The analysis of tin diffusion steps in the preparation of Nb3Sn-Cu superconductors

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THE ANALYSIS OF TIN DIFFUSION STEPS IN THE PREPARATION OF NIOBIUM(3)TIN-COPPER SUPERCONDUCTORS

Iowa State University

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The analysis of tin diffusion steps
in the preparation of Nb$_3$Sn-Cu
superconductors

by

Chann-Chen Cheng

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Since the discovery of superconductivity by Kamerling Onnes in 1911, a great deal of effort has been concentrated on the means of developing this "material of the future". The capacity of a superconductor to carry a current without resistance suggests the possibility of generating electric power with 100% efficiency and transmitting it without any loss. All pure metal superconductors have relatively low critical temperatures ($T_C$), less than $10^0$K. In addition, they have a distinct and sharply defined critical field strength ($H_C$), which is less than 0.1 tesla. Thus early attempts to build magnets from these materials were disappointing.

Several small-scale magnets were successfully fabricated by utilizing ductile superconducting alloys, mainly Nb-Ti. In the 1960s, owing to a need for improvements in the design of magnets for superconducting synchrotrons and for magnetic fusion reactors, metallurgical methods for producing large-scale filamentary conductors with brittle A15 compound superconductors were developed. A method for fabricating A15 compounds, Nb$_3$Sn and V$_3$Ga, was successfully developed during this period of time and is now called the bronze process$^{1-3}$. This discovery was made independently by different metallurgists in three countries at approximately the same time. They are K. Tachikawa$^1$ of Japan, A. R.
Kaufman and Pickett$^2$ of the U.S.A. and E. W. Howlett$^3$ of Great Britain. The bronze process is based on the fact that these A15 compounds can be formed at the interface of Nb(V) and Cu-Sn(Ga) when these composites are heat treated at appropriate temperatures. The $T_c$ of Nb$_3$Sn is as high as 18.5°K and that of V$_3$Ga is 16.8°K. Due to the high cost of Ga, there is more interest in the development of Nb$_3$Sn at the present time. In the bronze process, aligned Nb-bronze composite wire is produced from a bronze billet which is filled with an array of Nb rods. This composite billet is extruded. Further processing consists of several annealing and drawing steps to produce a wire. The main difficulty of the bronze process is that it requires several time-consuming annealing steps. Despite this difficulty, historically, the bronze process is the first reliable process for large-scale A15 superconductor fabrication.

Since the original discovery of the bronze process, a number of modifications have been introduced. They are listed as follows:

a. The Ta Diffusion Barrier. In order to stabilize the superconductor, high thermal conductivity Cu is required next to the superconducting filaments. Since the bronze process necessitates the presence of a high-resistivity matrix (e.g., bronze) next to the superconducting filaments, it is desirable to place high-purity Cu as close to the filaments as
possible. Harwell and Airco groups\(^4\) use Ta as a barrier to stop Sn diffusion to the Cu stabilizer from the bronze matrix.

b. The External Diffusion Process. This process consists of extruding a Nb-Cu composite and drawing it to final size, e.g., 300 \(\mu\)m. Then, the wire is coated with a layer of tin before heating it to make a Cu-Sn alloy matrix and then \(\text{Nb}_3\text{Sn}\) filaments. The main advantage of this process over the original one is that the Nb-Cu composite can be drawn to a small size without any intermediate annealing. The process was independently introduced by M. Suenaga and W. B. Sampson\(^5\), and W. Fietz and R. Scanlan as cited in Suenaga\(^6\). In this process, new problems have been encountered in the tin-plating process and subsequent heat treatments to diffuse the Sn into the Cu matrix to form a Cu-Sn alloy. The primary difficulty, which will be detailed later, is the delamination of the outer layer of wire\(^7,8\). Another problem is that this process can not be used with the Ta-diffusion barrier and the Cu stabilizer at the outside portion of a wire.

c. The Internal Diffusion Process. In 1974, a new modification to the bronze process was reported by Hashimoto et al.\(^9\) This process consists of assembling Cu-clad Nb bars and a Cu-clad (Sn-20at.%Cu) alloy rod in a Cu tube such that the Sn-Cu rod will be at the center. The assembly is then cold drawn to final size for heat treatment to form the \(\text{Nb}_3\text{Sn}\) as in the case of the external diffusion process. The main
advantage of this process over the bronze process is the elimination of the intermediate annealing steps in the bronze process. In addition, this has an advantage over the external diffusion process in that the Cu stabilizer and the Ta barrier can be placed outside a wire since Sn is contained at the center of the wire. More recently, this process has been further modified and has shown potential to become one of the most important processes. This process will be further discussed.

d. Others. Several modifications to the original bronze process have been proposed, such as putting bronze in Nb tubing\textsuperscript{10}, or wrapping a Sn–Cu alloy by a flattened Cu–Nb composite\textsuperscript{6} etc. These modifications have introduced some advantageous aspects in the fabrication of the multifilamentary A15 compound wires, but they have also added complications.

In 1973, C. C. Tsuei\textsuperscript{11} proposed an interesting approach to the fabrication of A15 filamentary conductors. This process consists of casting a Nb–Cu melt to form a dendritic network of Nb in Cu and of drawing to wire. Tin can be added in the initial melt or added afterward before the heat treatment to form Nb\textsubscript{3}Sn. The J\textsubscript{C} of his wires was relatively low, because the superconducting filaments were too short and were not present in sufficiently high volume fraction. Nevertheless, an interesting aspect of this processing method is that the
mechanical properties of this composite, such as yield strength, are greatly enhanced over the conventional multifilamentary Nb$\textsubscript{3}$Sn wires due to the close proximity of finely divided (<100 nm) filaments. An alternate method which is similar to Tsuei's has been developed and come to be called the in situ process$^{12-17}$. These superconducting wires are prepared by casting and drawing a Cu-Nb ingot into wire. Therefore, Nb filaments are dispersed in a Cu matrix and aligned with the axis of wires. These wires are coated with Sn and then annealed at elevated temperatures. Nb$\textsubscript{3}$Sn filaments are formed by the reaction of Nb filaments and Sn during diffusion heat treatment. This process was developed independently by Verhoeven et al.$^{12}$ together with Finnemore et al. at Ames$^{13}$, Harbison and Bevk$^{14,15}$, Foner et al.$^{16}$ and Roberge et al.$^{17}$

Harbison and Bevk$^{14}$ developed a levitation melting technique to prepare a material with uniform distribution of the Nb precipitates. Uniformity of the Nb$\textsubscript{3}$Sn filament distribution accounts for the unusual high strength of their composites$^{18}$. They also have reported that a Nb$\textsubscript{3}$Sn-Cu tape with filaments aligned in the rolling direction gives a strong anisotropy in $J_{c}$ at the field close to $H_{c2}$ of in situ formed Nb-Cu tapes$^{19}$.

Foner et al.$^{16}$ and Roberge and Fihey$^{20}$ have developed techniques to prepare materials by chill casting the
composites in graphite molds and by directional solidification to produce Nb dendrites aligned in a Cu matrix. They have done extensive work with strain effects on $J_c$, and on the effects of impurity additions.

Verhoeven et al. and Finnemore et al. prepared a Cu-Nb ingot, ~80 gm, by chill casting the composites in a water-cooled copper chill mold. They developed the arc casting technique to scale up Cu-Nb ingots to 15 Kg for commercial application. In addition, Verhoeven et al. have also done a wide variety of work on the morphologies and grain size of Nb$_3$Sn filaments, the control of Nb filament shape for optimization of $J_c$, calorimetric measurements of ac loss, and flux pinning mechanisms in in situ wire. Nagata et al. pointed out that 550-600°C is an optimum reaction temperature for high $J_c$ which is in agreement with previous results of Verhoeven et al.

Airco and I.G.C. have concentrated on large scale wire drawing, tin plating, and casting for commercial purposes. At Westinghouse, Braginski et al. and Bevk et al. are working towards full understanding of the ac loss.

In all, the in situ process is a promising process for fabricating superconducting wire with superior mechanical properties and comparable $J_c$ in economical cost. However, several metallurgical problems still require further investigation. For instance, during the external diffusion
step in producing \textit{in situ} wire, a ball-up problem\textsuperscript{36} is encountered. This problem is common to any process using the external tin diffusion technique. A dewetting phenomenon makes the Sn layer on the wire surface nonuniform and thus the wire becomes extremely brittle and drops $J_c$ after heat treatment. The solid state diffusion method\textsuperscript{37} was reported to be the most effective way to eliminate the ball-up problem. The method employs a 3 stage heat treatment which may be explained by using the Cu-Sn phase diagram\textsuperscript{38} shown in Figure 1. This technique can be outlined by the following stages:

Stage I. Heat to a temperature just below 227°C (around at 200°C) until the Sn is converted to layers of $\eta$ and $\epsilon$ phases.

Stage II. Increase the temperature to just below 415°C (usually at 375 or 400°C) until the $\eta$ phase is converted to layers of $\epsilon$ and $\delta$ phases.

Stage III. Finally, heat to a temperature which may be as high as the $\gamma$ solidus for the 2 phases composition in order to complete the diffusion process.

Figure 2 is a schematic representation of the compound layer formation which occurs during the three stages of the process. As shown at the top of the figure, the process is initiated by having a Sn layer of width $W_{Sn}$ on the surface of pure Cu. During stage I, this layer is converted into $\eta+\epsilon$ layers as Sn diffuses into the Cu. When Sn is gone, one is
Figure 1. The copper-tin phase diagram
Figure 2. The 3 stage of the solid state diffusion process
left with two layers of intermetallic compounds having a total width, $W_{\eta} + W_{\varepsilon}$, considerably thicker than the original Sn layer. When the temperature is raised to carry out stage II, the $\eta$ is converted into $\varepsilon$ as Sn continues to diffuse into the Cu. Stage II is completed when the $\eta$ phase is converted into $\varepsilon$ phase as shown in Figure 2. Stage III may be carried out at any higher temperatures below the $\gamma$ solidus, but for the sake of simplicity and to illustrate the physical picture which is involved, stage III is assumed to be done at 510°C. The sequence of events in this stage may be divided into 3 steps. In step 1, $\delta$ phase forms and as the $\varepsilon$ phase is depleted the $\delta/\alpha$ boundary moves into the Cu. During the step 2, the concentration gradients in the $\delta$ phase will drop and the $\delta/\alpha$ phase boundary motion must turn around and reduce the width of the $\delta$ phase. Hence, this step terminates when the width of the intermetallic compound layer on the Cu surface reaches a maximum value at the point of turnaround, $W_{\text{max}}$, as indicated at the bottom of Figure 2. Finally, the $\delta$ layer shrinks in size and eventually disappears, followed by continued diffusion until the sample is homogeneous, which completes step 3.

