Kinetics of Nb₃Sn, Cu₆Sn₅ and Cu₃Sn layer growth
Yogendra Singh* and Subrata Pradhan
Institute for Plasma Research, Bhat, Gandhinagar-382 428, India.

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 $S(t) = \frac{1}{b} \left(1 + \frac{1}{2} \left(\frac{B}{K}\right)^{\frac{1}{2}}\right)^{-\frac{1}{2}}$.’’$B$, ‘’$K$’’ 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 $C(x,t) = 1 - \frac{b}{(1+B/K)x}$. ‘’$x$’’ is the distance from Sn-Nb₃Sn interface. Kinetics of Cu₆Sn₅ 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.

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%.

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 interdiffusion 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. Cu₃Sn 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)

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

$C_n =$ Concentration of Sn in Nb after diffusion time of t.

a = radius of the niobium cylinder

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

\[
\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} (D \frac{\partial C}{\partial r})
\]  

(1)

**Figure 1**: Sn is shown to be diffusing in Nb having radius ‘a’.

Following boundary conditions have been adopted:
- \( C = C_0 \) at \( t = 0 \) and \( 0 < r < a \)
- \( C = C_s \) at \( r = a \) and \( 0 < t < \infty \)

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

\[
\frac{dt}{r^2} = -0.0675375 - 0.39889\log(1 - F)
\]  

(2)

Where, \( F = \frac{C - C_s}{C_s - C_0} \) 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.

**Figure 3**: Layer formation of Nb\(_3\)Sn after time \( t \) and Concentration Variation from surface to center.

### 1.3 Kinetics approach for the kinetics of Nb\(_3\)Sn formation:

In this section, the kinetics of Nb\(_3\)Sn formation has been described. Only Sn is considered to be moving towards Nb and forms Nb\(_3\)Sn. Reaction is written as

\[ \text{Nb}_3 + 3\text{Sn} \rightarrow \text{Nb}_3\text{Sn} \]

Initially the layer growth of Nb\(_3\)Sn 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 Nb\(_3\)Sn forms. At time \( t+\Delta t \) the thickness becomes \( x+\Delta x \).

**Figure 4**: At initial position

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.

Nb\(_3\)Sn layer forms at yellow reason where concentration of Sn at certain time \( t \) is 18-25 at% but value of C is only 8-10 at%\(^{3,4}\).

18-25 at% but value of Cs is only 8-10 at%\(^{3,4}\).

\[
C_s = 8-10 \text{ at%}
\]

\[
b = 18 \%
\]

\[
c = 25 \%
\]
As the Sn reaches Nb, the formation of Nb\(_3\)Sn takes place. The layer of Nb\(_3\)Sn gets formed. This results in shifting of Nb-Nb\(_3\)Sn interface towards center. These are schematically shown in figures (3), (4), (5). Reaction kinetics is shown in Fig. 6.

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

\[
S(t) = \frac{1}{B_i} \left[ 1 + 2B_i \left( \frac{B_i}{\pi} \right) \left( 1 + \frac{1}{2} B_i \frac{l^2}{D} \right) \right]^{1/2} \quad \text{--- (10)}
\]

Where \(\beta = M^2/CDT\),
\(M\)= 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 Nb\(_3\)Sn-Nb interface is given as [6]:

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

Where \(B_i = kl/D\),
\(K\)= rate constant of reaction.

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

\[ \text{Sn}_{\text{diff}} + 3 \text{Cu}_{\text{Surface}} = \text{Cu}_2\text{Sn} \quad (12) \]

**At interface 2:**

At interface 2, both Cu6Sn and Cu5Sn5 phases forms. Cu6Sn phase forms when Cu diffuses through Cu3Sn and reach at interface 2 and reacts with Cu3Sn. Thus, the reaction can be written as:

\[ 9\text{Cu} \text{diff} + \text{Cu}_6\text{Sn}_5 = 5\text{Cu}_2\text{Sn} \quad (13) \]

**At interface 3:**

Cu6Sn5 phase forms as Sn diffuses through Cu3Sn5 and reaches at interface 2. Then it reacts with Cu3Sn. Thus, the reaction can be written as shown below:

\[ 9\text{Sn} \text{diff} + 6\text{Cu}_3\text{Sn} = 3\text{Cu}_6\text{Sn}_5 \quad (14) \]

**2. Kinetics of Cu5Sn5, Cu6Sn layer growth**

Intermetallic compound of Cu-Sn formed during the heat treatment of Nb5Sn/Cu strands. These intermetallic compounds have been formed by heating the stack single thin layers of copper and tin also. 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 Cu5Sn and Cu6Sn5 at the Cu-Sn interface. Direct chemical reaction between primary components Cu and Sn clearly ceases after the formation of compound layers Cu5Sn 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.

