Formation Mechanism of Phase Interface for Diffusion Couple of Pb/Sn Layered Composite

Han Zhaohui[1], Yu Xiaohua[2], Zhu Peixian[2], Zhou Shenggang[2,*] and Yang Yi[3]

[1]College of metallurgy and energy engineering, Kunming University of Science and Technology, Kunming 650093,China
[2]College of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093,China
[3]Hubei Zhonggong Equipment Industry Investment Co. Ltd., Macheng, 430000, China

Abstract: *This paper prepares the diffusion couple of Pb/Sn layered composite by hot pressing, treat it at different holding times, and investigates the appearance characteristics and forming mechanism of the couple by means of SEM-EDS. The results show that Sn atoms preferentially diffuse into the Pb side under the heating temperature of 503K and the pressure of 0.5MPa. With the increase of the welding time, a eutectic liquid layer is formed on the interface of Pb/Sn and the diffusion-dissolution of Pb and Sn atoms are completed by simultaneous extension and homogenization. The research also demonstrates the star studded distribution of α-Pb and β-Sn solid solutions.*

1. INTRODUCTION

Thanks to special properties like stable performance, low melting point and good toughness, the Pn/Sn alloy has been extensively applied in electronics, aviation, coating, and so on[1-3]. With excellent electrical conductivity, the material is used in the metallurgy industry to Pb-Al layere d composite anode material[4-6]. Through the eutectic reaction, the elements Pb and Sn can form a solid solution, which falls in the category of partial solid solution in the binary alloy phase diagram of Pb-Sn[7]. The eutectic products of Pb and Sn mostly consist of α-Pb (Sn) and β-Sn (Pb). Under proper humidity conditions, the saturated solid solubility of Pb is 2.5% in Sn, and the saturated solid solubility of Sn is 19% in Pb. The above description lays the foundation for the preparation of Pb-Al layered composite electrode materials, and provides some data supports for the mutual incompatibility between Pb and Al.

Literature [8] probes into the microstructure characteristics of Pb and Sn by powder metallurgy sintering method, aiming to further disclose the diffusion-dissolution behavior of Pb/Sn, and demonstrate the diffusion-dissolution features and microstructures of Pb and Sn atoms in the powder sintering process. Therefore, this paper digs into the diffusion-dissolution characteristics and

formation mechanism of phase interface of Pb/Sn binary diffusion couple based on the research on the diffusion behavior of Pb/Sn which prepared by hot pressing and diffusion welding (HP-DW).

2. EXPERIMENTAL PROCEDURES

Targeted at the quaternary alloy of Pb (Pb-Ag-Ca-Sr) and Sn (99.95%), this paper studies the diffusion welding process taking place between 30mm×30mm×3mm Sn and Pb blocks in the argon-blanketed HP-DW furnace (vacuum degree: 10-3MPa; temperature control accuracy: ± 1ºC). In light of the melting points and phase diagrams of Pb and Sn and in reference to previous experiments, we formulate the process conditions for preparing the composite samples at different holding times (Table 1). Figure 1 is the schematic diagram of a Pb/Sn binary diffusion couple.

The diffusion coefficients of Pb and Sn elements at different

Table 1. Number of the Pn/Sn alloy samples prepared at different holding times

No.	Bonding temperature /K	Holding time /h	Static pressure /MPa
a		0	
b	503	2	0.5
c		4	
d		6	