Although this solid state diffusion method avoids the ball-up problem, one often finds severe porosity within the final reacted wire. It was found that during the solid state diffusion process, the problem of void formation could produce
catastrophic failures\textsuperscript{39,40}, such as the delamination of the outer layers of the wire. Verhoeven et al.\textsuperscript{41} clearly demonstrated that voids were nucleated in stage I. They concluded the void rows formed in stage I were nucleated in the presence of a positive divergence of the vacancy flux and were, therefore, thought to arise from tensile stresses produced by either volume changes when $\varepsilon$ formed or the steep Sn concentration gradient in the $\alpha$ phase. They\textsuperscript{41} also found that during stage II and/or stage III individual voids in the void rows sometimes either coalesced or formed connecting cracks, which separated the $\varepsilon$ layer and produced either blister formation or complete delamination with consequent spalling of Sn rich surface layers. However, their experience was that these detrimental effects of void row formation could be reduced by minimizing times at stage I and II temperatures. Therefore, there is one important practical problem which arises when utilizing the solid state diffusion process: What are the minimum times required in stage I and II in order to eliminate or reduce the void formation problem?

In 1980, Intermagnetics General Corporation (I.G.C.) developed a modified method to produce internal tin wire\textsuperscript{42,43} in long lengths. This internal tin process involves the manufacture of two major components, (1) a composite element and (2) a stabilizer tube. A composite tube is hot-extruded from a tubular billet, consisting of many Nb filaments in a
pure Cu matrix. The tube is then filled with Sn and drawn to a hexagonal shaped wire of a size suitable for restacking. The stabilizer is also a tubular extrusion consisting of a Cu tube with a thin diffusion barrier placed near the inside of the tube. The barrier usually is made of pure Nb or Ta. Several of the sub-element rods are assembled inside the stabilizer tube and co-drawn to wire. Figure 3 displays the cross-section of a unreacted internal tin wire supplied by I.G.C.

This new composite, consisting of Cu, Sn cores, Nb rods and Ta barrier, requires no intermediate annealing during drawing, eliminating a significant fabrication cost. Multifilamentary Nb$_3$Sn composites based on $\alpha$-brass of sufficient ductility to be extruded and drawn only if the Sn concentration in the bronze is < 14wt.% Sn$^{44}$. This modified method provides an opportunity to overcome the 14wt.% Sn concentration limitation. Also, unlike conductors produced from external tin diffusion technique, the internal tin wires are not restricted to composite diameters smaller than 0.5 mm$^{45}$. Therefore, the internal tin process because of its higher current density$^{46}$, ease of fabrication and comparatively low cost$^{43}$, will probably become one of the dominant processes to fabrication multifilamentary Nb$_3$Sn-Cu superconductor.

Because of its advantage, there is a major interest in
Figure 3. A cross section view of unreacted internal tin wire. (250X)
this internal tin wire. Groups at Brookhaven National Laboratory\textsuperscript{47} and Lawrence Berkeley Laboratory\textsuperscript{48} tried to optimize the heat treatment steps. They concluded that the $J_c$ of internal tin wire was increased when low temperature diffusion heat treatments were performed prior to a high temperature reaction. The $J_c$ reported\textsuperscript{46} could be as high as 2000 A/mm$^2$. Suenaga et al.\textsuperscript{49} of Brookhaven National Laboratory and Imuizumi et al.\textsuperscript{50} of Mitsubishi Electric Co. tried to improve the $J_c$ of internal tin wire by adding Ti and In elements.

Undoubtedly, heat treatment plays a very important role in determining the superconducting properties of these wires, in spite of the Sn being placed externally or internally. Advantages of the internal tin process over external one on this aspect are (1) having the soft Sn inside where it will not become scraped off during processing, (2) avoiding the ball-up problem because the molten Sn can be held in place by the surrounding Cu-Nb material, and (3) blistering is not expected to be a problem because the stresses are compressive\textsuperscript{51}. One may be reminded of the practical questions mentioned for the external tin wire: What are the minimum times required in stage I and II in order to eliminate or reduce the void formation problem? Here, alternately, this question becomes: What are the minimum times required in stage I and II for the internal tin wire and how do they compare to
those of external tin wire?

To answer these important questions, numerical analysis is a powerful tool. For many situations, phase layer growth kinetics can be predicted analytically using Fick's second law and invoking conditions of local equilibrium at each interface boundary. Closed-form solutions to such problems are well known for planar geometries in systems of infinite or semi-infinite extent. More complex situations which involve nonplanar geometries of finite extent typically are treated by numerical methods and computer techniques. For example, Hickl and Heckel studied the phase layer growth during aluminide coating of Ni, since many Ni-base superalloy parts are subjected to aluminization treatments prior to their use in environments which could produce severe surface degradation. Also, Cable and Evans numerically solved the diffusion-controlled growth and dissolution of a spherical particle which could be applied to study the sintering step in powder metallurgy.

Mathematical and numerical analyses formulated by either of these methods are useful in predicting the time dependence of concentration-distance profile in the diffusion zone and thicknesses of the corresponding phase layers. Furthermore, they may be able to answer the minimum times required in stage I and II for the external and internal tin wires.

In this presentation, the Sn diffusion step at low
temperature will be studied experimentally as well as mathematically for both the external and internal tin wires. Wires containing equal amounts of tin will be investigated and the minimum times required in stage I will be evaluated and compared. The exact closed-form solution for planar geometry will be presented in order to confirm the accuracy of the numerical solution. The possible relationship of Sn diffusion step among planar, external and internal geometries also will be discussed.
II. EXPERIMENTAL PROCEDURES

The experimental procedures are composed of two parts. First, the sample preparation for the planar sheet, internal and external tin wires will be described. Secondly, the mathematical and numerical analyses are explained.

A. Sample Preparation

The external tin wires were prepared as follows: four different Cu wire diameters, 0.25 mm, 0.5 mm, 1.0 mm and 3.0 mm were drawn from C101 Cu and cleaned in a 1:1 HNO₃:H₂O solution for 30 seconds. They were plated with Sn from a sodium stannate bath and in order to insure uniformity of plated thicknesses the wires were rotated during the plating operation. Based on weight gain measurements, the plate thicknesses were 10.03±0.72 μm, 11.18±0.92 μm, 10.86±0.65 μm and 9.83±0.69 μm for 0.25 mm, 0.5 mm, 1 mm and 3 mm wires, respectively. The Sn plated wires were cut to 2.5 cm lengths, sealed in 5 mm pyrex tubes under helium and given a heat treatment at 200±1°C for various times. The heat treatment took place in a box furnace and the specimens were held in a 15 cm diameter, 15 cm long Al block with 19 holes, 10 mm O.D., 13 cm deep.
The planar sheet samples were prepared in a similar way from a 0.12 mm thick sheet which was rolled from Cl01 Cu. The thickness of tin plating was 9.43±0.18 μm. The cleaning, plating and heat treatment procedures were the same as described above for the external tin wires.

The internal tin wires were prepared as follows: a 4 mm diameter 99.999% Sn rod was cast in a 4 mm I.D. quartz tube. A piece of 4 mm Sn rod (4 cm long) was put into a 4.1 mm hole which was drilled in a 6.35 mm Cu rod (18 cm long). This assembly was then cold drawn to 1.875 mm. Another assembly was made thereafter by putting a piece of this as-drawn 1.875 mm sample into another as-drilled 6.35 mm Cu rod and was cold drawn to 1.875 mm. The drilling and drawing procedures were repeated exactly as above twice except for the last drawing step. The last drawing step reduced the assembly to four different sizes, 0.8 mm, 1.32 mm, 1.59 mm and 2.31 mm in diameters. The tin core diameter of these wires were measured as 8.6 μm, 16 μm, 19.2 μm and 29 μm, respectively. The internal tin wires were cut to 2.5 cm lengths, sealed in 5 mm pyrex tubes under helium and given a heat treatment at 200±1°C in Al block for various times as described above.

The heat treated samples were mounted and metallographically polished to examine and measure the intermetallic layer thicknesses. The thicknesses of the Sn layers were determined by measurements at 25 different areas on each
sample. The effective original Sn plate thicknesses for evaluation of time to deplete the Sn layer, $T_d$, were taken by adding the average thicknesses and the standard deviations. The standard deviations were added because the thickest area should be the last area to deplete the Sn layer. Phase identification was done using Grard's etchant and verified with energy dispersive x-ray spectroscopy (EDS) in a scanning electron microscope.

B. Mathematical and Numerical Analyses

1. Mathematical Closed-form Model

The Sn diffusion process can be characterized as semi-infinite, multiphase, volume diffusion. Both the concentration-distance profiles and the interface positions change with time as the phase layers grow. Description of stage I of the diffusion process requires solution to Fick's second law in each of the intermediate phases, $\eta$, $\epsilon$ and $\alpha$.

$$\frac{3C}{\delta t} = \frac{1}{x^n} \times \frac{3}{\delta x} \left( x^n \times D_i \times \frac{3C}{\delta x} \right) \quad (1)$$
Figure 4. Phase formation and composition profiles expected in stage I
where $C$ is the volume concentration of Sn in the phases, $t$ is time, $x$ is position, and $D_i$ refers to the interdiffusion coefficients in the respective phases. Also, $m=0$ is for a planar geometry, 1 for a cylindrical and 2 for a spherical geometry. The initial condition for stage I is shown at the top of Figure 4 and formation of $\eta$ and $\epsilon$ phases during stage I is shown at the bottom of Figure 4. The boundary conditions involve specification of the Sn concentrations and a Sn flux balance at each of the three interfaces.

Sn/$\eta$ interface ($Z=Z_{Sn}$):

$$(C)_{Sn}=C_1 ; (C)_{\eta}=C_2$$

$$\frac{dZ_{Sn}}{dt} (C_1 - C_2) = D_\eta \frac{dc}{dx} |_{\eta} \cdots \cdots \cdots \cdots \cdots (2a)$$

$\eta/\epsilon$ interface ($Z=Z_{\eta}$):

$$(C)_{\eta}=C_3 ; (C)_{\epsilon}=C_4$$

$$\frac{dZ_{\eta}}{dt} (C_3 - C_4) = -D_\epsilon \frac{dc}{dx} |_{\eta} + D_\epsilon \frac{dc}{dx} |_{\epsilon} \cdots \cdots \cdots \cdots \cdots (2b)$$

$\epsilon/\alpha$ interface ($Z=Z_{\epsilon}$):
\((C)_e = C_5 \); \((C)_\alpha = C_6\)

\[
\frac{dZ_e}{dt} (C_5 - C_6) = -D_e \frac{dC}{dx}|_e + D_\alpha \frac{dC}{dx}|_\alpha \ldots \ldots \ldots \ldots (2c)
\]

The final two boundary conditions require that the initial Sn concentration is zero in the Cu and 100% Sn in the Sn layer.

