Effect of the TiO₂ nanoparticles on the growth behavior of intermetallics in Sn/Cu solder joints

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Abstract In order to investigate the effect of TiO₂ nanoparticles on growth behavior of interfacial Cu₆Sn₅ intermetallics compounds (IMCs) in Pb-free Sn/Cu system, the solder joints are fabricated by using flux doped with different content (0.0 - 2.0 wt. % of flux) and particle diameter (5 nm and 50 nm) of TiO₂. In context of isothermal reflow soldering at 250 °C and subsequent air cooling, the increase in reflow duration from 10 -120 s was characterized with an increment in IMC layer thickness and grain size, due to the enhancement of Cu flux contribution for Ostwald ripening during constant temperature reflow and precipitation kinetics during cooling. The increased proportion of TiO₂ nanoparticles in flux was found to reduce the growth of IMC layer and grain size. The suppression effect on IMC was more pronounced for 5 nm particles as compared to the 50 nm TiO₂. The TiO₂ nanoparticles, adsorbed on IMC plane can retard the growth of the latter. Presence of sufficient amount of a given sized TiO₂ nanoparticles among IMCs, by increasing the effective stress at the localized interfaces, and causing the breaking of brittle Cu₆Sn₅ during growth stage; can help in the inhibition of IMC whisker formation. Particle di-

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ameter and mass proportion of TiO_2 nanoparticles are important for soldering materials design.

Keywords TiO_2 nanoparticles · Intermetallic compounds · Ostwald ripening · vonMises stress · Solder · Interface

1 Introduction

In electronic packaging industry, the environmental concern of Pb material, miniaturization trend of electronic devices and technology transitioning from 2D to 3D Integrated Chip (IC) framework, have sought the requirement of feasible and reliable Pb-free solder joints. Interfacial Cu_6Sn_5 intermetallic compounds (IMCs) in solder /substrate system is characterized by inherent brittle property and thus, it plays a significant role in determining the overall solder joints strength. There is a broad discussion ongoing in the scientific and research community that solder joint properties could be enhanced by suppressing the interfacial Cu_6Sn_5 IMC layer [1],[2],[3],[4],[5]. Recently, researchers are implementing nanomaterials for controlling the layer thickness of IMC.

TiO_2 nano materials are inert and non-toxic , and utilizing them in solder materials design , can be a good approach from the human health and enviromental perspective. It has been found from the studies by many researchers [6],[7],[8],[9],[2],[10] that the use of TiO_2 nanoparticles in the Pb-free solder joints can be used to suppress the size of Cu_6Sn_5 IMCs layer. These research works provide a hallmark on the potentiality of TiO_2 nanoparticles as controlling or suppressing agent for IMC layer evolution. However, most of these research works have not considered the role of nanoparticle size on the IMC growth behaviour on one hand. Moreover, there is still insufficiency on existing literatures on how the suppression effect is holistically established. Influence on mass transfer of diffusing species at the interfacial regimes , and elastic effects on IMC material are the two important aspects , which help us in gaining insight on the IMC growth suppression. Performing experimental or numerical works in any one or both of these aspects can contribute a lot in developing a model of how IMC growth is suppressed by using nanomaterials.

In this study, TiO_2 nanoparticles of particle diameters of 5 and 50 nm, are introduced at several weight proportion in the organic flux and solder joints of Sn/Cu are prepared using this flux. The IMC grain layers and diameter are measured. Finite element analysis is performed to simulate stress at the vicinity of nano-pit or depression in the IMC material around the TiO_2 nanoparticle.

Fig. 1 The SEM characterization of purchased TiO₂ nanoparticles:(a) 5 nm; (b) 50 nm.

2 Experimental method

2.1 Materials

The TiO₂ nanoparticles of particle diameters 5 nm (Type A) and 50 nm (Type B), were purchased from Haoxi Research Nanomaterials Inc., Shanghai, China. The field emission scanning electron microscopy (NOVA Nano-SEM 450) was used to observe the morphology of 5 nm and 50 nm nanoparticles. The SEM results show in Fig. 1(a) and Fig. 1(b). Fig. 2 is the TiO₂ X-ray diffraction patterns obtained from X-ray diffractometer (XRD-6000). The peaks of the TiO₂ X-ray diffraction patterns are very close to those reported in the Joint Committee on Powder Diffraction Standards (JCPDS), TiO₂ file No.89-4921. Comparing the XRD peaks of the standard pdf, it is conformed that this nanoparticle is TiO₂.

