lattices. Therefore, the study of diffusion must involve the geometry and physics of crystal lattices as well as their energies.

Until very recently the study of crystal structure had been reserved for the physicists. It is now a problem for the metallurgist.

Early History of Diffusion. The earliest scientific record of the production of an alloy by the union of solid metals is of work credited to Faraday and Stodart in 1820. They successfully formed a solid solution of platinum and iron by welding the two metals together at a temperature below the melting point of iron.

The earliest systematic investigation of diffusion in solid metals was carried out by Spring in 1882. His work consisted of forming solid solutions from mixtures of powdered metals at a high pressure. The pressure was used to insure intimate contact between the particles, and the temperature used was kept below the melting point of either constituent.
The first quantitative investigation on the mutual penetration of metals in the solid state was reported by Roberts-Austen in 1896. These results were derived from work on the interpenetration of gold and lead. His work showed that gold and lead would form a solid solution at room temperature. This was the first attempt to quantify the rate of diffusion. At the time, his results were unbelievable, but were later proved to be very accurate.

In 1909, Masing proved that two metals will unite to form a solid solution at a temperature below the melting point of either.

The Problem. The purpose of this study was to determine and to explain the changes in microstructure due to diffusion. These changes in the microstructure were correlated with the physical properties of alloys of the same composition but formed under different conditions. The original intention was to compare the physical properties of the alloy layers formed by diffusion with the known physical properties of like alloys. The materials used for comparison were galvanized sheet and tin plate. Any advantages or disadvantages of diffused layers to be arrived at have to be evaluated on the basis of comparison and are, therefore, relative.

The actual problem was to electroplate samples of
low carbon steel with coatings of Cd, Sn, or Zn. The samples were diffused at various temperatures and times, then mounted and polished. The diffusion temperature used in all cases was kept below the melting point of the particular metal coat. These polished specimens were studied closely to determine the microstructure as well as the rate of diffusion.

Discussion of the Problem. Any study of the problem of diffusion coatings must include a complete review of the present state of the problem. This review must, of necessity, come from the volumes of published literature on the subject.

The study of diffusion coatings is justified because of the single fact that all previous investigators freely admit that the problem is unsolved. Experimental data is far too inadequate at the present time to allow these investigators to draw any general conclusions on the subject. The definite state of practical information that is available has been summarized by F. N. Rhines.¹

This summary includes;

a. A list of the systems that have been studied
b. Whether or not diffusion was successful

¹ All superscripts in this paper refer to the bibliography at the end of the report.
c. The procedure used, and  
d. In some cases, observations, with regard to the structures formed and their rates of formation.

The present state of the scientific knowledge of diffusion has been pointed out by R. F. Mehl.²

His summation follows:

a. The theory of atomic mechanism is fairly well understood. The old theory of atom interchange is being replaced with the new 'hole' theory of diffusion.

b. The valuation of 'D' (diffusion coefficient) is inadequate and unsound. It is based on the very few systems that have been studied. However, it has been concluded that 'D' is greater the farther apart the solute and solvent are in the periodic chart. That is, the greater the chemical affinity between solute and solvent the greater 'D' will be.

c. The effect of concentration is known. The problem of why the concentration gradient affects 'D' as it does is not clearly understood.

d. Information on the effect of grain size on 'D' is not at all understood. In some cases 'D' varies directly as grain size and in some cases it varies inversely as grain size.
e. The significance of isotropic diffusion as compared to anisotropic diffusion is an unanswered problem. The same is true for intergranular and intra-granular diffusion.

f. The question of what determines whether a metal such as zinc will diffuse into iron or whether the iron diffuses into the zinc is unanswered.

g. The effect of adding a third element to any diffusion system is unknown due to the lack of work along these lines.

Previous Investigations. All the work that has been done on the many phases of diffusion cannot possibly be reviewed here. This work has already been briefly summarized. A few specific cases will be studied to elucidate some of the points in question.

The Fe-Sn diffusion system was studied closely by Bannister and Jones. Their work was conducted above the melting point of tin. However, some interesting points were brought out by this investigation. First of all, in their review of previous work, it was pointed out that only body-centered cubic metals would diffuse into iron. This was disproved by these investigators in that tin is body-centered tetragonal. This fact will be developed in subsequent reviews. Their main work was concerned with the so-called
diffusion line. This line will exist whenever diffusion takes place regardless of diffusion temperature. This line is shown in the reproduced photomicrographs shown below. (Reproduced from the paper written by Bannister and Jones).