It is often found\(^{52,60}\) that growth of intermetallic phase boundaries are observed proportional to \(t^{1/2}\). Therefore, the solution for this Sn diffusion process can be found by assuming that three interfaces move as,

\[
Z_{Sn}(t) = Z_0 - 2a_1 \times (D_{n} t)^{\frac{1}{2}} \ldots \ldots \ldots \ldots (3a)
\]

\[
Z_{\eta}(t) = Z_0 + 2a_2 \times (D_{n} t)^{\frac{1}{2}} \ldots \ldots \ldots \ldots (3b)
\]

\[
Z_{\epsilon}(t) = Z_0 + 2a_3 \times (D_{\epsilon} t)^{\frac{1}{2}} \ldots \ldots \ldots \ldots (3c)
\]

Figure 5 shows the locations of the 3 interfaces formed during stage I relative to the original Sn/Cu interface. In order to evaluate the three constants, \(a_1\), \(a_2\) and \(a_3\) for stage I of this process, the following interface concentration values were taken from Hansen\(^{36}\).
Figure 5. Location of the 3 phase boundaries formed in stage I relative to the original boundary at $Z_0$. 
$C_1 = 100 \times 0.03701; \ C_2 = 45.4 \times 0.04839; \ C_3 = 44.7 \times 0.04839$

$C_4 = 24.9 \times 0.06947; \ C_5 = 24.45 \times 0.06947; \ C_6 = 0.7 \times 0.07863$

where the first factor is the Sn concentration in atom percent from the phase diagram, and the second factor is the molar density in atom/A$^3$ calculated from crystal structure data. Also, the interdiffusion coefficients were obtained using the data of Onishi and Fujibuchi$^{61}$ as follows:

$$D_\eta = 2.15 \times 10^{-11} \text{ cm}^2/\text{sec}$$

$$D_\alpha = 1.30 \times 10^{-11} \text{ cm}^2/\text{sec}$$

$$D_\alpha = 2.10 \times 10^{-20} \text{ cm}^2/\text{sec}$$

a. **Planar geometry**  The m value of Fick's second law is zero for planar geometry; thus, it can be solved by the use of eqns (2a) to (2c) as well as the assumed square root time dependent interface position of equations (3a) to (3c) as follows$^{62}$:
$$C_\eta = A + B \times \text{erf} \frac{z-z_0}{2 \times (D_\eta t)^{\frac{1}{2}}} \quad \text{(4a)}$$

$$C_e = C + D \times \text{erf} \frac{z-z_0}{2 \times (D_e t)^{\frac{1}{2}}} \quad \text{(4b)}$$

$$C_\alpha = E + F \times \text{erf} \frac{z-z_0}{2 \times (D_\alpha t)^{\frac{1}{2}}} \quad \text{(4c)}$$

where the constants are:

$$A = \frac{C_3 \text{erf}(a_1) + C_2 \text{erf}(a_2)}{\text{erf}(a_1) + \text{erf}(a_2)} \quad \text{(5a)}$$

$$B = \frac{C_3 - C_2}{\text{erf}(a_1) + \text{erf}(a_2)} \quad \text{(5b)}$$

$$C = \frac{C_4 \text{erf}(a_3) - C_5 \text{erf}(a_2 R)}{\text{erf}(a_3) - \text{erf}(a_2 R)} \quad \text{(6a)}$$

$$D = \frac{C_5 - C_4}{\text{erf}(a_3) - \text{erf}(a_2 R)} \quad \text{(6b)}$$
The velocity of each interface can be derived from equations (3a), (3b) and (3c).

\[
\frac{\partial Z_{Sn}}{\partial t} = -a_1 \times \left[ \frac{D_n}{t} \right]^{1/2} \quad \text{(10a)}
\]

\[
\frac{\partial Z_n}{\partial t} = a_2 \times \left[ \frac{D_n}{t} \right]^{1/2} \quad \text{(10b)}
\]

\[
\frac{\partial Z_e}{\partial t} = a_3 \times \left[ \frac{D_e}{t} \right]^{1/2} \quad \text{(10c)}
\]

Mass balance equations at each interface take into account the mass flux to and from each interface as well as the interface motion,

\[
\frac{\partial Z_{Sn}}{\partial t} = -J_{Sn+} \quad \frac{1}{(C_1 - C_2)} \quad \text{(11a)}
\]
\[ \frac{\partial \eta}{\partial t} = \frac{(J_{\eta^-} - J_{\eta^+})}{(C_3 - C_4)} \] ...............(11b)

\[ \frac{\partial \varepsilon}{\partial t} = \frac{(J_{\varepsilon^-} - J_{\varepsilon^+})}{(C_5 - C_6)} \] ...............(11c)

With \( J_{\eta^-} \) being the flux at the \( z_i \) interface computed from the negative side and \( J_{\eta^+} \) the flux from the positive side.

\[ J_{\eta^+} = -D_{\eta^+} \frac{\partial \eta}{\partial x} \bigg|_{z_{\eta^+}} \] ...............(12a)

\[ J_{\eta^-} = -D_{\eta^-} \frac{\partial \eta}{\partial x} \bigg|_{z_{\eta^-}} \] ...............(12b)

\[ J_{\varepsilon^+} = -D_{\varepsilon^+} \frac{\partial \varepsilon}{\partial x} \bigg|_{z_{\varepsilon^+}} \] ...............(12c)

\[ J_{\varepsilon^-} = -D_{\varepsilon^-} \frac{\partial \varepsilon}{\partial x} \bigg|_{z_{\varepsilon^-}} \] ...............(12d)

Taking the partial differentials of equations (4a) to (4c), as indicated in equations (12a) to (12e), fluxes at the interfaces are determined. These fluxes, when substituted into equations (11a) to (11c), yield on rearranging:
\[
\frac{\partial z_s}{\partial t} = \frac{\frac{1}{2}D_n B \exp(-a^2)}{n^2 t^{\frac{1}{2}} (C_1 - C_2)} \quad \text{(13a)}
\]

\[
\frac{\partial z_h}{\partial t} = \frac{-\left[\frac{1}{2}D_n B \exp(-a^2) - \frac{1}{2}D_\varepsilon D \exp(-a^2 R)\right]}{n^2 t^{\frac{1}{2}} (C_3 - C_4)} \quad \text{(13b)}
\]

\[
\frac{\partial z_e}{\partial t} = \frac{-\left[\frac{1}{2}D_\varepsilon D \exp(-a^2) - \frac{1}{2}D_\alpha F \exp(-a^2 G)\right]}{n^2 t^{\frac{1}{2}} (C_5 - C_6)} \quad \text{(13c)}
\]

These three equations, when combined with equations (10a) to (10c), give the following expressions for \(a_1\):
Solving for $a_1$ with the aid of a computer will allow for the characterization of either the interface positions or the concentration-distance profiles for any given time.

Using the diffusion coefficients given on page 24 the value of $G$ is found to be $2.5 \times 10^4$. It was shown by Verhoeven et al. that for such large value of $G$ equation (14c) can be simplified somewhat to the form,
One may thereafter solve the problem for the $a_1$, $a_2$ and $a_3$ values as a function of $R$ by the use of equations (5) to (9) and (14), where $R$ is the square root of the ratio of $D_\eta$ and $D_\varepsilon$. The $a_i$ values were determined for $R$ values ranging from 1 to 10 with a computer. The least square fit method was applied to the resulting data to obtain the following equations for the $a_i$ values as a function of $R$.

\[ a_1 = c_{1,0} + c_{1,1}(\ln R) + c_{1,2}(\ln R)^2 + c_{1,3}(\ln R)^3 + c_{1,4}(\ln R)^4 \]  \hspace{1cm} (15a)

\[ a_2 = c_{2,0} + c_{2,1}(\ln R) + c_{2,2}(\ln R)^2 + c_{2,3}(\ln R)^3 + c_{2,4}(\ln R)^4 \]  \hspace{1cm} (15b)

\[ a_3 = c_{3,0} + c_{3,1}R + c_{3,2}R^2 + c_{3,3}R^3 \]  \hspace{1cm} (15c)

where

- $c_{1,0} = 0.1064$;
- $c_{2,0} = -1.5287 \times 10^{-3}$;
- $c_{3,0} = 0.0527$

- $c_{1,1} = -0.0390$;
- $c_{2,1} = 0.0796$;
- $c_{3,1} = 0.0388$

- $c_{1,2} = 0.0255$;
- $c_{2,2} = -0.0430$;
- $c_{3,2} = 2.4528 \times 10^{-3}$

- $c_{1,3} = -8.1188 \times 10^{-3}$;
- $c_{2,3} = 0.0106$;
- $c_{3,3} = -4.1402 \times 10^{-4}$

- $c_{1,4} = 1.0363 \times 10^{-3}$;
- $c_{2,4} = -9.8394 \times 10^{-4}$;
The magnitude of the error for these least square fit curves is in the range of 0.1%. The R value for Cu-Sn system is between 1.2 to 1.4.

Experimentally, one may evaluate the time dependence of the widths of the \( \eta \) phase, \( W_\eta \), and the \( \epsilon \) phase, \( W_\epsilon \), which are defined on Figure 5. Such experiments have been done by Onishi et al. who found that the values of \( W_\eta \) and \( W_\epsilon \) both increase at \( t^{1/2} \). They express \( W_\eta = k_\eta t^{1/2} \) and \( W_\epsilon = k_\epsilon t^{1/2} \). The ratio \( W_\eta/W_\epsilon \) predicted by this analysis may be expressed as,

\[
W_\eta/W_\epsilon = \frac{a_1 + a_2}{(a_3/R - a_2)} \tag{16}
\]

One may evaluate \( W_\eta/W_\epsilon \) as a function of \( R \) from the data of equations (15). This has been done with a computer for several values of \( R \) and the equation is as follows:

\[
W_\eta/W_\epsilon = 1.089(R)^{1.867} \tag{17}
\]

Therefore, by applying the experimental value of \( W_\eta/W_\epsilon \) to equations (15) and (17), one may evaluate \( R \) and the corresponding \( a_1 \), \( a_2 \) and \( a_3 \) values. The diffusion coefficients may then be evaluated from the following:
\[ D_n = k_n^2/[4(a_1+a_2)^2] \quad D_e = k_e^2/[4(a_3-a_2R)^2] \] .......(18)

For example, one may take Onishi's data to evaluate the \( D_n \) and \( D_e \) values. Their \( W_n/W_e \) ratio was 1.7078 for a 200°C heat treatment. From equation (16), one obtains the \( R \) value to be 1.2725. From this \( R \) value, one also obtains the following \( a_i \) values from equation (15).

\[
\begin{align*}
  a_1 &= 0.0984 \\
  a_2 &= 0.0154 \\
  a_3 &= 0.1059
\end{align*}
\]

Consequently, the \( D_n \) and \( D_e \) can be evaluated from equations (18) and are found to be:

\[
\begin{align*}
  D_n &= 2.17 \times 10^{-11} \text{ cm}^2/\text{s} \\
  D_e &= 1.29 \times 10^{-11} \text{ cm}^2/\text{s}
\end{align*}
\]

These values are essentially the same as those computed in reference 62 and shown on page 24. The small difference results because the \( a_i \) and \( R \) values used here were calculated from equations (15) and (17) rather than from equations (5) to (9) and (14).
b. **Cylindrical geometries**  
For cylindrical geometries, the m value in equation (1) is unity. If the diffusion coefficients are independent of concentration, Fick’s second law becomes,

\[
\frac{\partial C}{\partial t} = D_1 \times \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \times D_1 \times \frac{\partial C}{\partial r} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (19)
\]

There is no complete solution involving compound layer growth for this equation. One may again assume the growth rate of intermediate layers proportional to \( t^{1/2} \) as equations (3a) to (3c). Intuitively, the \( \alpha_i \)'s are not constants for wire geometries. The \( \alpha_i \)'s could be functional to \( (\Delta r/r)_i \), where \( \Delta r \) is the movement of the interface positions and \( r \) is the interface radius. For the external Sn wire, \( (\Delta r/r)_{Sn} \) is relatively small, especially for large size wire, and the \( \alpha_i \)'s are close to constant. However, in case of internal Sn wire \( (\Delta r/r)_{Sn} \) is significantly larger because of the much smaller \( r \) values. Thus, the \( \alpha_i \)'s for the internal Sn wire deviate substantially from a constant value.