*To whom correspondence should be addressed: Email: 15987187676@163.com
  Phone:+8687165126513
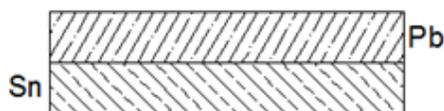
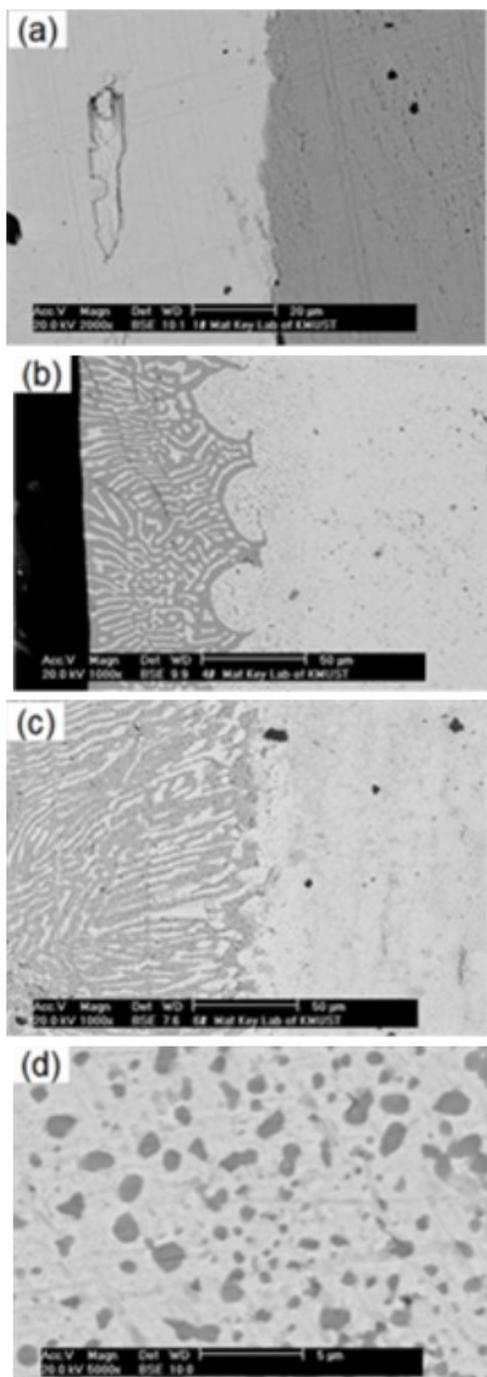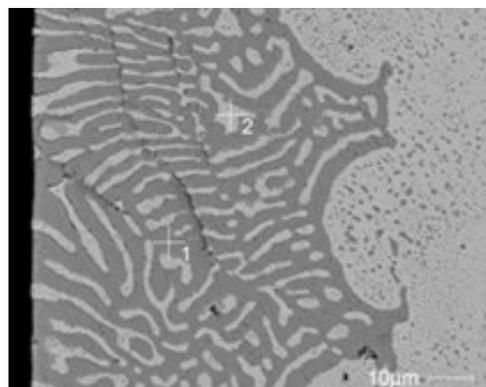Figure 1. Schematic diagram of Pb/Sn binary diffusion couple

Figure 3. EDS microanalysis of the reaction zone at 503K and 2h

temperatures are obtained by the Arrhenius equation, laying the basis for the research on the diffusion behavior of Pb and Sn elements. Meanwhile, the formation enthalpy of the solid solution on the Pb/Sn interface is calculated according to the Miedema theory, providing theoretical support for the analysis of interfacial reaction products. Furthermore, the morphology of the diffusion-dissolution layer and the combination of phase interface are observed with Philips XL-30 ESEM scanning electron microscope (SEM). Based on the phase diagram of Pb-Sn alloy, we analyze the formation mechanism of the diffusion-dissolution layer of Pb/Sn diffusion couple.

3. RESULTS AND DISCUSSION

3.1. Phase interface morphology of Pb/Sn diffusion couple

Welded under 0.5 MPa and 503K and held for different times, the samples are studied to understand the different process conditions on the interface of Pb and Sn in the diffusion zone. Figure 2 displays the morphologies and microstructures of Pb/Sn interphase diffusion solution layer at different holding times (0h, 2h, 4h and 6h).

