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Numeric simulation of thickness of intermetallic compounds in interface zone of diffusion bonding for Cu and Al①

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[Abstract] Numeric model of intermetallic compound formation and growth in the vacuum diffusion bonding of copper and aluminum was established, and proved by EPMA and micro-hardness test etc. The numeric simulation of thickness of the intermetallic compound results in accord with the tests well. This study provides some references to determine welding parameters in the vacuum diffusion bonding of Cu/Al dissimilar materials.

[Key words] vacuum diffusion bonding; intermetallic compounds; numeric simulation
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1 INTRODUCTION

Copper and aluminum are widely used in industry and their joining is an important part in the metal welding. Brazing method is also adverse for copper's thermal conductivity rate is high, the expansion coefficients of copper and aluminum are different and it is easy to form oxidation film on aluminum surface[1~3]. Vacuum diffusion welding is an advanced method that can join the materials joined hard by the common methods in vacuum and obtain perfect joint[4,5].

The diffusion transition zone tends to form some new phases different with the base materials during diffusion bonding of dissimilar materials. It is easy to produce brittle intermetallic compounds near the interface zone in Cu/Al diffusion bonding. These brittle intermetallic compounds will obviously decrease performance of the weld joint[4,6~8]. Analyzing formation and growth mechanism of the new phase in the interface and controlling effectively the kinds, content, shape, distribution of the brittle phase are important in diffusion bonding research of dissimilar materials. So it is significance in practice and theory for determining reasonable technology parameters to study the brittle phases formation and growth mechanism and seek the inner relation between the microstructure change and diffusion mechanism.

2 BUILDING OF NUMERIC MODEL

The main factors that affect Cu-Al intermetallic compounds and its structure are electronic concentration and atom size[9]. Different electronic compounds with different crystal lattice type are formed according to electron concentration for Cu and Al (see Table 1).

Table 1 Possible electronic compounds nearby interface of Cu/Al vacuum diffusion bonding

Item	Cu-Al intermetallic compounds		
	Cu_3Al	Cu_9Al_4	Cu_5Al_3
Electronic concentration	21:14 β-phase	21:13 γ-phase	21:12 ε-phase
Crystal lattice type	Body-centered cubic lattice	Complex cubic lattice	Hexagonal close-packed lattice

During initial stage of Cu/Al vacuum diffusion bonding the amount of intermetallic compounds is too little to decrease the joint performance obviously. At this stage for the new phase formed the homogeneous core has not occurred, but occurred catalyzed core[10]. The lower the activation energy, the easier the separating out of new phase. When the constituent and microstructure locally change, there is different unit cubage of phase between the intermetallic compounds and base metal. Metal distortion energy should be thought as a part that causes heat-work corresponding change. The forming time (t) of new intermetallic compounds core is in direct proportion with the effective activation energy of process and activation energy of separating out atom, but in inverse proportion with reaction temperature. The equation is

$$t = k\exp\left|\frac{E_e + E}{RT}\right| \quad (1)$$

where E_e is the effective activation energy of process; k is the separating out constant; E is the activation energy of separating out atom; R is the gas constant; T is the absolute temperature.

After separating out the intermetallic compounds phase, the atoms around them are impoverished, the

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further separating will depend on diffusion of surrounding solute atoms. The impoverished atoms will be supplied through atomic diffusion from the surrounding base metal. So the main factor for further separating out is the diffusion rate. If the difference between the grains of intermetallic compounds and base metal during this course is not only on component and atom arraying style, but also on the crystal structure, the situation will be more complex. The larger the difference between the crystal structures is, the larger effect the microstructure factor has, particularly at the initial stage of the intermetallic compound growth[11]. The relationship between the base metal ductility distortion and crystal direction becomes more complex, which makes the delay time longer during the grain growth. With the prolonging of time, the effects of diffusion factor increase till the last stage. For Cu and Al are both face-centered cubic lattices, the diffusion mechanism is void diffusion. The diffusion factor is the main element for the Cu/Al intermetallic compound growth.

The initial growth of the intermetallic compounds is mainly along the interface of Cu and Al, for the diffusion rate along the interface is larger. It will form continuous interlayer when the first intermetallic compounds converge nearby the interface and then grow into the depth. The experience equation about the relation of the width of intermetallic compounds and the time is[12]

$$W^n = K(t - t_0) \tag{2}$$

where W is the width of the intermetallic compounds; K is the growth rate; t_0 is the time of the latent period. The time of latent period can be calculated in the following way.