The closed-form solution for the wire geometries is more complicated than that for the planar geometry. A numerical solution, which will be analyzed next, is a better approach to solve this Sn diffusion problem.
2. **Numerical Analysis**

Finite-difference techniques\(^{63,64}\) are usually utilized to model complex, finite, multiphase diffusion problems. The basic finite-difference approximation can be derived from Taylor's theorem as follows: when a function \(u\) and its derivatives are single-valued, finite and continuous functions of \(x\), then by Taylor's theorem,

\[
 u(x+h) = u(x) + hu'(x) + \frac{1}{2} h^2 u''(x) + \frac{1}{6} h^3 u'''(x) + \ldots \quad (20a)
\]

and

\[
 u(x-h) = u(x) - hu'(x) + \frac{1}{2} h^2 u''(x) - \frac{1}{6} h^3 u'''(x) + \ldots \quad (20b)
\]

addition of these expansions gives,

\[
 u(x+h) + u(x-h) = 2u(x) + h^2 u''(x) + o(h^4) \quad \ldots \quad (21)
\]

Where \(o(h^4)\) denotes terms containing fourth and higher powers of \(h\). Assuming these are negligible in comparison with lower powers of \(h\) it follows that,

\[
 u''(x) = \frac{d^2 u}{dx^2} \bigg|_{x=x} = \frac{1}{h^2} \left[ u(x+h) - 2u(x) + u(x-h) \right] \quad \ldots \quad (22)
\]

Subtraction of equation (20b) from equation (20a) and neglect of terms of order \(h^3\) leads to
\[ u'(x) = \frac{du}{dx} \bigg|_{x=x} = \frac{1}{2h} \; [u(x+h) - u(x-h)] \ldots \ldots (23) \]

Assume \( u \) is a function of the independent variables \( x \) and \( t \). Subdivide the \( x-t \) plane into sets of equal rectangles of sites \( \Delta x=h, \Delta t=k \), as shown in Figure 6, and let the coordinates \((x,t)\) of the representative grid point \( P \) be \( x=ih; t=jk \), where \( i \) and \( j \) are integers.

Denotes the value \( u \) at \( P \) by

\[ u_P = u(ih,jk) = u^j_i \]

Then, by equation (23),

\[ \frac{\partial^2 u}{\partial x^2} \bigg|_{i,j} = \frac{u^j_{i+1} - 2u^j_i + u^j_{i-1}}{h^2} \ldots \ldots (24a) \]

Similarly,

\[ \frac{\partial^2 u}{\partial t^2} \bigg|_{i,j} = \frac{u^j_{i+1} - 2u^j_i + u^j_{i-1}}{k^2} \ldots \ldots (24b) \]

And,

\[ \frac{\partial u}{\partial t} = \frac{u^j_{i+1} - u^j_i}{k} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (25) \]

**a. Planar geometry** Since three intermediate layers, \( \eta, \epsilon \) and \( \alpha \), are observed during stage I heat treatment of the Cu-Sn system, Fick's second law, equation (26), must be satisfied simultaneously for these three layers during the
Figure 6. The schematic drawing of the finite-difference formula.
Furthermore, the interface mass balance equation, equation (27), also must be satisfied for the Sn-\( \eta \), \( \eta - \epsilon \) and \( \epsilon - \alpha \) phase boundaries.

\[
\frac{d\xi}{dt} (C_{\beta\alpha} - C_{\alpha\beta}) = -D_{\beta} \left[ \frac{dc}{dx} \right]_{\beta} + D_{\alpha} \left[ \frac{dc}{dx} \right]_{\alpha} \quad \text{(27)}
\]

Where \( \xi \) is the interface position, \( \beta \) is the solute-rich phase corresponding to the certain interface, \( \alpha \) is the solute-poor phase corresponding to the certain interface, and \( C_{\beta\alpha} \) and \( C_{\alpha\beta} \) are the solute concentrations of \( \beta \) and \( \alpha \) phases in equilibrium with \( \alpha \) and \( \beta \) phases, respectively.

The numerical calculation is started from the calculation of interface positions by equation (27). At the interface position, the solute of the solute-rich phase (\( \beta \) phase) will diffuse through the interface into the solute-poor phase (\( \alpha \) phase). Meanwhile, the interface moves toward the solute-rich phase (i.e., the thickness of the solute-rich phase is reduced). The interface mass balance equation, equation (27), can be expressed in finite-difference form:
\[
\frac{\xi^{j+1} - \xi^j}{\Delta t} = \frac{1}{c_{\beta_\alpha} - c_{\alpha_\beta}} \times \left[ D_{\alpha} \times \frac{(-c_3^j + 4c_2^j - 3c_1^j)}{2 \times (Z_{\alpha}/I_{\alpha})} \right. \\
- \left. D_{\beta} \times \frac{(c_{I_{\beta_{-2}}} - 4c_{I_{\beta_{-1}}} + 3c_{I_{\beta_{-1}}})}{2 \times (Z_{\beta}/I_{\beta})} \right] \quad (28)
\]

Where \(\xi^{j+1}\) is the \(\alpha/\beta\) interface position at time \(j+1\), \(\xi^j\) is the \(\alpha/\beta\) interface position at time \(j\), \(\Delta t\) is the time interval, \(I_{\alpha}\) and \(I_{\beta}\) are grid numbers in the \(\alpha\) and \(\beta\) phases, respectively, and \(Z_{\alpha}\) and \(Z_{\beta}\) are thicknesses of the \(\alpha\) and \(\beta\) phases, respectively.

In order to rewrite Fick's second law for planar geometry in finite-difference form, a fixed number of equally spaced grids need to be assigned to each phase through the entire process. Nevertheless, the size of the grid spacing changes after every iteration due to the changes in interface positions. The grid points, therefore, cannot be thought of as fixed, but must be considered moving. The shift in grid position with each time step required an adjustment in the indexed concentration value corresponding to the new grid position. This complicates the application of the governing equation for it is based upon an external frame of reference. This difficulty was overcome by employing the Murry-Landis correction to equation (26) by requiring for each grid point.
in each phase:

\[ \frac{dC_i}{dt} = \frac{\partial C_i}{\partial t} + \frac{\partial C_i}{\partial x_i} \times \frac{dx_i}{dt} \] (29)

Where \( \frac{\partial C_i}{\partial t} \) is the contribution of equation (26) and where the rate of travel of a grid point is functionally related to the interface velocity by:

\[ \frac{dx_i}{dt} = \left( \frac{x_i}{\xi} \right) \times \frac{d\xi}{dt} \] (30)

Comparing equations (29) and (30), one arrives at a relationship for the time rate of change of the \( \beta \) phase concentration at a grid point, \( i \):

\[ \frac{dC_\beta^i}{dt} = \frac{x_i}{z_\beta} \times \frac{\partial C_i}{\partial x_i} \times \frac{d\xi}{dt} + \frac{\partial C_\beta^i}{\partial t} \] (31)

In analogous fashion, the total concentration derivative at a grid point relative to the \( \alpha \) phase boundary is:

\[ \frac{dC_\alpha^i}{dt} = \left[ \frac{z_\alpha - x_i}{z_\alpha} \right] \times \frac{\partial C_i}{\partial x_i} \times \frac{d\xi}{dt} + \frac{\partial C_\alpha^i}{\partial t} \] (32)

At the interface, equations (31) and (32) are coupled through
equation (27), the interface mass balance, whose solution yields the interface velocity. Rewriting these equations in finite-difference form leads to the following expressions for the planar geometry.

\[ \beta \text{ phase: } \frac{c_{i}^{j+1} - c_{i}^{j}}{\Delta t} = \frac{i}{z_{\beta}} \times \frac{c_{i+1}^{j} - c_{i-1}^{j}}{2} \times \frac{d\xi^{j+1}}{dt} \]

\[ + D_{\beta} \times I_{\beta}^{2} \times \frac{c_{i-1}^{j} - 2c_{i}^{j} + c_{i+1}^{j}}{(z_{\beta})^{2}} \] \hspace{1cm} \ldots \ldots (33a) \]

\[ \alpha \text{ phase: } \frac{c_{i}^{j+1} - c_{i}^{j}}{\Delta t} = \frac{i_{\alpha} - i}{z_{\alpha}} \times \frac{c_{i+1}^{j} - c_{i-1}^{j}}{2} \times \frac{d\xi^{j+1}}{dt} \]

\[ + D_{\alpha} \times I_{\alpha}^{2} \times \frac{c_{i-1}^{j} - 2c_{i}^{j} + c_{i+1}^{j}}{(z_{\alpha})^{2}} \] \hspace{1cm} \ldots \ldots (33b) \]
Besides several essential constants being required to input for calculation, initial concentration-distance profiles are required to initiate the calculation. Linear profiles are utilized for the first try and it turns out to be an acceptable assumption. Furthermore, standard finite-difference techniques require that $\Delta x^2/4D_1 \geq \Delta t$. The time increment for each iteration varies since the grid spacings change with time. Thus, after every iteration, new $\Delta x$ and $\Delta t$ must be re-established. Since there are three interfaces in this Cu-Sn system, every iteration includes relocating these interfaces by utilizing equation (28) three times. Also, the concentration-distance profiles of $\alpha$ and $\beta$ phases need to be re-established along with the interface movements. Thus, in all, every iteration requires to apply each of equations (29), (33a) and (33b) three times in order to calculate the interface positions and concentration-distance profiles. The major calculation sequence is outlined in Figure 7.

b. Cylindrical geometries The finite-difference form of the interface mass balance equation for wire geometries is exactly identical to that for planar the geometry, equation (28), but Fick's second law is different from the planar geometry. Equation (19) is Fick's second law for wire geometries and the finite-difference form can be expressed:
Figure 7. The calculation sequence of the numerical analysis
Where the - sign in the last term is for internal tin wire and the + sign is for external tin wire.