Plate I, figure 4 shows the structure resulting from heat treatment at 800°C for 3 hours. At the left is shown the unaffected iron base. To the right of the compound Fe3Sn2 is shown the tin core. The light crystals in the tin core were unexplained.

Plate II, figure 5 is a similar sample heated to 1000°C for 24 hours. This shown the diffusion line at the termination of the columnar crystals growing in from the Sn layer on the left. These columnar crystals are a solid solution of tin in iron.
Plate III. Diffusion of tin plate into iron. Reproduced, 175X.

Plate III, figure 6. Sample was heated to 1150°C for 5 hours. This shows the diffusion line at the ferrite end of the columnar crystals. The upper part shows a dendritic structure of FeSn₂ and Sn in solid solution.

These investigators further concluded that only that amount of metal can diffuse inwardly which is in immediate contact with the iron sample.

The Fe-Zn system was studied by Rigg⁴. His work agrees with the previously mentioned idea that only B.C.C. and the B.C.T. metals will diffuse into Fe, since the Fe diffuses into Zn. Since Zn is C.P.H., as is Cd, this phenomenon was expected in both cases. Mr. Rigg was the first investigator to attempt an explanation of this phenomenon. He explains it by eliminating the idea that the type of
crystal lattice is all important. Instead, he applied the theory that the more nearly alike the physical properties of two metals are the lower the diffusion rate will be until a point is reached where the direction of diffusion reverses itself. Why such a reversion of diffusion would take place was not explained.

Plate IV, figure 9 and 10 below are reproduced from Rigg's work. Figure 9 shows two layers on either side of the unaffected Zn. (Dark band in the center.) The bands closest to the pure Zn are rich in that metal. These bands are solid solutions of FeZn$_7$ and Zn plus a second phase of excess Zn. This band contains a maximum of 6.3% iron. The other bands contain from 6.3 to 11.0% iron and are one solid solution of iron into Zinc. Reproduced, 75X.
FeZn$_7$ and Zn. The narrow dark bands next to the steel interface is possibly FeZn$_3$ (up to 17% iron). Figure 10 shows just one half of figure 9. In this case diffusion has carried the intermediate phase of FeZn$_7$ and Zn much farther in to the Zn core.

Another important conclusion from Rigg's work is that Zn vapor does not effect any of the changes. This means that the reactions definitely take place between solids and not between vapor and solid.

The case of Cu-Zn diffusion system goes one step further. This system shows practically equal amounts of diffusion in either direction from the original interface.

The diffusion of indium into Cd base alloys and of Cu into the Al layer on Alclad sheet are extremely important practical problems today. The diffusion of In into Cd base alloys is accomplished below the melting point of either. This diffused alloy produces a bearing metal that cannot be reproduced by any other methods. The problem in Alclad is one of prevention of the diffusion of Cu from the alloy core to the surface.

The actual theory behind these particular cases will be elaborated upon to considerable extent.
The three main divisions of diffusion are given as:

a. Solids in solids
b. Liquids in solids, and
c. Gases in solids.

The experimental work of this paper is confined to the solids in solids divisions.

The most important and best known of diffusion phenomena are: calorizing, carburizing, chromizing, siliconizing, galvanizing, sherardizing, and nitriding. Of the various treatments listed above, only sherardizing is carried out in the solid division, and is therefore, of particular interest here.

It is the general belief that every metal will diffuse into every other metal to some extent. Whether or not this diffusion will be beneficial in any way is yet to be determined in the majority of the possibilities. This supposition has not been supported by experimental results for every possible combination, but enough results are available to lead to the following general statement. That is:

While diffusion will take place, it is improbable that the diffusion process will affect any of the physical properties of the metals except in instances where the corresponding phase diagrams of the alloy show considerable
solid solubility or compound solubility.

There are, at the present time, four known and recognized types of diffusion. These types are:

1. Self-diffusion
2. Surface diffusion
3. Inter-granular diffusion, and,

Both inter-granular and intra-granular diffusion result from simple penetration. This penetration may, in turn, be one of two known types. These types are interstitial diffusion and substitutional diffusion. Self-diffusion is a combination of self-diffusion and inter-granular movement.