For preparation of materials for soldering, the pure Sn solder ball (Dalian Golden Saddle Welding Limited Company, China; purity: 99.99%, Melting point: 231.89 °C), polycrystalline Cu substrate (Qingyuan Metal Materials Limited Company, China; purity: 99.99%, Melting point: 1083.4 °C), rosin flux (AMTECH:NC-559-ASM) and purchased TiO₂ nanoparticles were used for this experiment. The dimension of Cu sheet used in this experiment was 15 mm × 5 mm × 100 μm. Before the Cu sheet was used as the substrate for soldering, it was cleaned in 5% HCl solution (vol.%) with ultrasonic vibration to remove the surface oxide film and then rinsed with deionized water and dried in Nitrogen condition. At the same time, the 1400 μm pure Sn solder ball was cleaned in ethanol solution and dried in air.

For the preparation of the composite flux, TiO₂ nanoparticles (NPs) at mass proportion in the range of 0 - 2 wt.% were then mixed with rosin flux (AMTECH:NC-559-ASM) in a flask, and, then subjected to stirring as well as ultrasonication for 30 min. The composite flux containing TiO₂ nanoparticles was applied over the Cu substrate according to the methodology described in Ref. [11]. Then solder ball was placed over the substrate. Ceramics chips, at a sufficiently larger distance from solder material, were utilized as the mask to fix the volume of applied flux. And then, the sample was put into the reflow oven (Forced Convection, FT02) at 250 °C for time durations of 10 , 60 and 120 s. After the reflow soldering procedure, the samples underwent air

Fig. 2 The XRD patterns of TiO_2 nanoparticles.

cooling. The joints were then ultrasonically cleaned in nitric acid solution (10 vol.%) followed by ethanol. The top-view and cross-sectional morphologies of the joints were observed by field emission scanning electron microscopy (Zeiss Supra 55). For characterization of the cross-section morphology as well as elemental compositions of interfacial Cu_6Sn_5 , the solder joint samples which were first polished and etched by 5% HNO_3 + 2% HCl + 93% $\text{C}_2\text{H}_5\text{OH}$ (in volume) and then the field emission scanning electron microscopy (Zeiss Supra 55) equipped with energy dispersive X-ray spectroscopy (OXFORD, EDX) was employed. For the observation of top-view results, the polished samples were etched by 10% HNO_3 solution (in volume) and then morphology and microstructure were obtained from the SEM. Image processing software was utilized to convert the SEM image's data from pixel to micrometers.

3 Results and Discussion

3.1 IMC microstructure evolution with content of TiO_2 nanoparticles

For the comparison of the morphology and the thickness of solder joint, corresponding to flux + x- TiO_2 (2R=5 nm and x=0, 0.2, 0.5, 1 and 2 wt.%) nanoparticles, reflow soldering was performed for 10 s, 60 s and 120 s at 250 °C. The cross sectional micrographs of interface are shown in Fig. 3. For higher reflow duration (t=120 s) and lower TiO_2 content (0-0.2 wt.%), Cu_6Sn_5 IMCs tend to appear as elongated prismatic whiskers. At lower reflow duration (t=10s), the IMCs are still in early nucleation stage and thus, whiskers cannot attain full growth (Fig. 3 (a1)-(a5)); and for higher reflow duration

Fig. 3 The SEM cross sectional images of the interfacial IMC morphology of samples with flux doped with 0 wt.%, 0.2 wt.%, 0.5 wt.%, 1 wt.% and 2 wt.% Type A (2R=5 nm) TiO₂ nanoparticles soldering for 10 s, 60 s and 120 s at 250 °C.

(t=120 s) with larger content of TiO₂ (1.0-2.0 wt.%), whiskering might have been suppressed due to the presence of the nanoparticles (Fig. 3 (c4),(c5)).