In this case, the + sign in the last term is for the internal tin wire and the - sign is for the external tin wire.
Equations (34a) and (34b) are suitable for both internal tin and external tin wires. The only difference between these two equations is the last term of the equations. It is clear that the \( \xi \) values are bigger for the external tin wire than those for internal tin wire. Therefore, the concentration-distance profile for these two wires should not be identical, and this implies different interface movement for external and internal tin wires.

In case of the \( \xi \) value approaching infinity, the last term of equations (34a) and (34b) become zero. And these two equations become exactly the same as equations (33a) and (34b) for planar geometry. Hence, simply based upon the relationship between these equations, one might expect that the planar geometry serves as the upper bound for the external tin wire.

The computer programs for the planar sample, the internal and the external tin wires are given in the VIII. Appendix.

c. **Boundary conditions and physical parameters utilized**

In order to initiate a solution by numerical analysis, the following input data are specified for each phase: initial concentration profiles, initial thicknesses, interface concentrations, interdiffusion coefficients, and internal node spacings. With this information, the numerical solutions yield a continuous trace of the interface location and
concentration profiles in each phase. It should be noted that the solutions presented in this study assume that: (1) the interdiffusion coefficients are independent of concentration; (2) the interface concentrations are time-independent; (3) the molar volumes of both phases are equal and (4) volume diffusion is the only diffusion mode. These assumptions were employed to minimize the number of input variables in the problem and were not the result of the numerical techniques that were used. The numerical methods developed in this study can be used also for situations where the effects of the time and concentration dependence of the above variables are of interest.

The initial concentration profiles and initial thicknesses determined from the analytical solution at 3 hours and the concentration-distance profiles were assumed to be linear. For both the internal and external cylindrical geometries, the initial thicknesses of \( \eta \) and \( \epsilon \) phases were taken from experimental data of 0.5 days at 200\(^{\circ}\)C. This is the major shortcoming of this numerical model. The measurement of intermetallic phase thicknesses can not be extremely accurate due to the fact that (1) the interface boundaries between \( Sn/\eta \), and \( \eta/\epsilon \) are not smooth, and (2) the thicknesses of intermetallic phases at this stage are very thin. Referring to equation (28), one may realize that the uncertainty of these two phase thicknesses will cause the uncertainty of the
produced interface positions. Furthermore, volume diffusion usually is not the controlling factor in determining the flux of atoms until an incubation period has elapsed. The thickness of these intermetallic phases were varied from regions to regions on the same wire. Thus, different regions of the same wire experienced various incubation times. This thickness variation makes the problem more complicated. In this study, the initial thickness of intermetallic phases were taken from the average values of over 25 measurements of scanning electron micrographs. The uncertainty on the initial thicknesses may be a major cause for the inconsistency between numerical and experimental results in this study.

It is readily ascertained that only the diffusion coefficients of the η and ε phases and the concentration boundaries of the η and ε phases have any significant effect on the growth rates of the individual phases. The η phase was taken to have a fractional composition range extending from 44.7 to 45.4 at.%Sn and the ε phase from 24.45 to 24.9 at.%Sn. One would not expect large fractional errors in the mean values of the compositions of the two phases, but the width of the composition range (e.g., 45.4–44.7=0.7 at.%Sn for η phase) might well be subject to significant error. However, Verhoeven et al. have proved that changing the value of the composition range of η and ε phases does not significantly affect the calculated values of $T_d$, the tin depletion time.
The finite difference technique can be utilized to establish effective diffusion coefficients and concentration boundaries for intermetallic phases where this information is missing or incomplete. One certainly is able to establish those parameters for each diffusion conditions. The values of $D_\eta$ and $D_\varepsilon$ were adapted from Verhoeven et al.\textsuperscript{62} and were given on page 24. Verhoeven et al. also have explained that these $D_\eta$ and $D_\varepsilon$ values agree reasonably well with several other studies.

The size and number of grid spacings were chosen so as to insure convergence of the numerical solution with minimal computer time. It was found that the optimum number of grid points was 10 for both $\eta$ and $\varepsilon$ phases. Standard finite-difference techniques require that $\Delta x^2/4D_i \geq \Delta t$ in order to insure convergence. The time increment for each iteration varied since the grid spacings changed with time. Since the time factor varied for each phase, the actual time increment used was taken as the minimum for the two different phases at each iteration. This process insured that the solution maintained convergence in both of the phases. Solution convergence was also checked by selection of grid points such that half the chosen number (twice the grid spacing) resulted in essentially the same calculated results.
III. RESULTS

A. Planar Geometry

The closed-form and numerical solutions for this geometry were developed to analyze the experimental results. Four thickness of Sn coatings, 5 \( \mu \text{m} \), 10 \( \mu \text{m} \), 15 \( \mu \text{m} \) and 20 \( \mu \text{m} \), respectively, were analyzed to obtain Sn depletion times and the thicknesses of Sn, \( \eta \) phase and \( \epsilon \) phase at any period of the diffusion process. Figure 8 presents the Sn thickness versus time\(^{1/2} \) for these four thickness coatings. Solid lines represent numerical results and circles the closed-form solution. The difference between these two methods is less than 0.5%. Figure 9 displays the time dependence of Sn layer thickness and the Sn depletion time, \( T_d \), is found to be:

\[
D_0 = 2.7 \times (T_d)^{1/2}
\]

where \( D_0 \) is the original Sn coating thickness, \( T_d \) is the Sn depletion time at 200\(^{\circ}\)C.

The growth rate of intermetallic phases and the depletion of Sn in the process of diffusion are shown as Figure 10 for 10 \( \mu \text{m} \) Sn coated sheet. As shown in Figure 10, the Sn/\( \eta \) and \( \epsilon/\alpha \) interface positions were consistently predicted by both methods. However, the \( \eta/\epsilon \) interface position was slightly
Figure 8. Parabolic relation between the depletion of Sn and diffusion time for the planar geometry case. Temperature = 200°C. Line = numerical solution, circles = analytical solution
Figure 9. Parabolic relation between the thickness of Sn coating and the depletion time for the planar geometry case. Temperature = 200°C. Lines = numerical solution, circles = analytical solution.
Figure 10. Parabolic relation between the Sn depletion, intermetallic phases growth and diffusion time for the planar geometry case. Temperature = 200°C. Lines = numerical solution, circles = analytical solution.
different. The results for 5 μm, 15 μm and 20 μm Sn coated samples were similar to that of the 10 μm sample shown in Figure 10.

The experimental results for 10 μm Sn coated sheet samples are shown as circles in Figure 11. The original Sn layer thickness was 9.43 μm and to convert the data to a 10 μm layer thickness a value of 0.42 μm was added to each data point in Figure 11. The solid lines give a least square fit, from which $k_\eta$ and $k_\varepsilon$ can be determined. The $k_\eta$ and $k_\varepsilon$ values for this experiment are 1.09 x 10^{-6} and 5.72 x 10^{-7} cm/s^{1/2}, respectively. One may go through the same procedure as given on page 31-32 to evaluate the corresponding $D_\eta$ and $D_\varepsilon$ values for this experiment, and the following results are obtained:

$$D_\eta = 2.22 \times 10^{-11} \text{ cm}^2/\text{s}$$
$$D_\varepsilon = 1.16 \times 10^{-11} \text{ cm}^2/\text{s}$$

where the $a_i$ values are $a_1=0.0968$, $a_2=0.01876$, and $a_3=0.1094$.

B. Internal Tin Wire

Because the layer growth rate was not proportional to the square root of the reaction time, the interface positions of four different internal tin wires were plotted versus the reaction time. Figures 12 to 15 are for Sn core diameters of
Figure 11. The experimental results of the depletion of Sn and the growth of intermetallic phases for the planar sheet sample with 10 μm Sn coating. Temperature = 200°C. Lines = least square fit, circles = experimental data.
Figure 12. The depletion of Sn and growth of intermetallic phases for the internal tin wire with 8.6 \( \mu \text{m} \) Sn core. Temperature = 200°C. Lines = numerical solution, circles = experimental data.
Figure 13. The depletion of Sn and growth of intermetallic phases for the internal tin wire with 16 µm Sn core. Temperature = 200°C. Lines = numerical solution, circles = experimental data.
Figure 14. The depletion of Sn and growth of intermetallic phases for the internal tin wire with 19.2 \( \mu m \) Sn core. Temperature = 200°C. Lines = numerical solution, circles = experimental data.
Figure 15. The depletion of Sn and growth of intermetallic phases for the internal tin wire with 29 μm Sn core. Temperature = 200°C. Lines = numerical solution, circles = experimental data.
Figure 16. The exponential relationship between the original diameter of Sn core and the Sn depletion time for the internal tin wire. Temperature = 200°C
8.6 \( \mu \text{m} \), 16 \( \mu \text{m} \), 19.2 \( \mu \text{m} \) and 29 \( \mu \text{m} \) Sn core, respectively. Solid lines give the numerical analysis results and the circles are experimental data. The numerical model predictions correlate only moderately well with the experimental results. Generally speaking, the numerical model predicts less time to finish heat treatment than found by experiment. Also, the deviation between these two results becomes greater with larger Sn core diameter.

Figure 16 displays the relationship between the depletion time and the original Sn core diameter, \( D_0 \). They are related exponentially to each other. The equations describing this relationship for the experimental and numerical results are found to be:

**Experimental:** \[ D_0 = 5.94 \times (T_d)^{1/1.89} \] ........................................(36)

**Numerical:** \[ D_0 = 5.84 \times (T_d)^{1/1.76} \] ........................................(37)

**C. External Tin Wire**

The depletion of Sn and layer growth of intermetallic phases were found to be proportional to the square root of the reaction time for the four different diameters of 10 \( \mu \text{m} \) Sn coated Cu wires. Figures 17 and 18 display the experimental results of Sn thickness and total thickness of intermetallic
Figure 17. Parabolic relation of experimental results between the Sn thickness and diffusion time for the external tin wire. Temperature = 200°C. Symbols = data points, lines = least square fit.
Figure 18. Parabolic relation of experimental results between the total intermetallic layer thickness and diffusion time for the external tin wire. Temperature = 200°C. Symbols = data points, lines = least square fit.
Figure 19. Parabolic relation of numerical results between the Sn thickness and diffusion time for the external tin wire. Temperature = 200°C
Figure 20. Parabolic relation of numerical results between the growth of intermetallic phases and diffusion time for the external tin wire. Temperature = 200°C
Figure 21. The exponential relation of experimental and numerical results between the Sn depletion time and wire diameter for the external tin wire. Temperature = 200°C
phases versus the square root of the reaction time. The original Sn layer thicknesses for these wires were 10.03 µm, 11.18 µm, 10.86 µm, and 9.83 µm for 0.25 mm, 0.5 mm, 1 mm, and 3 mm wires respectively. The thickness values shown on Figures 17 and 18 were obtained by changing the original data by an amount equal to the difference between the original plate thickness and 10 µm. The η phase grows in hillocked morphology, and it makes the measurement of η and ε thicknesses complex. However, the α/ε interface grows relatively smoothly and the ratio of η phase to ε phase thickness is around 1.7.