**Self-diffusion.** This is the simplest type of diffusion. It is the movement of atoms within their own crystal lattice. It is a phenomena common to all crystal lattices regardless of their stability. This self-diffusion is the first sign or basis of weakness within a crystal lattice that will lead to its breakdown. This movement within any lattice leads to the eventual invasion of that lattice by foreign atoms. If these atoms were not in movement within their own perfectly balanced structure, there would be no chance for any subsequent changes within that lattice.

This contained energy within a lattice site leads
to the second type of diffusion.

**Surface Diffusion.** As has already been stated, surface diffusion is a combination of self-diffusion and one or more unknown forces.

Surface diffusion can be actuated by one of two methods. First, the atoms that diffuse may result from self-diffusion. That is, if the contained energy in any crystal lattice becomes too great, one or more of these atoms will escape the lattice leaving behind vacant sites. This method of diffusion is confined to the one-component system. Second, in the two component system the atoms of one crystal lattice may be replaced by other atoms. The system of thorium-tungsten can be used to illustrate this phenomenon. The thorium atoms vacate the lattice site that had contained thorium and tungsten as an alloy. The vacated sites within the lattice are refilled with tungsten atoms. This is actually a simple process of substitution within crystal lattices.

In either case, the atoms eventually reach the grain boundaries. These atoms are then propelled along the grain boundaries by unknown forces until they finally reach the surface. If the temperature is below the vaporizing point of the atoms, they will move along the surface until it is covered one atom deep or until the supply of diffusing atoms
is exhausted. The atoms will not again penetrate the grains or grain boundaries. This type of diffusion is an exact reverse of the inter-granular and intra-granular type of diffusion.

**Inter-granular Diffusion.** Grain boundary diffusion is perhaps the best known of the diffusion phenomena. However, only one explanation for this process is offered. At the same time, it must be understood that this theory is not entirely acceptable.

The theory advanced is as follows. Grain boundaries contain an infinite number of imperfect crystal lattices. These crystal lattices are definitely not as stable as are the perfect ones within the grains. The energy maintaining such a lattice is not as great as if the lattice were perfect. Therefore, the grain boundary lattices are much more susceptible to breakdown or to invasion than are the intra-granular lattices. From this, it is apparent that the rate of inter-granular diffusion is much greater than that for intra-granular diffusion.

The factor or factors that propel the invading atoms from the lattice next to the surface to succeeding lattices inward along the grain boundaries are not at all clearly defined. These forces that propel the atoms inward along the grain boundaries involve diffusion through crystal
lattices or intra-granular diffusion.

**Intra-granular Diffusion.** Intra-granular diffusion utilizes two preceding actions. The first is inter-granular diffusion. This is necessary to deliver the invading atoms to the certain grains. The second factor is self-diffusion. This provides the needed opening in the lattice for the invading atoms.

Intra-granular diffusion is possible in two ways; substitutional or interstitial diffusion.

Substitutional diffusion is the replacement of one atom in a lattice by another atom of a different component. This is possible only when both atoms are nearly the same size.

Interstitial diffusion is the invasion of a crystal lattice by atoms that are small enough to fit into the lattice without disrupting the stability of the lattice. These solute atoms in the undisturbed lattice of the solvent atoms result in the formation of alloys and compounds. The alloys and compounds are of the same general type as those formed by substitution.

**Rate of Diffusion.** It becomes very apparent that knowledge of the above types of diffusion is useless without some quantitative measure of these types.

Much work has been done on this phase of the problem.
The important conclusions are that the rate of diffusion depends on:

1. Temperature
2. Concentration gradient, and,
3. Activation energy.

The rate of diffusion is also dependent on:

1. The amount and kinds of impurities
2. Grain size, and,
3. Structural changes.

These factors have been reduced to the following mathematical equation.

\[
dm = D \times A \times \frac{dc}{dx} \times dt \quad \text{or:} \quad \frac{dm}{dt} = D \times A \times \frac{dc}{dx}
\]

where:

\( dm \) = amount of diffusing material,
\( dt \) = unit of time,
\( D \) = the amount of substance diffused, in grams, per second across one square centimeter, through unit unit concentration gradient,
\( A \) = cross-sectional area in square centimeters,
\( \frac{dc}{dx} \) = concentration gradient.

