

Kinetics of Nb₃Sn, Cu₆Sn₅ and Cu₃Sn layer growth

Yogendra Singh* and Subrata Pradhan

Institute for Plasma Research, Bhat, Gandhinagar-382 428, India.

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Abstract

Niobium tin intermetallic compounds are formed by diffusion of Tin (Sn) from bronze matrix to niobium (Nb). Formation of Nb₃Sn is governed by uphill diffusion. Concentration of Sn is uniform in the layer of Nb₃Sn. Rate of Nb₃Sn layer growth is given by the equation $dx/dt=1/(x/D+1/k)$ where K is the rate constant in kinetic regime in m/s and D is the diffusion coefficient of Sn in Nb₃Sn in m²/s. By integrating this equation, the layer thickness at particular time can be found out. Alternate approach of Nb₃Sn layer formation can be described by finite element method. In this approach the mass concentration is considered. Kinetics of Nb₃Sn layer formation is governed by the kinetic regime

and diffusion regime of these chemical reactions. Layer growth is governed by the equation $S(t) = \frac{1}{B_1} \left[\left(1 + 2B_1 \left(\left(\frac{B_1}{\beta} \right) t + \frac{1}{2} B_1 b^2 \right) \right)^{\frac{1}{2}} - 1 \right]$. 'B₁', 'β' and 'b' are the constants and S(t) is the layer thickness of Nb₃Sn. Concentration of Sn at particular time and distance at Nb-Nb₃Sn interfaces given by the equation $C(x, t) = 1 - \frac{B_1}{(1+B_1 S(t))} x$. 'x' is the distance from Sn-Nb₃Sn interface. Kinetics of Cu-Sn is also elaborated. Equations are derived for the phase formation of Cu₆Sn₅ and Cu₃Sn. Rate of reaction can be calculated at interfaces with experimental data obtained from such binary systems.

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Introduction

Internal tin method is widely adopted at manufacturing multifilamentary superconductor materials involving Nb₃Sn. In the internal Sn process, solid pure or a slightly impure Sn is used as a source of Sn. In this process, there is basically no limit to the amount of Sn, though the bronze processed wire has to use bronze with the Sn content of up to 15.8%¹.

Owing to the reactive diffusion of tin during the annealing, Nb₃Sn intermetallic compound formed as a layer at the interface of Nb and the Cu-Sn alloy. The growth behaviour of the Nb₃Sn layer has been studied by several investigators. In most of these investigations mono-filamentary and multifilamentary diffusion couples have been employed. In such diffusion couples, the inter-diffusion of the constituent components takes place in rather complicated manners. Hence formation of Nb₃Sn layer with a uniform thickness is quite challenging to be formed. Further, the filamentary diffusion couples are not adequate for kinetics investigations of the Nb₃Sn layer.

Appreciating these limitations, we have attempted to kinetically study this Nb₃Sn layer formation theoretically with the help of some experimental data. Two different approaches have been considered. Cu-Sn system is critical in internal tin route on the Nb₃Sn formation is often governed by multi step heat treatment. Two phases Cu₆Sn₅ and Cu₃Sn found in Cu-Sn system when Nb₃Sn is formed by two step heat treatment. First step is recommended in range of 150 °C to 230 °C and second step is carried out at a temperature greater than 600 °C. Rate of formations of phases are attempted to be found out at various interfaces of Cu-

Sn system in this investigation. The basic kinetics of Nb₃Sn formation has been described next.

Experimental

1. Kinetics of Nb₃Sn formation

Two different approaches have been emphasized. First one is focused at diffusion regimes and kinetic regimes of the chemical reactions. The behavior of layer growth of Nb₃Sn is then described with finite element method.

1.1 Diffusion of Sn in Nb cylindrical system

Cylindrical geometry is the most practical geometry to be considered in. Mostly a right circular cylinder shaped billet of oxygen free high conductivity copper is considered to begin with. In these billets, the high homogeneous Nb rods are inserted in precisely drilled holes after which the tin filling is done in the center. The entire composite billet is then extruded and drawn. Nb₃Sn is formed by the diffusion of Sn from bronze matrix to niobium. The Sn concentration is uniform near the Nb in bronze matrix. It is generally 8-10 at%. This is schematically shown in Fig.1 and 2.

As shown in figure (1) and (2).