The numerical model predicts the Sn depletion and layer growth of intermetallic phases have the same relationship, proportional to the square root of the reaction time. The numerical results are shown in Figures 15 and 20. The thickness ratios between η and ε phases range from 1.6 to 1.85.

The time to eliminate the Sn layer thickness, $T_d$, was evaluated by extrapolating a least square fit line of the original data to zero thickness. These $T_d$ values were then corrected to an original Sn layer thickness of 10 µm using the following relation,

$$T_d(10\mu m) = \left(\frac{10}{W_{Sn}}\right)^2 \times T_d(\text{original}) \quad \text{...(38)}$$
where $W_{Sn}$ was the original Sn plate thickness for the particular wire. The experimental $T_d(10\mu m)$ values are compared to the numerical predictions on Figure 21. The experimental results show the relationship between the depletion time and the diameter of Cu wire as follows:

\[
T_d = 14.5 \times e^{-0.082} \frac{r}{e} \quad \text{(39)}
\]

Also, that for the numerical results is

\[
T_d = 14.0 \times e^{-0.092} \frac{r}{e} \quad \text{(40)}
\]

Both of equations (39) and (40) show the depletion times have a limiting value when the diameter of Cu wire approaches infinity.
IV. DISCUSSION

The experimental results in Figure 11 show that the depletion of Sn and the growth of the intermetallic phases are proportional to $t^{1/2}$. The values of $k_{\eta}$ and $k_{\xi}$ of this experiment are $1.09 \times 10^{-6}$ and $5.73 \times 10^{-7}$ cm/s$^{1/2}$, and the corresponding $D_{\eta}$ and $D_{\xi}$ values are $2.22 \times 10^{-11}$ and $1.16 \times 10^{-11}$ cm$^2$/s. Onishi's data\(^6\) give $k_{\eta}=1.06 \times 10^{-6}$ cm/s$^{1/2}$, $k_{\xi}=6.20 \times 10^{-7}$ cm/s$^{1/2}$, $D_{\eta}=2.17 \times 10^{-11}$ cm$^2$/s, and $D_{\xi}=1.29 \times 10^{-11}$ cm$^2$/s. The agreement between these two experiments is good.

The analytical solution given here, which was developed in reference 62, predicted that the time to deplete a 10 $\mu$m Sn layer using Onishi's data would be 14.0 days. This study obtained an experimental value of $T_d=13.0$ days for the 9.43 $\mu$m Sn layer, which converts to $T_d=14.6$ days for 10.0 $\mu$m Sn layer. These results demonstrate the validity of using the analytical solution for the planar geometry to calculate $T_d$.

For the external wires the experimental and numerical results agree fairly well as shown on Figure 21. The experimental values of $T_d$ are consistently higher than numerical results by around 3 to 4%. The source of the error is unknown. There are two major sources of error in these experiments, the appropriate value to use for the original Sn layer thickness, $W_{Sn}$, and the exact time of depletion of the Sn layer, $T_d$. One would expect variations in $T_d$ due to
experimental error to be random. However, the experimental $T_d$ values are consistently higher than the numerical results. Therefore, it seems likely that the major source of error is the value of $W_{Sn}$. The value of $W_{Sn}$ used for Figure 21 was the original average value plus one standard deviation. As mentioned before the standard deviation was added because the thickest area should be the last region to be depleted. If one were to take $W_{Sn}$ as the average plus 1.2 standard deviations, the experimental results fall directly on the numerical results. In view of this result, the agreement between experimental and numerical results seems satisfactory.

For the internal tin wires with small tin core, e.g., 8.6 $\mu$m, the experimental and numerical results show good agreement. However, the agreement becomes progressively poorer as the tin core size becomes larger. For the 16, 19.2 and 29 $\mu$m core wires, Figures 13 to 15, a significant discrepancy occurs for the tin layer thickness at long times. The final 3 to 4 $\mu$m of Sn seems to persist longer than expected, and then suddenly disappears. The cause of this behavior is unknown. It may, however, be related to the void problem discussed below, or perhaps to the fact that as the core thickness increased the final core became more and more distorted from a circular to an elliptical shape.

In the first portion of the mathematical and numerical analyses section, the mathematical closed-form and numerical
models were developed for the planar geometry case. Because the closed-form solution is well-developed[^52,^53,^54,^62], it serves here as a standard solution to confirm the accuracy of the numerical model. The almost exact agreement with the planar geometry case shown in Figures 8 and 10 assure the validity of the numerical model in this study.

A possible source of error between the experimental and numerical results is the formation of voids at the $\alpha/\varepsilon$ interface. Figure 22 is the metallographic cross section of external wire at 200°C for 12 days. According to Verhoeven et al.[^41], the nucleation of voids is probably a result of tensile stresses. They argued that there are two mechanisms which can cause stresses during Sn diffusion. First, when the $\varepsilon/\alpha$ interface advances into the Cu matrix, a given volume of Cu atoms is converted to $\varepsilon$ having a volume $1.59$ times larger. This volume expansion produces tensile stresses in the Cu matrix and can lead to void nucleation. A second mechanism for stress field formation arises from the very steep Sn concentration gradient in the Cu matrix at the $\varepsilon/\alpha$ interface required by the extremely small interdiffusion coefficient at 200°C, $\approx 10^{-20}$ cm²/s[^59]. It is well-established that steep concentration gradients such as these can produce significant strains, for example, in theories of spinodal decomposition[^66]. In the present case, the localized increased Sn content at the interface would expand the Cu matrix, and there produce a
Figure 22. A metallographic cross section view of the external tin wire at 200°C for 12 days. Void formation occurs at α/ε interface. (2000X)
tensile strain in the neighboring Cu region which would resist the expansion. These strains might be quite high due to the magnitude of the gradient caused by the very small D value.

This argument that the tensile stress nucleates voids seems reasonable, if one refers to the results of internal and external tin wires, Figures 22 and 23. In case of the internal tin wire, the ε and α phases all formed internally where the stresses are compressive. The compressive stress reduces the tensile stress produced by the volume expansion resulting from the high Sn concentration in α phase near the interface, and hence the void nucleation is expected to be reduced for the internal tin wire. Figure 23 displays the void formation in the internal tin wire and it is found to be only slightly less of a problem. However, Figures 16 and 21 show that the predictions of the numerical model for the external tin wire are better than that for the internal tin wire. Therefore, it seems unlikely that the void formation problem is the cause for the deviation between experimental and numerical results.

It is apparent from the physics involved that the planar geometry is the upper bound solution for the external tin wire, which means that no matter how large the wire is, its $T_d$ value will always be less than that for the planar geometry. The present results agree with this relationship. The numerical model for the planar geometry predicts 14.0 days,
Figure 23. A metallographic cross section view of the internal tin wire at 200°C for 12 days. Void formation problem is reduced. (1600X)
for a 10 μm Sn coating, which is exactly identical to the value for the numerical model for the wire geometry, extrapolated from equation (40) when r goes to infinity. Moreover, equation (39) of the experimental results presents a similar relationship between these two geometric cases. It is interesting to study how the $T_d$ values change when the geometry transfers from wire to planar (i.e. from small wire to very large wire). The term $\Delta T_d/T_d$ is defined as the fractional decrease the time to deplete Sn for a wire versus a sheet, where $T_d$ is the depletion time for the planar geometry and $\Delta T_d$ is the difference between the $T_d$ values of the planar and wire geometries. Figure 24 shows the fractional decrease in time to deplete Sn as the wire size is increased. The numerical and experimental data show a fairly good agreement in Figure 24. The figure also shows that when the diameter of the wire is larger than 7 mm the tin depletion time is almost as long as that for the planar geometry.

The relationship between the numerical results of internal and external wires is similar to the case described above, although it is not as straightforward. Referring to equation (2a), the mass balance equation for the Sn/η interface, one would realize that other than the direction of interface motion the only difference in calculating the interface positions for both external and internal wires is the
Figure 24. The fractional decrease of time to deplete 10 μm of Sn coating for a wire versus a sheet. Temperature = 200°C
concentration profiles in the intermetallic phases. Equation (40) shows $T_d$ decreases with smaller $r$ which also means that smaller external wire diameters have steeper concentration profiles in the intermetallic phases. As will be shown later, the concentration profile in the intermetallic phases of internal wire is always steeper than in external wire. Thus, the $T_d$ value of internal wire (with a 10 $\mu$m radius Sn core) is always smaller than that of external wire (with a 10 $\mu$m thickness Sn coating). In all, one concludes that the internal tin wire is a lower bound of the solution of the external tin wire in the numerical analysis for the case where the internal tin core radius equals the external tin plate thickness. The experimental results shown in Figures 16 and 21 seem to show this trend. Figures 25 and 26 present the concentration profile in $\eta$ and $\epsilon$ phases for the internal tin wire at times $0.1T_d$, $0.5T_d$ and $T_d$. Figures 27 and 28 reveal the concentration profile in $\eta$ and $\epsilon$ phases for the 0.25 mm external tin wire. The initial concentration-distance profiles were assumed linear while the Sn phase was assumed free of Cu. Figure 26 shows that the concentration profile in the $\epsilon$ phase for the internal tin wire is almost linear during the whole diffusion process. However, Figure 25 demonstrates that the concentration profile in the $\eta$ phase becomes non-linear as the process continues. In order to evaluate the effect of using a nonlinear initial composition profile, the
concentration profile at $T_d$ in Figure 25 was utilized as the initial concentration profile of the $\eta$ phase. This nonlinear initial concentration profile approaches a nearly linear profile within several iteration which means a linear concentration profile is a better choice for the initial $\eta$ phase profile. The profiles for external tin wire are nearly unchanged during the diffusion process.