This formula may be stated as the amount of diffusing material (\( dm \)) in unit time (\( dt \)) is equal to the product of the amount of substance (\( D \)), in grams, and the area (\( A \)) of the surface times the concentration gradient (\( \frac{dc}{dx} \)).
This formula is known as Fick's Law. It is the basis of all computation in diffusion rates. This formula is directly dependent on another one. This second formula deals with the probability of the atoms becoming loosened from their lattice site.

This probability accounts for the great difference in the rate of diffusion in the various types. In this way it can be explained why inter-granular diffusion is more rapid than intra-granular diffusion. In turn, this probability accounts for the difference in the respective rates of diffusion in the substitutional and interstitial types. In the substitutional type two atoms must become loosened before diffusion can occur. The probability of this happening greatly reduces the possibility of diffusion occurring. It has been concluded that surface diffusion is ten times as rapid as inter-granular diffusion and that the rate of inter-granular diffusion is 100 times that of intra-granular diffusion of the interstitial type. This, in turn, is faster than substitutional diffusion.

The effect the various factors of this equation have on the diffusion rate is not entirely understood.

The concentration gradient is important to the extent that as one atom diffuses inward from the interface, another atom must be available to replace it or all diffusion will stop.
The probability of loosening an atom increases with temperature increase. However, once the atom has sufficient energy to escape the lattice site the time required for it to escape is independent of the temperature.

The causes of activation energy are not understood. It is defined, however, as the energy an atom is capable of containing in order to escape from the lattice site. The vapor pressure of the metals must be considered in this connection.

Impurities along the interface reduce the diffusion rate due to the decrease in area \((A)\) in the formula.

The effect that grain size has is not known. This was mentioned previously in the summary of the physical knowledge of diffusion.

Anisotropic crystals show a much higher rate of diffusion along the crystal axis than at an angle to this axis. Therefore, the rate of diffusion in isotropic crystals is much greater than in those showing anisotropic properties.

Structural changes are of two types in the binary systems. First, the formation of columnar grains is usually associated with the appearance of a new phase. Second, recrystallization or grain growth can occur without the appearance of a new phase. One of the great difficulties that is encountered in the study of structural changes is the distinction between changes in microstructure due to
diffusion and changes due to heat treatment.

Columnar grains result from a particular mode of grain growth. That is, when a new phase forms the grains grow inward from their present site in the direction of penetration. This phase of diffusion is reserved for work carried out above the transformation temperature.

Summary. Two metals will diffuse into one another with the formation of alloy layers equal in number to the phases stable in the binary system at the chosen temperature. The rapidity with which these various layers form varies from layer to layer and from system to system. This rate of formation depends on the various diffusion coefficients.

These facts have been summarized by Dr. Mehl.\textsuperscript{5}

1. The rate of self-diffusion at a given temperature is the lower the higher the melting point of the metal.

2. In a series of binary alloys with a common base metal such as iron, the rate of diffusion is the greater the lower the melting point of the diffusing material.

3. In a binary system the rate of diffusion is the greater in the metal with the lower melting point.

While it is accepted that every metal will diffuse
into every other metal to some extent, it is improbable that the diffusion process will effect any changes in the physical properties of the metals except in certain instances. This one requisite is that the corresponding phase system must show considerable solid solubility. In the binary system solid solubility is usually greater in the metal with the higher melting point. From this, it can be concluded that diffusion should take place more readily in systems where the melting points are most divergent.

The main purpose of the study of the constitutional diagrams in connection with diffusion is the prediction of the phases that will occur. These phases all have their own particular set of properties and are therefore very important. This study of physical properties leads to the practical aspects of diffusion.

In general, it is known that the physical properties are different for each phase. Also that diffusion layers composed of solid solutions are much more ductile than are those of intermetallic compounds. The properties of the various layers, unless very thick, are affected by the adjacent layers.

The usefulness of diffusion coatings is evaluated on the basis of physical properties. Some of the properties affected are:

1. hardness,
2. corrosion resistance,
3. machinability,
4. surface appearance, and,
5. wear resistance.

Whether or not diffusion will alter all of these properties favorably or unfavorably is yet to be determined.

Plate V below shows the constitutional diagram for Fe and Zn in connection with a galvanized sheet.
The original interface is the alpha plus epsilon and epsilon boundary. It is readily seen that the various phases formed are easily predicted from the diagram. Two brittle phases are formed of intermetallic compounds. It has been shown that with proper diffusion these two phases can be closely controlled and the more ductile phases increased in comparative thickness. That is, by diffusion the epsilon and the alpha plus epsilon phases could be expanded. This would increase the ductility of the coating. At the same time the zinc-rich surface could be preserved to give the needed corrosion resistance properties.