Select three points from the curve of the width vs the heating time at certain temperature: $M_1(W_{\min}\ t_1)$, $M_2(W_{av}\ t_2)$, $M_3(W_{\max}\ t_3)$, their relation is

$$W_{av} = \sqrt{W_{\min} W_{\max}} \tag{3}$$

The results from Eqn. (2) is:

$$t_1 = t'_0 + \frac{1}{K} W_{\min}^H$$

$$t_2 = t'_0 + \frac{1}{K} W_{av}^H$$

$$t_3 = t'_0 + \frac{1}{K} W_{\max}^H$$

Put these Eqns. into Eqn. (3):

$$t_2 - t'_0 = \sqrt{(t_1 - t'_0)(t_2 - t'_0)}$$

$$t'_0 = \frac{t_1 t_3 - t_2^2}{t_1 + t_3 - 2t_2} \tag{4}$$

In the same way, calculate the time of t''_0 latent period at other temperature T'_0 then put t'_0 and t''_0 into Eqn. (1), the results are:

$$t'_0 = k\exp\left(\frac{E_e + E}{RT_0}\right),$$

$$t''_0 = k\exp\left(\frac{E_e + E}{RT'_0}\right)$$

So we can get parameter $(E_e + E)$ and k of the latent period time:

$$E_e + E = \frac{T_0 T'_0}{T'_0 - T_0} R \ln \frac{t'_0}{t''_0} \tag{5}$$

$$k = \frac{\left[t''_0\right]^{T'_0/(T'_0 - T_0)}}{\left[t'_0\right]^{T_0/(T'_0 - T_0)}} \tag{6}$$

$$t_0 = t_0(T) = k\exp\left[\frac{T_0 T'_0}{T'_0 - T_0} R \ln \frac{t'_0}{t''_0}\right] / RT \tag{7}$$

To the most of intermetallic compounds, the n in Eqn. (2) usually is 2, then Eqn. (2) change into

$$W^2 = K[t - t_0(T)] \tag{8}$$

$$K = K_0 \exp\left(-\frac{Q}{RT}\right) \tag{9}$$

where K_0 is growth constant of reaction phase; Q is growth activation energy of reaction phase.

Measure the width W_1 of the intermetallic compounds at different time and temperature T_1, then can calculate the growth rate K_{T_1} at T_1 temperature through Eqn. (8) and K_{T_2} at T_2 temperature in the same way. According to the Eqn. (9), the results are

$$Q = \frac{(\ln K_{T_2} - \ln K_{T_1}) RT_1 T_2}{T_2 - T_1} \tag{10}$$

$$K_0 = \frac{\left[K_{T_1}\right]^{T_1/(T_1 - T_2)}}{\left[K_{T_2}\right]^{T_2/(T_1 - T_2)}} \tag{11}$$

Then the equation of width growth rate of intermetallic compounds is

$$W = \sqrt{\left[K_{T_1}\right]^{T_1/(T_1 - T_2)} / \left[K_{T_2}\right]^{T_2/(T_1 - T_2)}} \cdot \sqrt{\exp\left[\frac{(\ln K_{T_1} - \ln K_{T_2}) T_1 T_2}{(T_2 - T_1) T}\right] [t - t_0(T)]} \tag{12}$$

3 EXPERIMENT AND VERIFICATION

The base metals in the test were industrial aluminum (L_4) and copper (T_2), which were 4 mm thickness. The chemical compositions and thermophysical performance of two materials are shown in Table 2. The size of test plate was 50 mm × 50 mm × 4 mm. The surface oxide film of the two materials should be cleared away before the diffusion welding. Using Workhorse-Ⅱ type vacuum diffusion bonding equipment, was conducted welding. The heating power was 45 kVA. The vacuum degree in the test can arrive 6.7×10^{-4} Pa.

Technology parameters of vacuum diffusion bonding in the test for Cu and Al were heating temperature 520~540 ℃, pressure 12.5 MPa and diffusion time 60 min. The relation between temperature and time in the test is shown in Fig. 1.