To compare the crystal grain morphology and size of IMC of solder, the SEM micrographs of the top-view of IMC layers of solder with four types of fluxes (flux + x wt.% TiO₂, x= 0 wt.%, 0.2 wt.%, 0.5 wt.%, 1 wt.% and 2 wt.%) and reflow durations 10, 60 and 120 s, are shown in Fig. 4. In general in all the samples, the increase in reflow duration is associated with an enlarged grain diameter. The increase in reflow time, will enhance the contribution of the radial flux J_r of Cu with diffusivity ($D_{Cu}=6.4 \times 10^{-9}$ m²/s) given by the following equation, for Ostwald ripening induced growth of IMC :

$$J_r = -D_{Cu}\rho_l \frac{dC(r)}{dr} = -\frac{-2D_{Cu}\rho_l\Omega\gamma C_0}{\epsilon RT} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (1)$$

where, ρ_l is the density of liquid solder. C_0 ($=1.6 \times 10^{-3}$ mol/cc) means the equilibrium concentration of Cu in liquid solder. $\frac{dC(r)}{dr}$ is the concentration gradient along the radial direction of initially spherical IMCs during isothermal reflow. γ denotes the interfacial energy per unit area between Cu₆Sn₅ (with NPs adsorbed) and molten solder, and Ω ($=1.18 \times 10^{-4}$ m³/mol) represents the molar volume of Cu₆Sn₅. T is the temperature, and R is the gas constant. For two interacting IMCs with different radii r_1 and r_2 . ϵ means the average separation among interfacial grains.

In context of Fig. 4 (a1, a2, a3, a4, a5), the nodular IMCs corresponding to the reflow time of 10 s are characterized by the absence of distinct facets on their surface whereas the prismatic Cu₆Sn₅ grains represented by Fig. 4 (b1-b5, c1-c5) that correspond to reflow duration of 60 and 120 s possess obviously observable faceted planes. For reflow duration of 10 s, the solder bulk is not

Fig. 4 The SEM top-view images of the IMC morphology of sample with flux doped with 0 wt.%, 0.2 wt.%, 0.5 wt.%, 1 wt.% and 2 wt.% of Type A NPs ($2R = 5$ nm) soldering for 10 s, 60 s and 120 s at 250 °C.

fully saturated with Cu species in context of reflow temperature of 523.15 K and due to this the prismatic IMC growth cannot take place during air cooling stage. At longer soldering duration of $t = 60$ s or 120 s, the solder solution is supersaturated with Cu, and this will accelerate the mechanism of screw dislocation driven growth of Cu_6Sn_5 at interface, thus enabling the appearance of faceted planes at the surface of after-cooled Cu_6Sn_5 [12,13].

3.2 Influence of particle size of TiO_2 on IMC growth behavior

For the investigation of the effect of different sized TiO_2 nanoparticles on the IMC evolution behavior, the SEM micrographs for samples processed with flux containing with Type A (5 nm) or Type B (50 nm) TiO_2 nanoparticles are shown in Fig. 5 6. The wt % of nanoparticles A and B, is chosen to be

Fig. 5 The SEM cross-section images of the IMC morphology of samples using flux doped with 2 wt. % of Type A (a - c) and Type B (d - f) TiO₂ nanoparticles. Type A and Type B correspond to particle diameter of 5 and 50 nm respectively.

Fig. 6 The SEM top-view figures of Cu₆Sn₅ IMC morphology of samples utilizing flux doped with 2 wt. % of Type A (a - c) and Type B (d - f).

fixed as 2.0, the reflow temperature is 250 °C and the reflow duration is chosen as 10, 60 and 120 s. From the cross-section images of interface in Fig. 5, it can be observed that at a given weight percentage of NPs in proportion to the total flux solution, the suppression of whiskered growth of IMCs at larger reflow duration of 120 s is more pronounced for smaller sized nanoparticles. This is because of two reasons-(i) smaller particles owing to larger surface area to volume ratio, have larger adsorption kinetics (detailed in Section 3.3) on Cu₆Sn₅, and (ii) given weight percentage of flux implies greater particle number and distribution density for Type A nanoparticles. Comparing the result of t=10 s of top-surface morphology in Fig. 6, it can be observed that IMCs nucleate with larger grain diameter for Type B nanoparticles.

Fig. 7 Variation in the average thickness of IMC layers and size of IMC grain as a function of the content and size of TiO_2 NPs added into flux. Average thickness of IMC layers (a) and average IMC grain width (c) of solder joint with 5 nm (type A) TiO_2 NPs soldering for 10 - 120 s at 250 °C; Average thickness of IMC layers (b) and average IMC grain width (d) of solder joint without TiO_2 NPs, with 2 wt.% 5 nm (type A) and 2 wt.% 50 nm (type B) soldering for 120s at 250 °C.