The solubility of zinc in iron is high and that of iron in zinc is very low. Also the two melting points are very divergent. It should be concluded then, that the rate of diffusion should be high.
EXPERIMENTAL PROCEDURE

The experimental work is divided into three phases. These are:

1. Electroplating of samples,
2. Diffusion treatment,
3. Mounting, polishing, and study of specimens.

Electroplating. The samples of 1/8 inch stock of low carbon steel were cut into pieces 2 x 2 inches in area. These were used as the cathode and were completely submerged in the electrolyte. The anodes used were of the pure metal that was being plated.

The surfaces of the cathode were carefully prepared. They were ground and polished to remove all oxide film and then pickled to insure a clean surface. The anodes were cut from sheets of the respective metal.

The electrical set-up is shown below.

The power source used was a 6-volt rectifier capable of furnishing 2 amps, continuously. This was ample current
for all cases. The electrolyte in each case was chosen on the basis of operating temperature and available chemicals.

The electrolytes used were as follows:

**Cadmium**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdO</td>
<td>30 g/liter</td>
</tr>
<tr>
<td>NaCN</td>
<td>100 &quot;</td>
</tr>
<tr>
<td>Glue</td>
<td>trace</td>
</tr>
<tr>
<td>Operating temp.</td>
<td>20-30°C</td>
</tr>
<tr>
<td>Current density</td>
<td>1.5-5.4 amps./dm.²</td>
</tr>
</tbody>
</table>

Cadmium anodes.

**Tin**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl₂ · 2H₂O</td>
<td>30 g/liter</td>
</tr>
<tr>
<td>NaOH</td>
<td>75 &quot;</td>
</tr>
<tr>
<td>Glucose</td>
<td>60 &quot;</td>
</tr>
<tr>
<td>Operating temp.</td>
<td>60°C</td>
</tr>
<tr>
<td>Current density</td>
<td>1 amp./dm.²</td>
</tr>
</tbody>
</table>

Tin anodes.

**Zinc**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄ · 7H₂O</td>
<td>360 g/liter</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>30 &quot;</td>
</tr>
<tr>
<td>NaH₂C₂O₂</td>
<td>15 &quot;</td>
</tr>
<tr>
<td>Glucose</td>
<td>120 &quot;</td>
</tr>
<tr>
<td>Operating temp.</td>
<td>20-30°C</td>
</tr>
<tr>
<td>Current density</td>
<td>1.5-3 amps./dm.²</td>
</tr>
</tbody>
</table>

Zinc anodes.
The cell was operated in each case until a deposit of about 0.002 inch was obtained. The cathodes were then cut into small specimens that were properly numbered and made ready for diffusion treatment.

**Diffusion.** The diffusion furnace set-up is shown in Plate VI.

Plate VI. Furnace set-up as originally designed.

The furnace train as shown was used at first. However, the diffusion furnace at the right burned out when heat treating a specimen of Ni plate. This portion of the
experimental work was abandoned, and the single furnace was used for all subsequent work.

The furnace, as shown, was arranged as follows: The nitrogen tank is at the left, followed by $\text{H}_2\text{SO}_4$ and $\text{CaCl}_2$ drying tubes. These are followed by the preheat furnace which is packed with Cu gauze. The drying tube between the furnaces prevents condensation at this point. The main furnace is equipped with the thermocouple for temperature control. At the extreme right is shown the cooling coil on the furnace tube.

Both furnaces are equipped with the necessary resistances and ammeters. The preheat furnace used 110-volt A. C. current. The diffusion furnace used 220-volt A. C. current.

The various times and temperatures for heating are shown later.

Mounting and Study. The heat treated specimens were mounted in lucite. The size of the specimens made it possible to mount three specimens in each mount. They were mounted so that the specimens with the same metal coating were in each mount. This was necessary to facilitate etching.

The specimens were polished in the usual manner.

Considerable difficulty was experienced in developing a suitable etch for the various coatings. The etchants that were used are as follows:
Ferric chloride for tin.

$$\text{FeCl}_3$$-------------------------10 grams
$$\text{HCl}$$--------------------------2 ml.
$$\text{H}_2\text{O}$$----------------------98 ml.