C_s = Surface concentration of tin near the Nb cylinder i.e. 8-10 at% (Assumed to be constant for all the time)

C₀ = Concentration of Sn in Nb at t=0 which is considered to be zero.

C = Concentration of Sn in Nb after diffusion time of t.

a = radius of the niobium cylinder

The concentration varies as a function of time in Nb cylindrical system in accordance with Fick's second law:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(rD \frac{\partial C}{\partial r} \right) \quad \text{----(1)}$$

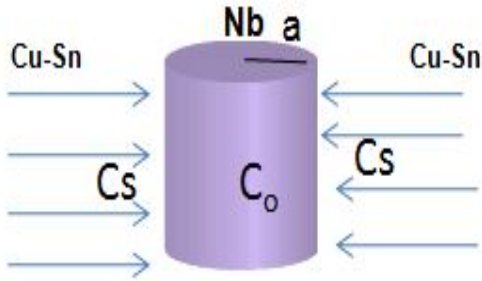


Figure 1: Sn is shown to be diffusing in Nb having radius 'a'.

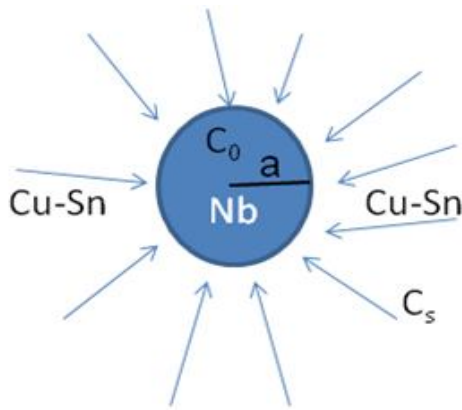


Figure 2: Sn diffusion to Nb as seen from top

Following boundary conditions have been adopted:

$$C=C_0 \text{ at } t=0 \text{ and } 0 < r < a$$

$$C=C_s \text{ at } r=a \text{ and } 0 < t < \infty$$

Solving equation (1) with given boundary conditions yields equation (2).²

$$\frac{Dt}{r^2} = -0.0675375 - 0.3988 \log(1 - F) \quad \text{---- (2)}$$

Where, $F = \frac{C-C_0}{C_s-C_0}$; known as the Fractional concentration of Sn in Nb after diffusion time of t.

1.2 Uphill Diffusion

The uphill diffusion is best described when the diffusion is not governing by concentration of gradient by the gradient of free energy. In such cases atoms diffuse from lower concentration to higher concentration as per the available free energy with them. In this case atoms diffuse from lower concentration to higher concentration. As Sn starts to diffuse layer formation takes place according to Fig. 3.

Nb₃Sn layer forms at yellow reason where concentration of Sn at certain time t is 18-25 at% as per Nb-Sn phase diagram but value of C_s is only 8-10 at%^[3-4].

The value of 'F' in equation (2) as described in the previous section is necessarily required to be less than unity to ensure a positive diffusion However, Considering C= 25, C₀ =0, C_s = 8, the value of 'F' is found to be 3.12. Then equation (2) is unphysical.

This indicates the chemical reaction described above cannot be explained adequately following Fick's law. This need to be described by another approach described in section 2.3.

Nb₃Sn layer forms at yellow reason where concentration of Sn at certain time t is 18-25 at% but value of C_s is only 8-10 at%³⁻⁴.

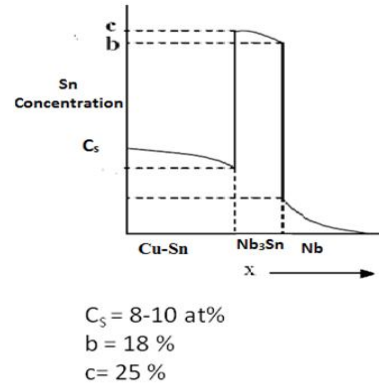
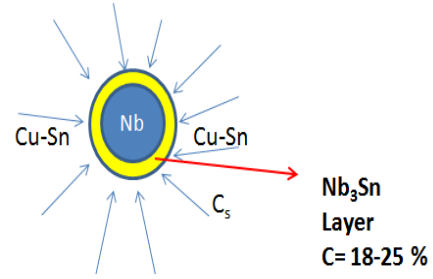
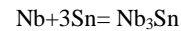


Figure 3: Layer formation of Nb₃Sn after time t and Concentration Variation from surface to center.