The specimen of diffusion transition zone respectively was eroded using $FeCl_3$ hydrochloric acid alco-

Table 2 Chemical composition and thermophysical performance of aluminum and copper

Metal	Chemical composition/ %							
	Al	Cu	Fe	Si	O_2	Ni	Pb	Others
Al	99.3	0.05	0.3	0.35	–	–	–	0.1
Cu	–	99.9	0.005	–	0.06	0.006	0.005	–

Metal	Thermophysical performance				
	Melting point / ℃	Density /(g·cm^{-3})	Average specific heat capacity/(J·kg^{-1}·K^{-1})	Melt heat /(kJ·mol^{-1})	Thermal conductivity /(W·m^{-1}·K^{-1})
Al	657	2.70	917	10.47	238
Cu	1083.4	8.96	386	13.02	397

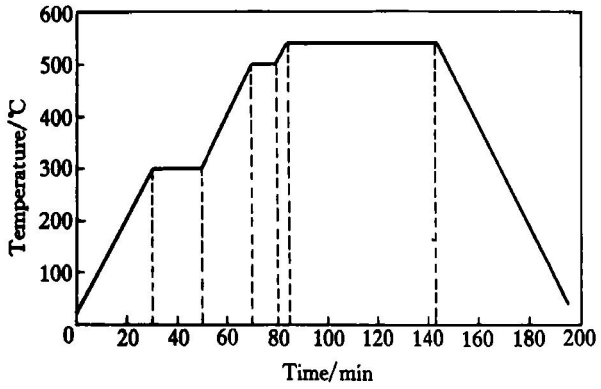

Fig. 1 Temperature vs time curve of vacuum diffusion bonding for Al and Cu

holic solution and hydrofluoric acid solution after diffusion bonding specimen polished. Fig. 2 shows the microstructures of Cu/Al diffusion joint interface.

The original crystal silicon with shape of polygon block can be observed after eroded with hydrofluoric acid solution. Regular twin microstructure can be observed in the copper base after eroded with $FeCl_3$ hydrochloric acid alcoholic solution. Under the condition of heating, pressing and vacuum, the oxide film (such as CuO, Cu_2O) on the copper surface is destroyed continuously and dissolved into Cu and Al forming spherical grain through diffusion. The amount of Al atoms transferring to Cu side is larger than that of Cu because of different diffusion rate of both materials. The surplus Al atom expands lattice of Cu side and Al atom lattice contracts, which results in interface transferred to Cu side.

The main elements nearby the interface of Cu/Al diffusion bonding were analyzed by the electron probe microanalysis (EPMA), and the test results are shown in Fig. 3. The thickness of diffusion transition zone is about 40 μm. In this zone copper side (about 28.8 μm) is thicker than aluminum side (about 11.8 μm) because the activity of Al atom is stronger than that of Cu atom. The main factors that affect the intermetallic compound and its structure are electric concentration and atom size. According to the difference of diffusion rate in the different range of