This etchant darkened the pure tin as well as the tin rich FeSn$_2$. It left the iron rich compounds and the iron unattacked. A solution of alcoholic nitric acid followed by picric acid was used to reveal the diffusion line. This required very deep etching.

Mixed acids in glycerine.

A solution of nitric and hydrofluoric acids were mixed in glycerine. This darkened the zinc and cadmium and left the iron as polished.
RESULTS

The results from the study of the various samples are tabulated below.

**Tin.** The time and temperature of diffusion and the depth of penetration of the tin into the iron are tabulated in Table I.

**Zinc.** The same information for zinc is tabulated in Table II.

**Cadmium.** The same is true for Cd in Table III.

**Curves.** The curves below the tables in each case is the plot of depth of penetration against time of heating. The curves are superimposed for each specific metal coat to show a sharper contrast.
<table>
<thead>
<tr>
<th>specimen no.</th>
<th>time</th>
<th>temp.</th>
<th>penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>4 hours</td>
<td>210°C</td>
<td>0.019 mm.</td>
</tr>
<tr>
<td>22</td>
<td>16</td>
<td>210</td>
<td>0.039</td>
</tr>
<tr>
<td>23</td>
<td>24</td>
<td>210</td>
<td>0.045</td>
</tr>
<tr>
<td>24</td>
<td>48</td>
<td>210</td>
<td>0.089</td>
</tr>
<tr>
<td>25</td>
<td>18</td>
<td>245</td>
<td>0.046</td>
</tr>
<tr>
<td>26</td>
<td>24</td>
<td>245</td>
<td>0.073</td>
</tr>
<tr>
<td>27</td>
<td>40</td>
<td>245</td>
<td>0.157</td>
</tr>
</tbody>
</table>

![Graph showing depth of penetration vs. time and temperature]

- curve A - 210°C
- curve B - 245°C

Depth of penetration of tin into iron
<table>
<thead>
<tr>
<th>specimen no.</th>
<th>time</th>
<th>temp.</th>
<th>penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4 hours</td>
<td>210°C</td>
<td>0.18 mm.</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>210</td>
<td>0.38</td>
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<td>3</td>
<td>24</td>
<td>210</td>
<td>0.59</td>
</tr>
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<td>48</td>
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<td>0.90</td>
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<td>18</td>
<td>245</td>
<td>0.52</td>
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<td>24</td>
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<td>245</td>
<td>0.99</td>
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<td>1.12</td>
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<td>16</td>
<td>420</td>
<td>1.09</td>
</tr>
<tr>
<td>12</td>
<td>24</td>
<td>420</td>
<td>1.55</td>
</tr>
<tr>
<td>13</td>
<td>40</td>
<td>420</td>
<td>2.01</td>
</tr>
</tbody>
</table>

![Graph showing penetration over time and temperature](image-url)
TABLE III
DEPTH OF PENETRATION OF CADMIUM INTO IRON

<table>
<thead>
<tr>
<th>specimen no.</th>
<th>time</th>
<th>temp.</th>
<th>penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>4 hours</td>
<td>210°C</td>
<td>0.07 mm.</td>
</tr>
<tr>
<td>42</td>
<td>16</td>
<td>210</td>
<td>0.38</td>
</tr>
<tr>
<td>43</td>
<td>24</td>
<td>210</td>
<td>0.54</td>
</tr>
<tr>
<td>44</td>
<td>48</td>
<td>210</td>
<td>0.88</td>
</tr>
<tr>
<td>45</td>
<td>18</td>
<td>245</td>
<td>0.58</td>
</tr>
<tr>
<td>46</td>
<td>24</td>
<td>245</td>
<td>0.67</td>
</tr>
<tr>
<td>47</td>
<td>40</td>
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<td>0.97</td>
</tr>
<tr>
<td>48</td>
<td>8</td>
<td>320</td>
<td>0.45</td>
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<tr>
<td>49</td>
<td>16</td>
<td>320</td>
<td>0.80</td>
</tr>
<tr>
<td>50</td>
<td>24</td>
<td>320</td>
<td>1.29</td>
</tr>
</tbody>
</table>

![Graph showing penetration of cadmium into iron at different temperatures and times.](image-url)
The three samples of tin in table I were heated slightly above the melting point of tin to experiment with diffusion rate curves crossing the melting point of the metal.