1.3 Kinetics approach for the kinetics of Nb₃Sn formation:

In this section, the kinetics of Nb₃Sn formation has been described. Only Sn is considered to be moving towards Nb and forms Nb₃Sn. reaction is written as



Initially the layer growth of Nb₃Sn is dominating by kinetic regime of reaction. Later the reaction of layer formation is governing by diffusion kinetics.

It is assumed that at time 't' a thickness 'x' of Nb₃Sn forms. At time t+dt the thickness becomes x+dx.

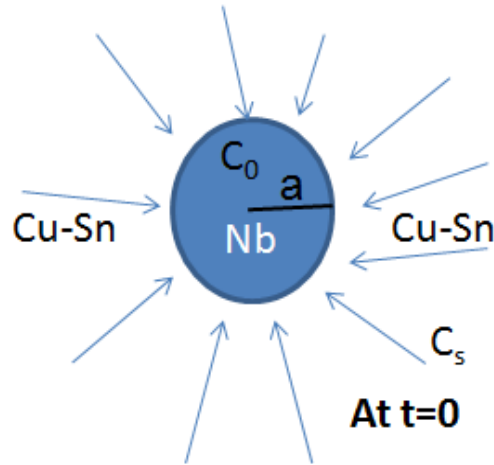


Figure 4: At initial position

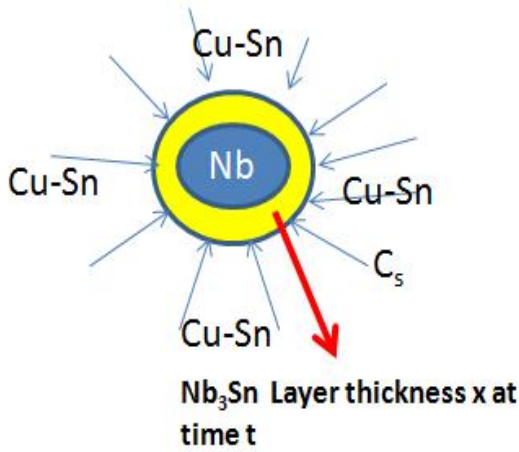


Figure 5: Layer forms at time 't' in kinetic regime

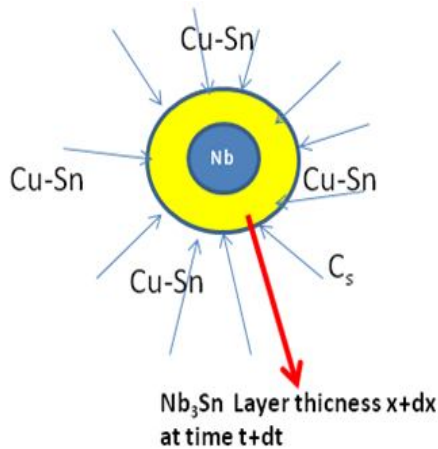


Figure 6: layer increment at t+dt in diffusion regime

As the Sn reaches Nb, the formation of Nb₃Sn takes place. The layer of Nb₃Sn gets formed. This results in shifting of Nb-Nb₃Sn interface towards center. These are schematically shown in figures (3),(4),(5). Reaction kinetics is shown in Fig. 6.

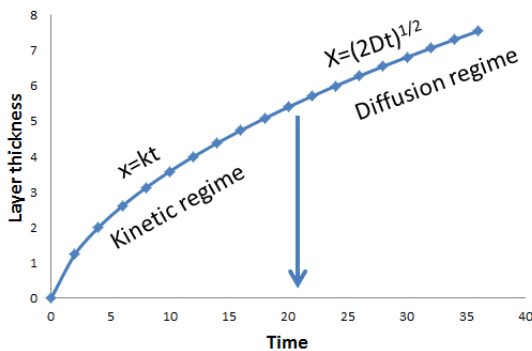


Figure 7: Kinetic regime and diffusion regime of reaction.

As illustrated in the above figures the layer thickness increment is described by the equations given below:

The total time 'dt' taken is given by

$$dt = dt_{reaction} + dt_{diff} \quad \text{----- (3)}$$

Where $dt_{reaction}$ = time for reaction at Nb- Nb₃Sn interface or Nb-Sn interface at $t=0$. dt_{diff} = time taken to reach the Sn up to Nb-Nb₃Sn interface. $dt_{reaction}$ is the time for reaction that is proportional to dx .

$$dt_{reaction} = \frac{dx}{K} \quad \text{---- (4)}$$

K = rate constant in m/s.