According to Figure 2, the original Pb/Sn interface is in a closely combined mechanical state under the action of the force in Figure 2(a). The phenomenon is attributable to the low hardness and high plasticity of Pb and Sn. The features make the elements deform easily and thus completes the interface combination. When the diffusion time increases to 2h, the diffusion-dissolution reaction between Pb and Sn atoms occur in the interface region. As shown in Figure 2(b), the irregular wavy phase interface is composed of alternating layered dark gray and light gray tissues. As the holding time continues to grow, perfect diffusion reaction occurs between Pb and Sn atoms to form an intermetallic compound in the interphase interface, and to produce α-Pb solid solution and β-Sn solid

Figure 2. Morphologies and microstructures of Pb/Sn interphase diffusion solution layer for different holding times: (a)0h; (b)2h; (c)4h; (d)6h

Table 2. EDS results of points composition of diffusion couple at 503K and 2h

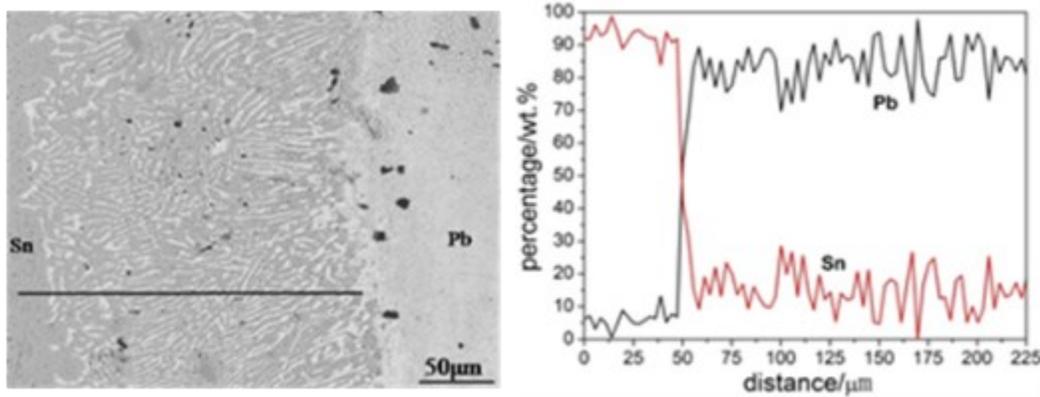| Location on micrographs	Elements in.ω_i%	
	Pb K	Sn L
1	07.11	92.89
2	96.73	03.27

Figure 4. EDS microanalysis of the reaction zone at 503K for 2h

solution (Figure 2(d)). The longer the holding time, the more the light gray tissue and the fewer the dark gray tissue.

3.2. Phase interface component of Pb/Sn diffusion couple

The phase structure and composition of Pb/Sn interface diffusion-dissolution layer at 503K and 2h are analyzed with the aid of electron probe microanalysis (EPMA) and electronic differential system (EDS).

According to Table 2 and Figure 4, there is an interface of metallurgical welding between Pb and Sn. It carries obvious diffusion characteristics resulted from the mutual diffusion reaction between Sn and Pb atoms in the interface. The EDS test analysis (Figure 3 and Table 2) shows that the contents of Pb and SN are 7.11% and 92.89%, respectively. In reference to the Pb/Sn alloy phase diagram, it can be seen that the dark gray tissue in Figure 3 is β-Sn and the light gray tissue in that figure is α-Pb solid solution. The isothermal solidification is accompanied by the formation of the diffusion-dissolution layer with stratified structure. The inter-diffusion is driven by the eutectic reaction of Pb and Sn and the mutual diffusion reaction between Pb and Sn atoms.

3.3. Phase boundary diffusion dynamics of Pb/Sn diffusion couple

According to the equation of Arrhenius[9]:

$$D = D_0 e^{-Q/RT} \qquad (1)$$

where D is the diffusion coefficient ($m^2 \cdot s^{-1}$)); D_0 is the diffusion constant ($cm^2 \cdot s^{-1}$); Q is the activation energy of diffusion ($kJ \cdot mol^{-1}$); T is diffusion temperature (K); R is the Boltzman constant (8.314J/mol·K).