The slope of curve B, table I, indicates that the rate of diffusion above the melting point of the diffusing metal is only slightly higher than it is below the melting point. This would indicate that the increase is due to the temperature change and not due to the change of state.

It is believed that, had methods of determination been more exact, the curves would have been straight lines. These straight lines would persist to a very definite depth. At this certain point, the slope of the curve would increase sharply. This sudden decrease in penetration can be attributed to an excess of carbon building up ahead of the penetration. The dotted portion of curve B illustrates this.

The photomicrograph below in Plate VII shows this penetration of tin into iron.
The original base iron is shown at the top. Next to the iron layer is a layer of FeSn. A narrow layer of FeSn₂ plus Sn is shown at the bottom of the print. The original tin layer has apparently all diffused into the iron.

Zinc. As has been previously stated, the actual penetration of Fe into the Zn or Cd could not be determined. The inter-granular diffusion was measured carefully. This inter-granular penetration of zinc or cadmium into the Fe has no relationship to the amount of iron that will penetrate the coatings. Again, it is believed that if the methods used had been more exacting, the penetration curves
would have been straight lines. Unlike the case of tin in Fe, the straight line should persist throughout the entire cross-section of the piece.

**Cadmium.** The depth of penetration of cadmium is slightly lower than that for zinc. Since the physical properties of the two metals are very similar, the depth of penetration should be very nearly the same. Cd is the less active of the two, also the lattice constants of Cd are greater than those for zinc. These factors all enter into the causes of this variation in depth.

The zinc and cadmium samples were unaffected by the etchant beyond the actual penetration in the grain boundaries. In either case, the coating showed definite signs of ferrite at all times and temperatures of diffusion.

In all cases, the plot of the temperature against the depth of penetration results in a straight line. These were not plotted due to the very few different temperatures used.

Plate VIII illustrates this inter-granular diffusion.
Plate VIII. Inter-granular penetration of zinc into iron. Glycerine etch. 300X.

This photomicrograph is of a sample of zinc that has been diffused at 245°C for 24 hours. The inter-granular material is Zn-rich, while the grains of ferrite are unaffected.
CONCLUSIONS

The coatings of cadmium and zinc show some ferrite. This ferrite is believed to be inter-granular material in the case of Cd and intra-granular material in the case of zinc. Since, for all practical purposes, cadmium and iron do not form a solid solution, intra-granular diffusion cannot occur. It is very essential that, for intra-granular diffusion to occur, the two elements must be capable of forming a solid solution.

It is concluded further, that in all metal pairs where diffusion does take place, it must result in diffusion to some extent in both directions.

Diffusion above the recrystallization temperature is necessary to form the columnar grain structure and the diffusion line.

Diffusion layers that are bounded by intermetallic compounds are more sharply defined than are those bounded by eutectics or solid solutions.

The most important factors determining whether or not diffusion will take place as well as the type of diffusion are listed below:

1. Temperature,
2. Whether or not the two metals will form a solid solution.
3. Lattice constants,
4. Crystal structure,
5. Vapor pressure (for diffusion above the melting point only).
SUGGESTIONS FOR FURTHER STUDY

The field of further study on this problem is unlimited. This field will be open until all the questions asked in this paper as well as the questions asked in all previous papers are answered.

A very interesting problem could be the study of the corrosion resistant properties of the coatings of Zn and Sn formed by diffusion as compared to the coatings in common use today.

The great problem in the tin can industry is the breaking of the continuity of the tin plate in forming the can. The same is true of galvanized zinc. It is possible that intermediate layers formed by diffusion would greatly increase the formability of plated materials. The problem for study would be the formability of plated material compared to the formability of diffused plates.

Fe and Cd show limited solubility for each other. However, no constitutional diagram for this system is available. It would be interesting to know the exact limit of this solubility, since it is claimed by several investigators that at least one intermediate phase exists in diffusion coatings of Cd on Fe. If the system of Fe and Cd shows no solubility and if this one intermediate phase does exist, then the accepted idea that solid solubility is necessary
for diffusion, is in error. The establishment of a reliable diagram for iron and cadmium would clear up this point.

The development of a suitable etchant is essential to absolute identification of the phases present. Such an etchant would have to be capable of attacking the various phases to a certain graduated degree. This is necessary to establish all the phases present.

The use of the X-ray to identify the phases present in the diffusion zone is limited by the available indexes. These are but a few of the specific problems connected with this paper.
BIBLIOGRAPHY