Here dt_{diff} is proportional to multiplication of Δx and dx .

$$dt_{diff} = x \frac{dx}{D} \quad \text{---- (5)}$$

D = diffusion coefficient of Sn through Nb₃Sn in m²/s.

So equation (3) can be written as:

$$dt = x \frac{dx}{D} + \frac{dx}{K} \quad \text{---- (6)}$$

Time required for formation of the Nb₃Sn of x layer thickness can be written as:

$$t = \frac{x}{K} + \frac{x^2}{2D} \quad \text{(by integrating above equation 6)} \quad \text{---- (7)}$$

Rate of layer growth can be written as:

$$\frac{dx}{dt} = \frac{1}{\frac{x}{D} + \frac{1}{K}} \quad \text{---- (8)}$$

Thickness of layer at particular time t also calculated by solutions of quadratic equation (7)

$$X = D \left(-\frac{1}{K} + \left(\left(\frac{1}{K} \right)^2 + \frac{2t}{D} \right)^{\frac{1}{2}} \right) \quad \text{---- (9)}$$

Above formulae are essential towards finding out the rate of layer growth, thickness of layer at particular time.

Heat treatment has been carried out of Nb₃Sn/Cu strand at 650°C for 40, 80, 160 and 200 hrs. Data of layer thickness of these heat treatments has been used to calculate the rate of layer growth. Rate of layer growth of Nb₃Sn is 4.62×10^{-12} m/s at 200 hrs at 650°C.

1.4 Kinetics of Nb₃Sn by finite element method

As explained earlier the kinetics of Nb₃Sn layer growth has also been explained by finite element methods. Quasi steady case has been solved by Paul Murray and G.F. Curray.

As per their formulation, the Position of Moving boundary at time t is given as⁶

$$S(t) = \frac{1}{B_i} \left[\left(1 + 2B_i \left(\left(\frac{B_i}{\beta} \right) t + \frac{1}{2} B_i b^2 \right) \right)^{\frac{1}{2}} - 1 \right] \quad \text{--- (10)}$$

Where $\beta = Ml^2/CDT$,

M = mass of reaction;

l = characteristic length of diffusion,

C = total Mass concentration,

t = time.

Mass concentration of Sn with respect to time and distance at Nb₃Sn-Nb interface is given as [6]:

$$C(x, t) = 1 - \frac{B_i}{(1+B_i S(t))} x \quad \text{---- (11)}$$

Where $B_i = kl/D$,

K = rate constant of reaction.

Behavior of position of moving boundary and concentration by taken $B_i = \beta = 1$ given in figure (7) and (8).

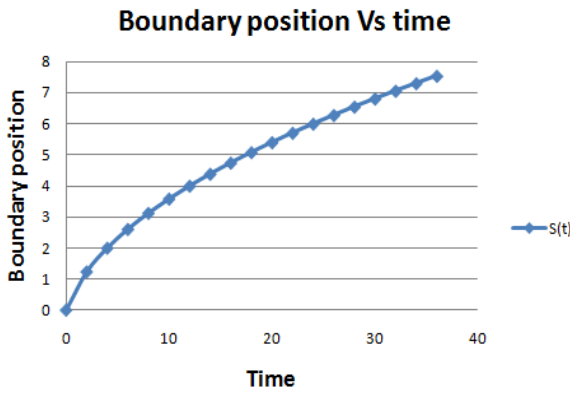


Figure 8: Boundary position behaviour

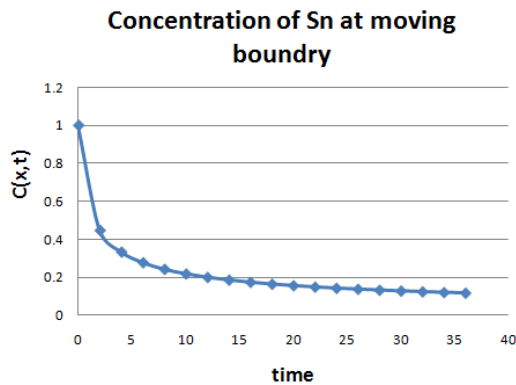


Figure 9: MassConcentration behaviour

Layer thickness of Nb₃Sn behaves linearly for short times and parabolically for large times.