Table 3. Diffusion constant ($\underline{D_0}$) and activation energy ($\underline{Q}$) of Pb and Sn

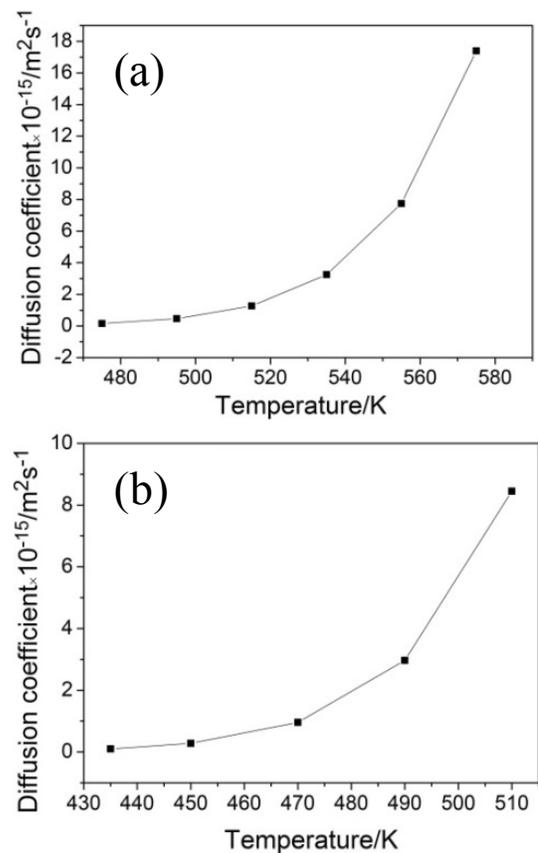| Element	$\underline{D_0}$/cm^2·s^{-1}	$\underline{Q}$/kJ·mol^{-1}
Pb	0.995	107.4
Sn	10.7	108.4
Sn in Pb	0.29	99.4

Figure 5. Relationship between self-diffusion coefficients of Pb (a) and Sn (b) and diffusion temperature

Based on the thermodynamic data in Table 3, we can calculate the diffusion coefficients of Pb and Sn elements at the different temperatures by formula (1). Figure 5 shows the relationship between the self-diffusion coefficients of Pb (Figure 5(a)) and Sn (Figure 5(b)) and the diffusion temperature; Figure 6 shows the relationship between the diffusion coefficient of Sn in Pb substrate and the diffusion temperature.
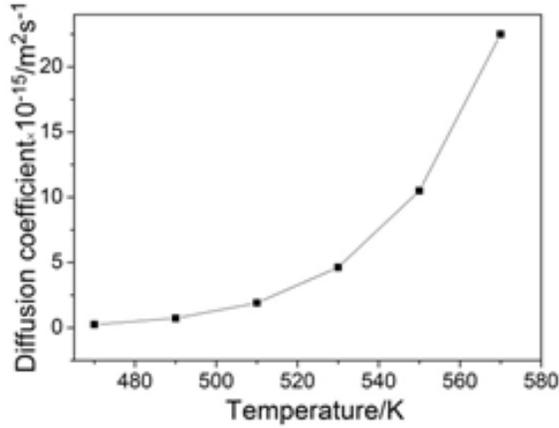
Figure 6. Relationship between diffusion coefficient of Sn in Pb substrate and diffusion temperature

Figure 7. Relationship between ΔH and the composition of the alloy

As shown in Figure 5, the self-diffusion coefficients of Pb and Sn grow exponentially with the diffusion temperature, that is, higher temperature is conducive to the diffusion of elements. At the welding temperature of 503K, the self-diffusion coefficient of Sn is greater than that of Pb. This means the Sn atoms are diffusing at a higher rate than the Pb atoms.

Figure 6 shows that the diffusion coefficient of Sn in the Pb substrate increases with the temperature, indicating that the Sn element diffuses faster and more fully than the Pb element near the interface under the same thermodynamic conditions.