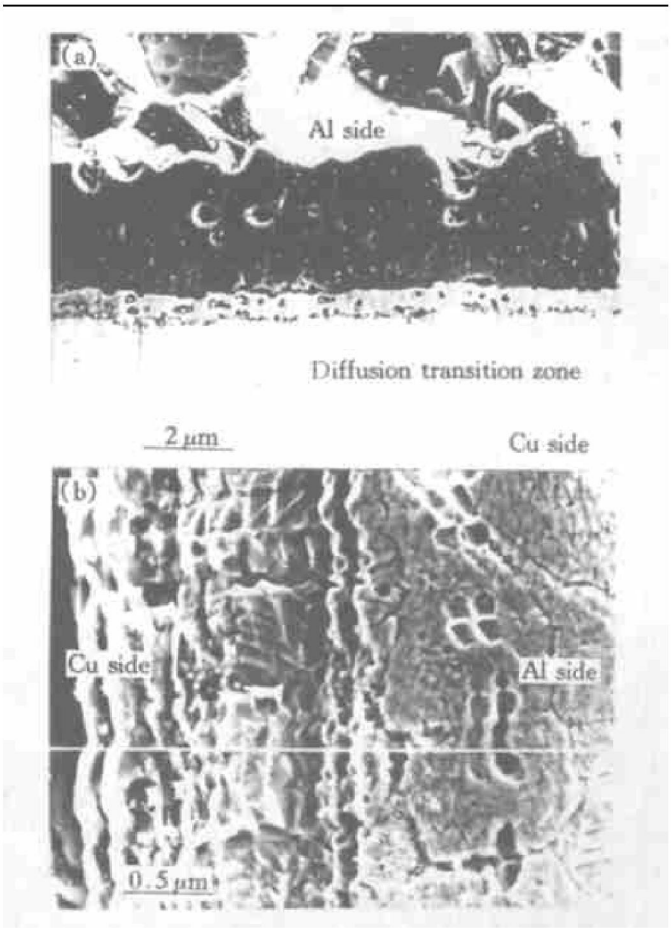

Fig. 2 Microstructures near interface of Cu/Al vacuum diffusion bonding (SEM)

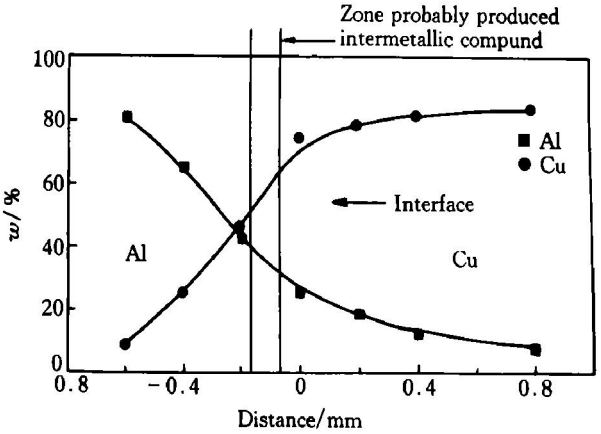

Fig. 3 EPMA analysis result on both sides of diffusion interface

temperature, the width of different electronic compounds can be roughly calculated.

The micro-hardness of Cu-base, Al-base, Cu side and Al side in the interface were measured by a micro-sclerometer using a 25 g load and at load time of 10 s, the results are shown in Fig. 4. The micro-hardness test result indicates that the micro-hardness (MH) of Al side in the transition zone is lower, but there is a peak zone (MH 780) in Cu side of transition zone that is obviously higher than that of Cu base. This phenomenon may be inferred from the intermetallic compounds in Cu side of the transition zone.

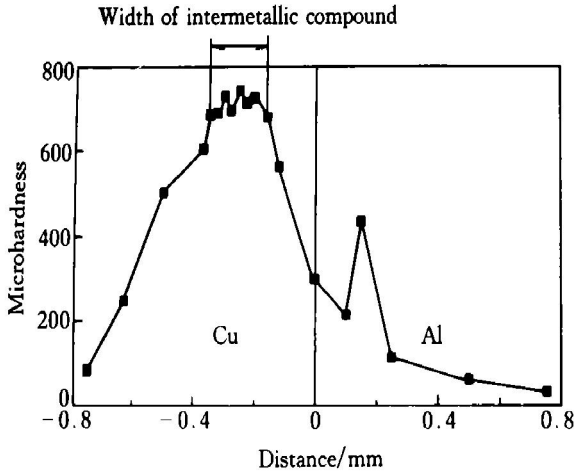

Fig. 4 Micro-hardness near diffusion interface of copper and aluminum

The main factors to form the intermetallic compounds are electric concentration and atom size. Al atom can transfer into Cu base through the interstitial place of the atoms during Cu/Al diffusion bonding. Cu and Al may combine and make the periphery electron reassign to form Al: Cu atom pair when Al meets with Cu ion. The transfer rate of Al: Cu atom pair in crystal is slow and the "trap" is formed in the dislocation, resulting in the increase of hardness nearby the interface. According to the difference of micro-hardness between the base metal and the interface transient zone, the width of the intermetallic compounds can be calculated.

The average error between test and calculating result is less than 12% using above two methods. This model can reflect the width of the intermetallic compounds nearby the interface and can provide test and calculation basis for determining technology parameters in Cu/Al vacuum diffusion bonding.

4 CONCLUSION

A numeric model of thickness of the intermetallic compound formed in the diffusion interface of Cu/Al dissimilar materials is presented. This calculation method is proved by optical microscope, EPMA and micro-hardness test etc.. The calculation result of numeric simulation accords with the test well. This study may provide test and calculation basis for determining technology parameters in Cu/Al vacuum diffusion bonding.

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