2. Kinetics of Cu₆Sn₅, Cu₃Sn layer growth⁷

Intermetallic compound of Cu-Sn formed during the heat treatment of Nb₃Sn/Cu strands. These intermetallic compounds have been formed by heating the stack single thin layers of copper and tin also⁸⁻⁹. So, it is important to understand the layer growth of these intermetallic compounds theoretically. Figure (9) shows a schematic diagram illustrating the growth process of the layers of two intermetallic compounds Cu₃Sn and Cu₆Sn₅ at the Cu-Sn interface. Direct chemical reaction between primary components Cu and Sn clearly ceases after the formation of compound layers Cu₃Sn and Cu₆Sn₅. These layers separate the reacting phases from each other. Subsequently, four chemical reactions take place at the layer interfaces. They described below at each of the interfaces.

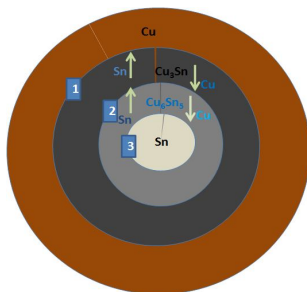
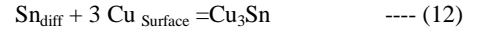


Figure 10: Layers of Cu₃Sn and Cu₆Sn₅ in Cu-Sn system

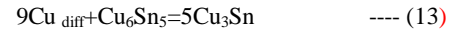
At interface 1:

Sn diffuses in both of the layers and reaches at interface 1 from center. It reacts with Cu at the surface of interface 1. Thus, the reaction can be written as shown below:



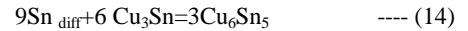
At interface 2:

At interface 2, both Cu₃Sn and Cu₆Sn₅ phases forms. Cu₃Sn phase forms, when Cu diffuses through Cu₃Sn and reach at interface 2 and reacts with Cu₆Sn₅. Thus, the reaction can be written as:



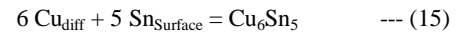
At interface 2:

At interface 2, Cu₆Sn₅ phase forms as Sn diffuses through Cu₆Sn₅ and reaches at interface 2. Then it reacts with Cu₃Sn. Thus, the reaction can be written as shown below:



At interface 3:

Cu diffuses from both of the layers and reaches at interface 3 from interface 1. Then it reacts with Sn at the surface of interface 3. Thus, the reaction can be written as



Assuming that layers of Cu₃Sn and Cu₆Sn₅ get formed at particular time t with thickness of x and y. During an infinitesimal period of time, dt the thickness of the Cu₃Sn layer increases by dx_{Sn} at interface 1 as a result of reaction (12) and by dx_{Cu} at Interface 2 as a result of reaction (13), (shown in Fig 10) At the same time, the thickness of the Cu₆Sn₅ layer increases by dy_{Sn} at interface 2 and by dy_{Cu} at interface 3 due to reactions (14) and (15) respectively.

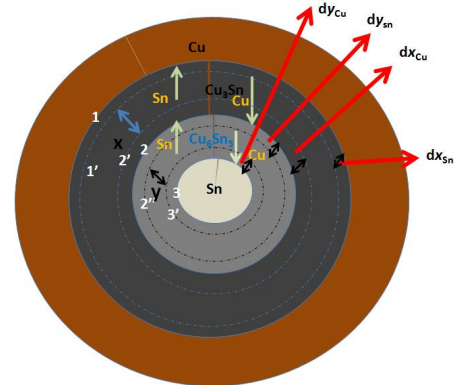


Figure 11: Increment in thickness of Cu₃Sn and Cu₆Sn₅ in infinitesimal time dt

In order to establish the equations relating dt to the increases, dx_{Sn}, dx_{Cu}, dy_{Sn} and dy_{Cu}, in thicknesses of the Cu₃Sn and Cu₆Sn₅ layers, the summation of the time of diffusion of the Cu or Sn atoms and the time of subsequent chemical transformations for each of chemical reactions are taken at phase interfaces 1, 2 and 3. This results in:

At interface 1:

$$dt = dt_{\text{diff}}(\text{Sn} \rightarrow \text{Cu}_3\text{Sn}) + dt_{\text{chem}}(\text{Sn} \rightarrow \text{Cu}_3\text{Sn}) \quad \text{--- (16)}$$

Where dt_{diff}(Sn → Cu₃Sn) is the time to reach interface 1 for forming Cu₃Sn and dt_{chem}(Sn → Cu₃Sn) is the time required in chemical reactions at interface 1.