Figure 8. Formation of the interfacial transition zone for Pb/Sn diffusion welding

3.4. Calculation of the enthalpy of formation of Pb/Sn alloy

The new phase precipitation of Pb/Sn diffusion couple on the phase interface is essentially the phase transformation of solids. The enthalpy of formation of the solid solution on the Pb/Sn interface is calculated by the Miedema theory.

The enthalpy of formation in the Miedema theoretical model is expressed as below:

$$\Delta H = x_A f_B^A \Delta H_{sol}^{AinB} \qquad (2)$$

Where as the Pb/Sn solid solution belongs to the disordered phase, we have:

$$f_B^A = C_B^S = 1 - C_A^S \qquad (3)$$

where f_B^A is the surface area ratio of B atoms to alloy atoms. The surface concentration of B atoms is as follows:

$$f_B^A = x_B V_B^{2/3} / (x_A V_A^{2/3} + x_B V_B^{2/3}) \qquad (4)$$

where x_A and x_B are mole fractions of A and B, respectively; V_A and V_B are mole volumes of A and B, respectively.

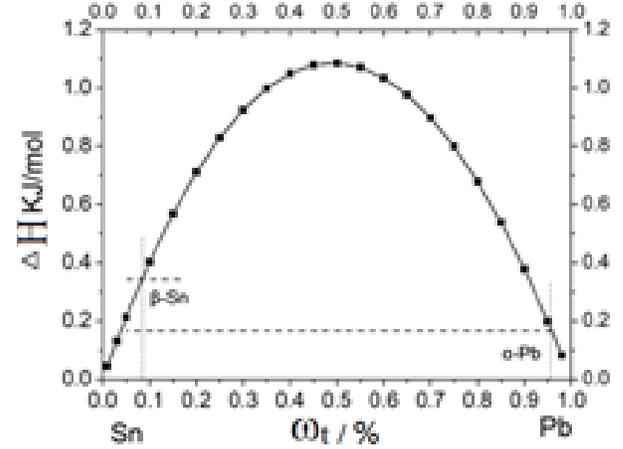The Miedema theory describes the thermal dissolution of metal A in B as below

$$\Delta H_{sol}^{AinB} = \frac{2PV_A^{2/3}}{(n_{ws}^{1/3})_A^{-1} + (n_{ws}^{1/3})_B^{-1}} \bullet [-(\phi_A - \phi_B)^2 + \frac{Q}{P}(n_{wsA}^{1/3} - n_{wsB}^{1/3})^2] \qquad (5)$$

Hence, ΔH is expressed as follows:

$$\Delta H = \frac{2x_A x_B P V_A^{2/3} V_B^{2/3}}{[(n_{ws}^{1/3})_A^{-1} + (n_{ws}^{1/3})_B^{-1}] \bullet (x_A V_A^{2/3} + x_B V_B^{2/3})} \bullet [-(\phi_A - \phi_B)^2 + \frac{Q}{P}(n_{wsA}^{1/3} - n_{wsB}^{1/3})^2] \qquad (6)$$

Since Pb and Sn are non-transition elements in the Miedema theory, we have P=10.6 and Q/P=9.4.

The enthalpy of formation (ΔH) is calculated according to formula (6) and Table 4. Figure 7 depicts the relationship between the enthalpy of formation and the composition of Pb-Sn alloy. The resulting enthalpy of formation is consistent with that given by Akira Takeuchi[11]. It is found that α -Pb solid solution is more stable than β-Sn solid solution (Figure 7). The discovery echoes the variation pattern of morphologies and microstructures in Pb/Sn interface.