**At interface 1:**

\[ \text{Sn} \text{diff} \text{Sn} + 3 \text{Cu}_{\text{Surface}} = \text{Cu}_2\text{Sn} \quad (12) \]

**At interface 2:**

At interface 2, both Cu6Sn and Cu5Sn5 phases forms. Cu6Sn phase forms when Cu diffuses through Cu3Sn and reach at interface 2 and reacts with Cu3Sn. Thus, the reaction can be written as:

\[ 9\text{Cu} \text{diff} + \text{Cu}_6\text{Sn}_5 = 5\text{Cu}_2\text{Sn} \quad (13) \]

**At interface 3:**

Cu6Sn5 phase forms as Sn diffuses through Cu3Sn5 and reaches at interface 2. Then it reacts with Cu3Sn. Thus, the reaction can be written as:

\[ 9\text{Sn} \text{diff} + 6\text{Cu}_3\text{Sn} = 3\text{Cu}_6\text{Sn}_5 \quad (14) \]

**Figure 11:** Increment in thickness of Cu5Sn and Cu6Sn5 in infinitesimal time \( dt \)

In order to establish the equations relating \( dt \) to the increases, \( dx_{\text{Sn}} \), \( dx_{\text{Cu}} \), \( dy_{\text{Sn}} \), and \( dy_{\text{Cu}} \), in thicknesses of the Cu5Sn 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:**

\[ \text{dt} = t_{d1}\text{diff} (\text{Sn}) + t_{d2}\text{chem} (\text{Sn}) \rightarrow \text{Cu}_2\text{Sn} \quad (16) \]

Where \( t_{d1}\text{diff} (\text{Sn}) \rightarrow \text{Cu}_2\text{Sn} \) is the time to reach interface 1 for forming \( \text{Cu}_2\text{Sn} \) and \( t_{d2}\text{chem} (\text{Sn}) \rightarrow \text{Cu}_2\text{Sn} \) is the time required in chemical reactions at interface 1. **At interface 2:**

\[ \text{dt} = t_{d1}\text{diff} (\text{Sn}) + t_{d2}\text{chem} (\text{Sn}) + t_{d3}\text{chem} (\text{Sn}) + t_{d4}\text{chem} (\text{Sn}) \rightarrow \text{Cu}_6\text{Sn}_5 \quad (17) \]

**At interface 3:**

\[ \text{dt} = t_{d1}\text{diff} (\text{Sn}) + t_{d2}\text{chem} (\text{Sn}) + t_{d3}\text{chem} (\text{Sn}) + t_{d4}\text{chem} (\text{Sn}) \rightarrow \text{Cu}_6\text{Sn}_5 \quad (18) \]
\[ dt = dt_{diff}(Cu \rightarrow Cu_{6}Sn) + dt_{chem}(Cu \rightarrow Cu_{3}Sn) \quad \ldots \quad (17) \]

Where, \( dt_{diff} \) (Cu \( \rightarrow \) Cu_{6}Sn) is the time to reach interface 2 for forming Cu_{6}Sn and \( dt_{chem}(Cu \rightarrow Cu_{3}Sn) \) is the time required in chemical reaction at interface 2.

At interface 2:
\[ dt = dt_{diff}(Sn \rightarrow Cu_{6}Sn_{5}) + dt_{chem}(Sn \rightarrow Cu_{3}Sn) \quad \ldots \quad (18) \]

Where \( dt_{diff} \) (Sn \( \rightarrow \) Cu_{6}Sn_{5}) is the time takes to reach interface 2 for forming Cu_{6}Sn_{5} and \( dt_{chem}(Sn \rightarrow Cu_{3}Sn) \) is the the time required for the chemical reactions at interface 2.