At interface 2:

$$dt = dt_{diff}(Cu \rightarrow Cu_3Sn) + dt_{chem.}(Cu \rightarrow Cu_3Sn) \quad \text{---- (17)}$$

Where, $dt_{diff}(Cu \rightarrow Cu_3Sn)$ is the time to reach interface 2 for forming Cu_3Sn and $dt_{chem.}(Cu \rightarrow Cu_3Sn)$ is the time required in chemical reaction at interface 2.

At interface 2:

$$dt = dt_{diff}(Sn \rightarrow Cu_6Sn_5) + dt_{chem.}(Sn \rightarrow Cu_6Sn_5) \quad \text{---- (18)}$$

Where $dt_{diff}(Sn \rightarrow Cu_6Sn_5)$ is the time takes to reach interface 2 for forming Cu_6Sn_5 and $dt_{chem.}(Sn \rightarrow Cu_6Sn_5)$ is the the time required for the chemical reactions at interface 2.

At interface 3:

$$dt = dt_{diff}(Cu \rightarrow Cu_6Sn_5) + dt_{chem.}(Cu \rightarrow Cu_6Sn_5) \quad \text{---- (19)}$$

Where $dt_{diff}(Cu \rightarrow Cu_6Sn_5)$ is the time to reach interface 3 for forming Cu_6Sn_5 and $dt_{chem.}(Cu \rightarrow Cu_6Sn_5)$ is the the time required for the chemical reactions at interface 3.

Time of the diffusion i.e. dt_{diff} is directly proportional to both the increase of the thickness of a given compound layer and its existing total thickness, whereas the time of chemical transformations is directly proportional to the increase of the thickness of the layer and is quite independent of its total thickness. Hence, equations (16),(17),(18) and (19) can we written as:

At interface 1:

$$dt = (x/D_{Sn-Cu_3Sn} + 1/K_{Sn1})dx_{sn} \quad \text{---- (20)}$$

Where D_{Sn-Cu_3Sn} is the diffusion coefficient of Sn in Cu_3Sn and K_{Sn1} is the rate constant of chemical reaction at interface1. 'x' is the existing thickness of Cu_3Sn at time 't' shown in figure2. 'dx_{sn}' is the increment in thickness after time dt.

At interface 2:

$$dt = (x/D_{Cu-Cu_3Sn} + 1/K_{Cu2})dx_{Cu} \quad \text{----(21)}$$

Where, D_{Cu-Cu_3Sn} is the diffusion coefficient of Cu in Cu_3Sn and K_{Cu2} is the rate constant of chemical reaction at interface2. 'x' is the existing thickness of Cu_3Sn at time 't' as shown in figure(10). 'dx_{cu}' is the increment in thickness after time dt.

At interface 2:

$$dt = (y/D_{Sn-Cu_6Sn_5} + 1/K_{Sn2})dy_{sn} \quad \text{----- (22)}$$

Where, $D_{Cu-Cu_6Sn_5}$ is the diffusion coefficient of Sn in Cu_6Sn_5 and K_{Sn2} is the rate constant of chemical reaction at interface2. 'y' is the existing thickness of Cu_6Sn_5 at time 't' as shown in figure (10). 'dy_{sn}' is the increment of thickness after time dt.

At interface 3:

$$dt = (y/D_{Cu-Cu_6Sn_5} + 1/K_{Cu3})dy_{Cu} \quad \text{----- (23)}$$

Where $D_{Cu-Cu_6Sn_5}$ is the diffusion coefficient of Cu in Cu_6Sn_5 and K_{Cu3} is the rate constant of chemical reaction at interface3. 'y' is the existing thickness of Cu_6Sn_5 at time t shown in figure2. 'dy_{cu}' is the increment of thickness after time 'dt'.

By above text the increment of thickness of Cu_3Sn in infinitesimal time dt is: $dx_{Sn} + dx_{Cu}$ and increment of thickness of Cu_6Sn_5 is the: $dy_{Sn} + dy_{Cu}$.