Table 4. Relevant thermodynamic parameters of the calculation

Element	$n_{ws}^{1/3}$	$V^{2/3}$/cm^2	ϕ
Sn	1.24	6.43	4.15
Pb	1.15	6.94	4.10

3.5. Formation mechanism of phase interface of Pb/Sn diffusion couple

As mentioned above, the diffusion-dissolution layer on the Pb/Sn diffusion couple interface is formed through the following stages. Figure 8 presents the formation process model of the interfacial transition zone of Pb/Sn diffusion welding:

3.5.1. Physical contact stage

According to the theory of diffusion welding and Figures 8(a) and 8(b), the atomic diffusion and recrystallization reaction take place when the contact surface spacing equals the interatomic distance in composite welding materials required to form combination bonds. When the diffusion welding begins, the heating temperature and welding pressure keep rising [12]. Under the concentration gradient of the Pb/Sn contact interface, the Pb and Sn diffuse from the original interface to other positions that are distributed irregularly and dotted with vacancies and micro voids.

3.5.2. Diffusion–solution stage

We can infer from Figure 8(c) that the diffusion reaction occurs between Pb and Sn under the combined action of diffusion pressure and temperature. At the same diffusion welding temperature, the diffusion rate depends on the atomic diffusion coefficient (D_S) in the solid phase and the concentration difference of components in the interface zone. According to the above diffusion kinetic analysis of Pb and Sn, the self-diffusion coefficient of Sn element ($9.6\times10\text{-}16 m^2/s$) is greater than that of the Pb element ($1.55\times10^{-16}m^2/s$). Thus, the Sn atoms will preferentially diffuse to the Pb side on the Pb/Sn interface. At the eutectic concentration, the eutectic reaction occurs to form a liquid phase structure. In this case, the atomic diffusion rate increases in Pb/Sn interface, and the diffusion rate of Sn atoms in liquid phase is faster than that in solid phase, thus increasing the liquefaction reaction rate in the eutectic reaction system of the alloy. As the diffusion time grows, the Sn eventually reaches the saturation concentration in the eutectic liquid of the near-liquid phase Pb. The ensuing dissolution of Pb from the solid phase into the liquid phase thickens the liquid layer. The dissolution rate is determined by the diffusion coefficient of Sn atoms ($2.6\times10^{-16}m^2/s$) in the solid phase Pb. Meanwhile, the homogenization process continues. The homogenization rate mainly depends on the diffusion coefficient of Sn atoms in the liquid phase. In this phase, the extension of eutectic liquid layer goes in parallel with the homogenization. At the completion of the homogenization process, the mutual diffusion of the Pb and Sn atoms is completed, i.e. the concentration of the Sn atoms reaches the liquid phase composition concentration of the eutectic liquid. At this point, the width of Pb/Sn eutectic liquid layer is maximized.

3.5.3. Isothermal solidification stage

In this phase, the diffusion of the solid phase Sn elements in the Pb substrate near the solid-liquid interface reduces the concentration of Sn atoms. Besides, Sn elements further diffuse to solid phase Pb, resulting in the decline of concentration of Sn atoms in liquid phase and the rise of the melting point. The width of the liquid phase reaction layer decreases until the solidification on the liquid solid interface is completed. As the atoms continue to spread and the diffusion mechanism remains stable, the crystalline transition tissue of alternating layered α-Pb solid solution and β-Sn solid

solution leads to low homogenization of the liquid layer in the subsequent solidification process. The rate of crystallization mainly relies on the diffusion coefficient of Sn atoms ($2.6\times10^{-16}m^2/s$) in the solid phase Pb on this stage. This explains the long time consumed in diffusion and homogenization on this stage.

4. CONCLUSION

1. With the increase of holding time, Pb atoms participate in the diffusion-solution reaction with Sn atoms. The irregular wavy phase interface is composed of alternating layered α-Pb solid solution and β-Sn solid solution.
2. According to the dynamics theory and the formation mechanism of the interface, Sn atoms preferentially diffuse to the Pb side, accompanied by the dissolution of Pb atoms in Pb/Sn interface. The mutual diffusion solution of Pb and Sn atoms is eventually realized by extension and homogenization on the liquid phase layer of the interface.

5. ACKNOWLEDGEMENT

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