It was discussed that the low temperature heat treatment was important to both internal and external tin wires. Therefore, it is interesting to compare the minimum depletion times for these two wires. Consider the external tin wire first. If one wants to increase the diameter of a superconducting wire the Sn coating thickness must be increased. Consider, for example, a Cu-Nb wire with a Cu/Nb ratio of 2.3. The thickness of Sn coating, $W_{Sn}$, required to convert all the Nb to $Nb_3Sn$, assuming that the Cu matrix retains 2 at.%Sn (a typical value) is found to vary with the Cu-Nb wire diameter, $D_0$, as,

$$W_{Sn} = 0.044D_0$$

where $W_{Sn}$ and $D_0$ are in mm. Hence, for $D_0$ values of 0.1 mm, 0.25 mm, 0.5 mm, 1.0 mm and 3.0 mm, one is considering Sn
Figure 25. The numerical calculated concentration-distance profile in the η phase of the internal tin wire. Temperature = 200°C
Figure 26. The numerical calculated concentration-distance profile in the $\varepsilon$ phase of the internal tin wire. Temperature $= 200^\circ$C
Figure 27. The numerical calculated concentration-distance profile in the η phase of the external tin wire. Temperature = 200°C
Figure 28. The numerical calculated concentration-distance profile in the ε phase of the external tin wire. Temperature = 200°C
layer thicknesses, $W_{Sn}$, of 4.4 $\mu$m, 11 $\mu$m, 22 $\mu$m, 44 $\mu$m, and 134 $\mu$m, respectively. Now, if one intends to manufacture the same outside diameter wires (0.1 mm, 0.25 mm, 0.5 mm, 1.0 mm and 3.0 mm) with the internal tin process, what size of Sn core can supply the same amount of Sn as external wires having the same outside diameters? Table 1 displays the thickness of the external Sn coatings and diameter of internal Sn cores for this purpose and Figure 29 is a plot of these data.

One may utilize equations (36) and (40) to calculate the depletion time for external and internal wires with the Sn coating thicknesses and the Sn core diameters shown in Table 1. The plots in Figure 30 show the ratio of the depletion time between external and internal wires versus the diameter of wires. The curve labelled Num. is the result calculated from numerical analysis. The curve labelled Expt. is the result obtained from extrapolation of the data equations, numbers 36 and 40. Refer to Figure 30, the internal tin wire has a relatively longer $T_d$, if it is compared to the external tin wire, when the wire is small. However, the $T_d,\text{int}/T_d,\text{ext}$ ratio gets smaller as the wire becomes bigger, and eventually the ratio seems to have a constant value when the wire diameter approaches 10 mm. For a 0.1 mm internal tin wire with 43 $\mu$m Sn core, which is the case of the commercial I. G. C. wire shown in Figure 3, the depletion time is 42 days which is prohibitively long. Fortunately, one of the advantages of
Figure 29. Exponential relation between Sn core diameter, $d_0$, of the internal tin wire and diameter, $D_0$, of the external tin wire. These two wires have same amount of Sn and are designed to have 2 at.%Sn retained in Cu matrix after heat treatment.
Figure 30. The ratio of Sn depletion time of external and internal tin wires versus the wire diameter, $D_0$. These two wires have same amount of Sn, and are designed to have 2 at.%Sn retained in Cu matrix after heat treatment
Table 1. The thickness of Sn coatings and diameters of Sn core for five wire diameters to retain 2 at.%Sn after heat treatment.

<table>
<thead>
<tr>
<th>Wire diameter (mm)</th>
<th>Thickness Sn coating (µm)</th>
<th>Diameter Sn core (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4.4</td>
<td>43</td>
</tr>
<tr>
<td>0.25</td>
<td>11</td>
<td>108</td>
</tr>
<tr>
<td>0.5</td>
<td>22</td>
<td>216</td>
</tr>
<tr>
<td>1.0</td>
<td>44</td>
<td>432</td>
</tr>
<tr>
<td>3.0</td>
<td>134</td>
<td>1316</td>
</tr>
</tbody>
</table>
the internal tin process is it avoids liquid Sn flow because the molten Sn can be held in place by the surrounding Cu-Nb material. Therefore, the 200°C heat treatment for the internal tin wire actually is not necessary. Nevertheless, Higuchi et al.\textsuperscript{47} and Dietderich et al.\textsuperscript{48} showed that the critical current density \(J_c\) of internal tin wire increases when low temperature diffusion heat treatments were performed prior to a high temperature reaction.

Alternately, it is possible to avoid the long time requirements of 200°C heat treatment for the external tin wire by plating speculum metal directly on the Cu\textsuperscript{41}. Speculum metal is an alloy of approximately 45 wt.%Sn-55 wt.%Cu which is utilized industrially because of its high reflectivity and plating techniques are well-developed\textsuperscript{67}. The major problem of this technique is that the as-plated specimen is brittle and presents problems of wire handling after plating.
V. SUMMARY AND CONCLUSION

1. Experiments on stage I, 200°C, of heat treatment in three geometric conditions, planar, internal tin and external tin, are studied. The relationship between the Sn depletion time and thickness of Sn coating or diameter of Sn core has been obtained. The depletion of Sn and growth of intermetallic phases are also measured with reaction time.

2. The experimental results for the time dependence of the Sn, η, and ε phase thicknesses on sheet samples were found to vary as $t^{1/2}$ and agreement with the literature data of Onishi were excellent.

3. The mathematical closed-form solution for the planar geometry condition has been compared to the finite-difference numerical analysis developed here. The closed-form solution predicts the Sn depletion time and thickness of each phases very close to experimental and numerical results for the planar geometric condition.

4. The numerical analysis can trace the interface positions and concentration-distance profiles of each intermetallic phases during the whole diffusion process. The numerical results show that the planar geometry is the upper bound solution of the external tin wire condition. It is also shown that the internal tin wire condition is the lower bound solution of the external tin wire condition.
5. The experimental results are only slightly different from the predictions of the numerical model for the external tin wire case. For the internal tin wire case agreement is good for small core sizes, but becoming increasing poorer at larger core sizes. The cause of the disagreement is uncertain.

6. The main shortcoming of the numerical analysis is probably the need to input initial thickness of intermetallic phases.
VI. REFERENCES


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VII. ACKNOWLEDGMENTS

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He also gratefully acknowledges Associate Professor K. A. Heimes of the Mathematics Department for developing the mathematical closed-form model and H. H. Baker for the metallographic work.

He wishes to give a special acknowledgment with deep appreciation to his parents and brothers, whose understanding and encouragement were essential ingredients during his studies. Finally, he also owes great appreciation to his wife, Yug-Yea Wang, for her constant encouragement and understanding.
A. The Computer Program for the Planar Geometry Case

This program is written to trace the interface positions and the concentration-distance profiles in the intermetallic phases of Cu-Sn system. The temperature of the heat treatment for this program is 200°C. The number of grid for γ and ε phases is 10.

***This program is for Z1 μm of tin coating on planar Cu sheet.***********************************************

```fortran
REAL C(1), D(11), EEP(11), DDP(11), E(11), DP(11), EP(11)
REAL T, Z1, Z2, Z3, D1, D2, D3, DT, Z, DZ, X1, X2, X3, X5, X6, A1
REAL A2, A4, A5, Y1, Y2, Y3, B1, B2, B3, B4, P1, P2, P3, ZSN, ZN
REAL ZE, Q3, OA, DA, TA, ZP, Q, Q1, Q2, DD, DX, DY, ZZ, TN, TE,
REAL ZTN, ZTE
INTEGER I, J, K(500), N, M

C to input the thickness of tin coating and the starting time.
READ (5.*) Z1, T
ZSN = Z1 - 2*0.073371*(2.15E-3*T)**.5
Z2 = 2*0.0407484*(2.15E-3*T)**.5 + Z1 - ZSN
Z3 = 2*1.384992*(1.3E-3*T)**.5 + Z1 - ZSN - Z2

C to input the diffusion coefficients
D2 = 2.15E-3
D3 = 1.3E-3
Z2 = Z1
Z3 = ZSN

C to set up the boundary conditions and assume the starting concentration profiles are linear.
C(22) = 1.00
D(2) = .454
DO 4 I = 2, 10, 1
  4 D(I+1) = Q
D(12) = .447
E(2) = .249
DO 7 I = 2, 10, 1
  7 E(I+1) = Q
G = .007
DO 39 J = 1, 500000, 1

C to set the time interval as Δx^2/4D_1 ≥ Δt.
DO 39 J = 1, 500000, 1
T2 = (Z2/10)**2/(4*2.15E-3)
T3 = (Z3/10)**2/(4*1.3E-3)

10 DT = T2
11 IF(DT - T2) 13, 13, 12
```
12 DT=T3

13 X1=4*D(3)-D(4)-3*.454
X2=Z2*2
X3=2.15E-3*10*X1/X2
X5=1.8315018
X6=X5*X3
Z=Z1+DT*X6
DZ=DT*X6
IF(Z-.00)40,40,17

17 DO 18 I=3,11,1
A1=(10-I)*(D(I+1)-D(I-1))*X6/(Z2*2)
A2=D2*10**2*(D(I-1)-2*D(I)+D(I+1))/Z2**2
A5=A1+A2
18 DP(I)=DT*A5
Z1=Z
T=T+DT

19 DO 18 I=3,11,1
A1=I*(D(I+1)-D(I-1))*X3/(Z2*2)
A2=D2*10**2*(D(I-1)-2*D(I)+D(I+1))/Z2**2
A4=A1+A2
22 DP(I)=DT*A4
DO 23 I=3,11,1
23 D(I)=DP(I)+DDP(I)+D(I)

21 DO 22 I=3,11,1
B1=(10-I)*(E(I+1)-E(I-1))*Y3/(Z2*2)
B2=D3*10**2*(E(I-1)-2*E(I)+E(I+1))/Z3**2
B4=B1+B2
24 EP(I)=DT*B4
Z2=Z

26 DO 24 I=3,11,1
B1=(10-I)*(E(I+1)-E(I-1))*P3/(Z3*2)
B2=D3*10**2*(E(I-1)-2*E(I)+E(I+1))/Z3**2
A4=A1+A2
28 EP(I)=DT*A4
DO 29 I=3,11,1
29 E(I)=EP(I)+EEP(I)+E(I)
Z3 = Z
IF(Z1 - .0001) 33, 33, 31
31 DO 32 I = 1, 500, 1
   K(I) = I * 1000
32 IF(J .EQ. K(I)) GO TO 33
   GO TO 39
33 DD = T / 86400
   DX = 2.15E-3
   DY = 1.30E-3
   TN = Z1 + Z2
   TE = TN + Z3
   ZP = ZZ - 2 * .073371 * (DX * T) ** .5
   ZN = ZZ - 2 * .0407484 * (DX * T) ** .5 - ZP
   ZE = ZZ + 2 * .1384992 * (DY * T) ** .5 - ZN - ZP
   Q1 = Z1 - ZP
   Q2 = Z2 - ZN
   Q3 = Z3 - ZE
   ZTN = ZP + ZN
   ZTE = ZTN + ZE
   WRITE (1, *) J
34 TYPE *, J
35 WRITE (1, *) LOG10(T), T, DD
36 TYPE *, LOG10(T), T, DD
37 WRITE (1, *) Z1, Z2, Z3, TN, TE
38 TYPE *, Z1, Z2, Z3, TN, TE
   WRITE (1, *) ZP, ZN, ZE, ZTN, ZTE
   TYPE *, ZP, ZN, ZE, ZTN, ZTE
   WRITE (1, *) Q1, Q2, Q3
   TYPE *, Q1, Q2, Q3
39 CONTINUE
40 STOP
END
B. The Computer Program for the Internal Tin Wire Case

**This program is for the internal tin wire with **21*2

C

\[ C(1), D(11), E(11), F(11), G(11), H(11), J(11), K(11), L(11), M(11) \]

REAL C(1), D(11), E(11), F(11), G(11), H(11), J(11), K(11), L(11), M(11)
REAL T, Z1, Z2, Z3, D1, D2, D3, D4, D5, D6, D7, D8, D9, D10
REAL X5, X6, A1, A2, A3, A4, A5, ZC, Y1, Y2, Y3, B1, B2, B3, B4, B5
REAL P2, P3, Q, ZSN, TN, TE
INTEGER I, J, K, N, M

C to set up the initial conditions and input diffusion coefficients.