Heat treatments for 25 hours and 50 hours at 210⁰C (as shown in figure (11) and (12)) has been carried out for Cu-Sn diffusion couples. Cu_3Sn (Layer 2) and Cu_6Sn_5 (Layer 1) has been formed.

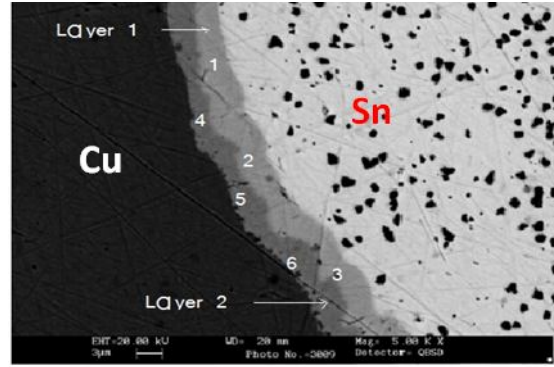


Figure 12: Heat treated at 210⁰C for 25 hrs

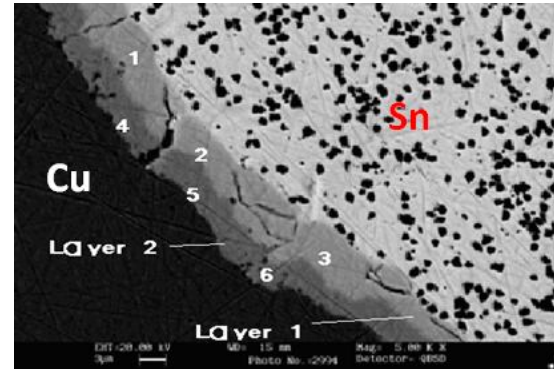


Figure 13: Heat treated at 210⁰C for 50 hrs

Some of the following assumptions have been made. Diffusion coefficients values have been taken from literature ¹⁰

$$\begin{aligned} dx_{Sn} &= 0.8 * 10^{-6} \text{ m} \\ dx_{Cu} &= 0.2 * 10^{-6} \text{ m} \\ dy_{Sn} &= 1.2 * 10^{-6} \text{ m} \\ dy_{Cu} &= 0.8 * 10^{-6} \text{ m} \\ D_{Cu-Cu_3Sn} &= 3.67 * 10^{-17} \text{ m}^2/\text{s} \\ D_{Cu-Cu_6Sn_5} &= 7.04 * 10^{-16} \text{ m}^2/\text{s} \\ D_{Sn-Cu_3Sn} &= 2.35 * 10^{-16} \text{ m}^2/\text{s} \\ D_{Sn-Cu_6Sn_5} &= 6.49 * 10^{-16} \text{ m}^2/\text{s} \end{aligned}$$

Rate constants at different interfaces as shown in figure (9) have been calculated as listed in Table 1:

Table 1: Rate constants at different interfaces

Interface	Rate constant	Significance of Rate constant	Numerical Value
1	K _{Sn1}	Rate of Cu ₃ Sn formation at interface 1 by diffusion of Sn	10-11 m/s
2	K _{Cu2}	Rate of Cu ₃ Sn formation at interface 2 by diffusion of Cu	2.7*10-12 m/s
2	K _{Sn2}	Rate of Cu ₆ Sn ₅ formation at interface 2 by diffusion of Sn	2.0*10-11 m/s
3	K _{Cu3}	Rate of Cu ₆ Sn ₅ formation at interface 3 by diffusion of Cu	9.0*10-12 m/s

Results and Discussions

Models for kinetics of Nb₃Sn, Cu₆Sn₅, Cu₃Sn has been prepared. Model for Nb₃Sn kinetics can be useful for understanding the growth kinetics for single diffusion couple of Nb and Cu-Sn alloy for cylindrical as well as slab system. Rate of layer growth of Nb₃Sn is 4.62×10^{-12} m/s at 200 hrs at 650°C. Model for kinetics of Cu₃Sn and Cu₆Sn₅ is also useful for calculating the rate of reaction at different interfaces of Cu-Sn system.

Conclusions

Formation of layers of intermetallic like Nb₃Sn, Cu₆Sn₅ and Cu₃Sn is governed by uphill diffusion. Various diffusion models are described in paper. These diffusion models are useful in calculating the layer growth, diffusion coefficient and rate constant etc. in cylindrical as well as slab geometry.

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