At interface 3:
\[ dt = dt_{diff}(Cu \rightarrow Cu_{6}Sn_{5}) + dt_{chem}(Cu \rightarrow Cu_{3}Sn) \quad \ldots \quad (19) \]

Where \( dt_{diff} \) (Cu \( \rightarrow \) Cu_{6}Sn_{5}) is the time to reach interface 3 for forming Cu_{6}Sn_{5} and \( dt_{chem}(Cu \rightarrow Cu_{3}Sn) \) 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:
\[ dt = (x/D_{Sn-Cu_{3}Sn} + 1/K_{Sn})dx_{Sn} \quad \ldots \quad (20) \]

Where \( D_{Sn-Cu_{3}Sn} \) is the diffusion coefficient of Sn in Cu_{3}Sn and \( K_{Sn} \) is the rate constant of chemical reaction at interface1. ‘x’ is the existing thickness of Cu_{3}Sn at time ‘t’ shown in figure2. ‘dx_{Sn}’ is the increment in thickness after time dt.

At interface 2:
\[ dt = (x/D_{Cu-Cu_{6}Sn_{5}} + 1/K_{Cu})dx_{Cu} \quad \ldots \quad (21) \]

Where \( D_{Cu-Cu_{6}Sn_{5}} \) is the diffusion coefficient of Cu in Cu_{6}Sn_{5} and \( K_{Cu} \) is the rate constant of chemical reaction at interface2. ‘x’ is the existing thickness of Cu_{6}Sn_{5} at time ‘t’ as shown in figure(10). ‘dx_{Cu}’ is the increment in thickness after time dt.

At interface 2:
\[ dt = (y/D_{Sn-Cu_{6}Sn_{5}} + 1/K_{Sn})dy_{Sn} \quad \ldots \quad (22) \]

Where, \( D_{Sn-Cu_{6}Sn_{5}} \) is the diffusion coefficient of Sn in Cu_{6}Sn_{5} and \( K_{Sn} \) is the rate constant of chemical reaction at interface2. ‘y’ is the existing thickness of Cu_{6}Sn_{5} at time ‘t’ as shown in figure (10). ‘dy_{Sn}’ is the increment of thickness after time dt.

At interface 3:
\[ dt = (y/D_{Cu-Cu_{6}Sn_{5}} + 1/K_{Cu})dy_{Cu} \quad \ldots \quad (23) \]

Where \( D_{Cu-Cu_{6}Sn_{5}} \) is the diffusion coefficient of Cu in Cu_{6}Sn_{5} and \( K_{Cu} \) is the rate constant of chemical reaction at interface3. ‘y’ is the existing thickness of Cu_{6}Sn_{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_{6}Sn in infinitesimal time dt is \( dx_{Sn} + dx_{Cu} \) and increment of thickness of Cu_{6}Sn_{5} is the: \( dy_{Sn} + dy_{Cu} \).

Heat treatments for 25 hours and 50 hours at 210\(^\circ\)C (as shown in figure (11) and (12)) has been carried out for Cu-Sn diffusion couples. Cu_{3}Sn (Layer 2) and Cu_{6}Sn_{5} (Layer 1) has been formed.

![Figure 12: Heat treated at 210\(^\circ\)C for 25 hrs](image)

![Figure 13: Heat treated at 210\(^\circ\)C for 50 hrs](image)

Some of the following assumptions have been made. Diffusion coefficients values have been taken from literature: \(^{10}\)

- \( D_{Cu-Cu_{6}Sn} = 3.67 \times 10^{-17} \, \text{m}^2/\text{s} \)
- \( D_{Cu-Cu_{6}Sn_{5}} = 7.04 \times 10^{-13} \, \text{m}^2/\text{s} \)
- \( D_{Cu-Cu_{6}Sn_{5}} = 2.35 \times 10^{-16} \, \text{m}^2/\text{s} \)
- \( D_{Sn-Cu_{6}Sn_{5}} = 6.49 \times 10^{-10} \, \text{m}^2/\text{s} \)

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

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<thead>
<tr>
<th>Table 1: Rate constants at different interfaces</th>
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<tr>
<td>Interface</td>
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<tr>
<td>1</td>
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Results and Discussions

Models for kinetics of Nb$_3$Sn, Cu$_6$Sn$_5$, Cu$_3$Sn has been prepared. Model for Nb$_3$Sn 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 Nb$_3$Sn is $4.62 \times 10^{-12}$ m/s at 200 hrs at 650°C. Model for kinetics of Cu$_6$Sn$_5$ and Cu$_3$Sn$_5$, is also useful for calculating the rate of reaction at different interfaces of Cu-Sn system.

Conclusions

Formation of layers of intermetallic like Nb$_3$Sn, Cu$_6$Sn$_5$, and Cu$_3$Sn 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.

References

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