READ (1, *) T, Z1, Z2, Z3
C(21)=1.
D2=2.15E-3
D3=1.30E-3
D(0)=.454
DO 2 I=0, 9, 1
Q=D(I)-7.E-4
2 D(I+1)=Q
D(10)=.447
E(0)=.249
DO 5 I=0, 9, 1
Q=E(I)-4.5E-4
5 E(I+1)=Q
E(10)=.2445
G=.007

C to set the time interval as \( \Delta x^2/4D_i \geq \Delta t \).

DO 7 J=1, 500000, 1
T2=(Z2/10)**2/(4*2.15E-3)
T3=(Z3/10)**2/(4*1.3E-3)
10 DT=T2
11 IF(DT-T3)13, 13, 12
12 DT=T3

C equation (24)

X1=4*D(1)-D(2)-3*.454
X2=Z2*2
X3=2.15E-3*10*X1/X2
X5=1.8315018
X6=X5*X3
ZA=Z1+DT*X6
DZ=DT*X6
IF(ZA=.00)40, 40, 17
C equation (30b)

DO 17 I=1, 9, 1
A1=(10-I)*(D(I+1)-D(I-1))*X6/(Z2*2)
A2=2.15E-3*10**2*(D(I-1)-2*D(I)+D(I+1))/Z2**2
A3=2.15E-3*10*(D(I+1)-D(I-1))/((Z1+Z2/10)*(Z2**2))
A5=A1+A2+A3
17 DP(I)=DT*A5
T = T + DT

C equation (24)

\[ Y_1 = 1.3E-3 \times 10^*(4*E(1) - E(2) - 3* .249)/(Z3*2) \]
\[ Y_2 = 2.15E-3 \times 10^*(D(8) - 4*D(9) + 3* .447)/(Z2*2) \]
\[ Y_3 = 5.0505051*(Y_1 - Y_2) \]
\[ ZB = DT*Y3 + Z2 - DZ \]
\[ DZ = DT*Y3 \]

C equation (30a)

DO 20 1 = 1, 9, 1
\[ A1 = 1*(D(I+1)-D(I-1))*Y3/(Z2*2) \]
\[ A2 = 2.15E-3*10^2*(D(I-1)-2*D(I)+D(I+1))/(Z2*2) \]
\[ A3 = 2.15E-3*10*(D(I+1)-D(I-1))/(Z1+(I*Z2)/10)*Z2*2 \]
\[ A4 = A1 + A2 + A3 \]

20 DDP(I) = DT*A4

DO 21 1 = 1, 9, 1
\[ D(I) = DP(I) + DDP(I) + D(I) \]

C equation (30b)

DO 22 1 = 1, 9, 1
\[ B1 = (10-I)*(E(I+1)-E(I-1))*Y3/(Z3*2) \]
\[ B2 = 1.3E-3*10^2*(E(I-1)-2*E(I)+E(I+1))/(Z3*2) \]
\[ B3 = 1.3E-3*10*(E(I+1)-E(I-1))/((Z1+Z2+(I*Z3)/10)*Z3*2) \]
\[ B4 = B1 + B2 + B3 \]

22 EP(I) = DT*B4

C equation (24)

\[ P1 = 1.3E-3 \times 10^*(E(8) - 4*E(9) + 3* .2445)/(Z3*2) \]
\[ P2 = 4.2105263 \]
\[ P3 = P2*(0-P1) \]
\[ ZC = DT*P3 + Z3 - DZ \]

C equation (30a)

DO 27 28 1 = 1, 9, 1
\[ A1 = 1*(E(I+1)-E(I-1))*P3/(Z3*2) \]
\[ A2 = 1.3E-3*10^2*(E(I-1)-2*E(I)+E(I+1))/(Z3*2) \]
\[ A3 = 1.3E-3*10*(E(I+1)-E(I-1))/((Z1+Z2+(I*Z3)/10)*Z3*2) \]
\[ A4 = A1 + A2 + A3 \]

28 EP(I) = DT*A4

DO 29 1 = 1, 9, 1
\[ E(I) = EP(I) + EEP(I) + E(I) \]
\[ Z1 = ZA \]
\[ Z2 = ZB \]
\[ Z3 = ZC \]
\[ IF(Z1 = .005)33,33,31 \]

31 DO 32 1 = 1, 500, 1
\[ K(I) = I*1000 \]

32 IF(J .EQ. K(I)) GO TO 33

GO TO 39

33 TN = Z1 + Z2
\[ TE = TN + Z3 \]
\[ DD = T/86400 \]
WRITE (3, *) J

35 WRITE (3, *) LOG10(T), T, DD
37 WRITE (3,*) Z1, Z2, Z3, TN, TE
39 CONTINUE
40 STOP
   END
C. The Computer Program for the External Tin Wire Case

**This program is for 1 mm copper wire with 10 μm of tin coating.**************

```fortran
REAL C(1),D(11),E(11),DP(11),EE(11)
REAL T,Z1,Z2,Z3,D1,D2,D3,DD,DT,DZ,G,X1,X2,X3,ZA,ZB
REAL X5,X6,A1,A2,A3,A4,A5,ZC,Y1,Y2,Y3,B1,B2,B3,B4
REAL P1,P2,P3,Q,ZSN,TN,TE,R,R1,R2,R3
INTEGER I,J,K(500),N,M

to set up the initial conditions and input the diffusion coefficients.
READ (1,*),T,Z1,Z2,Z3
R=515.+10.
R1=R-Z1
R2=R1-Z2
R3=R2-Z3
D2=2.15E-3
D3=1.3E-3
C(21)=1.
D(0)=.454
DO 2 1=0,9,1
  Q=D(I)-7.E-4
  D(I+1)=Q
  D(10)=.447
E(0)=.249
DO 5 1=0,9,1
  Q=E(I)-4.5E-4
  E(I+1)=Q
  E(10)=.2445
G=.007
to set the time internal as Δx^2/4D_i ≥ Δt.
7 DO 39 J=1,500000,1
  T2=(Z2/10)**2/(4*2.15E-3)
  T3=(Z3/10)**2/(4*1.3E-3)
10 DT=T2
11 IF(DT-T3)13,13,12
12 DT=T3

equation (24)
13 X1=4*D(1)-D(2)-3*.454
  X2=Z2*2
  X3=2.15E-3*10*X1/X2
  X5=1.8315018
  X6=X5*X3
  ZA=Z1+DT*X6
  DZ=DT*X6
  IF(ZA-.00)40,40,17

equation (30b)
17 DO 18 I=1,9,1
  A1=(10-I)*(D(I+1)-D(I-1))*X6/(Z2*2)
```

100
A2 = 2.15E-3 * 10**2 * (D(I) + D(I+1)) / Z2**2  
A3 = 2.15E-3 * 10**2 * (D(I+1) - D(I-1)) / ((R1 - I * Z2/10) * (Z2 * 2))  
A5 = A1 + A2 + A3  
18 DP(I) = DT * A5  
T = T + DT  
C equation (24)  
Y1 = 1.3E-3 * 10**2 * (4 * E(1) - E(2) - 3 * .249) / (Z3 * 2)  
Y2 = 2.15E-3 * 10**2 * (E(8) - 4 * E(9) + 3 * .447) / (Z2 * 2)  
Y3 = 5.0505051 * (Y1 - Y2)  
ZB = DT * Y3 + ZB - DZ  
DZ = DT * Y3  
C equation (30a)  
DO 20 I = 1, 9, 1  
A1 = I * (D(I+1) - D(I-1)) * Y3 / (Z2 * 2)  
A2 = 2.15E-3 * 10**2 * (D(I-1) - 2 * D(I) + D(I+1)) / Z2**2  
A3 = 2.15E-3 * 10**2 * (D(I+1) - D(I-1)) / ((R1 - (I * Z2)/10) * Z2 * 2)  
A4 = A1 + A2 + A3  
20 DDP(I) = DT * A4  
DO 21 I = 1, 9, 1  
21 D(I) = DP(I) + DDP(I) + D(I)  
C equation (30b)  
DO 22 I = 1, 9, 1  
B1 = (10 - I) * (E(I+1) - E(I-1)) * Y3 / (Z3 * 2)  
B2 = 1.3E-3 * 10**2 * (E(I-1) - 2 * E(I) + E(I+1)) / Z3**2  
B3 = 1.3E-3 * 10**2 * (E(I+1) - E(I-1)) / ((R2 - (I * Z3)/10) * Z3**2)  
B4 = B1 + B2 + B3  
22 EP(I) = DT * B4  
C equation (24)  
P1 = 1.3E-3 * 10**2 * (E(8) - 4 * E(9) + 3 * .2445) / (Z3 * 2)  
P2 = 4.2105263  
P3 = P2 * (E - P1)  
ZC = DT * P3 + ZC - DZ  
DZ = DT * P3  
C equation (30a)  
DO 28 I = 1, 9, 1  
A1 = I * (E(I+1) - E(I-1)) * P3 / (Z3 * 2)  
A2 = 1.3E-3 * 10**2 * (E(I-1) - 2 * E(I) + E(I+1)) / Z3**2  
A3 = 1.3E-3 * 10**2 * (E(I+1) - E(I-1)) / ((R2 - (I * Z3)/10) * Z3**2)  
A4 = A1 + A2 + A3  
28 EP(I) = DT * A4  
DO 29 I = 1, 9, 1  
29 E(I) = EP(I) + EEP(I) + E(I)  
Z1 = ZA  
Z2 = ZB  
Z3 = ZC  
R1 = R - Z1  
R2 = R1 - Z2  
R3 = R2 - Z3  
IF (Z1 < .005) 33, 33, 31  
31 DO 32 I = 1, 500, 1  
K(I) = I * 1000
32 IF(J .EQ. K(I)) GO TO 33
        GO TO 39
33  DD=T/86400
    WRITE (3,*) J
    WRITE (3,*) LOG10(T),T,DD
    WRITE (3,*) Z1,Z2,Z3
39  CONTINUE
40  STOP
    END