3.3 Kinetics of interfacial reaction

The interfacial Cu_6Sn_5 IMC layer thickness and the Cu_6Sn_5 grain size for samples with different weight percentage and particle sizes for TiO_2 NPs, are measured and the results are plotted in Fig. 7. As shown in the figure, the IMC layer thickness and grain size increase with an increase in reflow duration. For samples using Type A (5 nm) TiO_2 NPs, it can be observed from Fig. 7 (a), that the increase in content of nanoparticles, as compared to reference solder (without TiO_2 NPs), leads to the lowering of IMC layer thickness. In context of reflow for 120 s at 250 °C, the average thickness of IMC layer for solder without nanoparticles is 3.71 μm , is 3.67 μm for solder with 0.2 wt.% of Type A NPs in flux and is just 2.53 μm for sample with 2 wt.% TiO_2 nanoparticles in flux. The corresponding grain sizes at $t = 120$ s for these solders are 2.50 μm (0 wt %), 2.26 μm (0.2 wt %) and 1.68 μm (2.0 wt %).

As shown, in Fig. 7 (b) and (d), it is obvious that usage of either Type A or Type B, nanoparticles in soldering flux can suppress the layer thickness and grain sizes for interfacial IMCs. However the suppression effect is more pronounced in samples using smaller diameter (5 nm) TiO_2 nanoparticles. For

reflow at 120 s and nanoparticles occupying 2.0 wt % of applied flux, the IMC layer thickness is reduced by 1.38 μm (3.71-2.53) for samples with Type A NPs, whereas it is reduced by only 0.89 μm (3.71-2.82) in using Type B nanoparticles. Similarly, the reduction in grain width corresponding to Type A and Type B nanoparticles are 0.82 and 0.53 μm respectively. From these data, it is quite clear that the use of TiO₂ nanoparticles suppresses the layer and grain growth kinetics of interfacial IMCs, and the degree of suppression is more pronounced when particle diameter decreases at nanoscale.

Thus, physically there is the suppression of the grain ripening with the TiO₂ nanoparticles doped in flux. According to Ostwald ripening mechanism, the difference of the radius between neighboring grains of the IMC will cause the solder flux to diffuse to the direction of the bigger grain and away from the smaller one, thus shrinking the smaller grains while enlarging the bigger grains. The bigger the difference between the radii of the IMC grains, the higher the ripening rate.

3.4 The interaction between TiO₂ and the Cu₆Sn₅ IMC

The TiO₂ nanoparticles inserted into the solder in the experiments, are found to be present as chemically inert substances at the vicinity of the interfacial regime of solder/substrate. For experiment with flux doped TiO₂ nanoparticles, it is difficult not only to control the dispersion of nanosized particles over the IMC surface but also to, exactly locate them; and thus it remains the topic of future research to devise experiment to analyze the rule of TiO₂ nanoparticles distribution at the interfacial regime. However, from EDS technique, it has been possible to characterize the TiO₂ particles on the surface of Cu₆Sn₅ IMC. The Fig. 8 (a) shows the SEM image of specimens consisting TiO₂ nanoparticles. The EDS of Fig. 8 (b) verifies the presence of TiO₂ in the solder. In the Ref. [2], it also involves sintering of solder particles together with TiO₂ nanoparticles, the distribution of TiO₂ particles on IMCs has been characterized vividly using EDS technique. These all experimental evidences show that inert TiO₂ are adsorbed on Cu₆Sn₅ surface.

In order to analyze accurately about the process of how the TiO₂ nanoparticles interact with the Cu₆Sn₅ IMC, one TiO₂ nanoparticle adsorbed on the surface of Cu₆Sn₅ is considered in the study. As shown in Fig.8 (c1), because the size of TiO₂ nanoparticle is much smaller than that of Cu₆Sn₅, so the surface of Cu₆Sn₅ is taken as plane and the TiO₂ nanoparticles as the sphere. The surface energy relation between Cu₆Sn₅ and the TiO₂ nanoparticle can be deduced as [14]:

$$\gamma_{\text{solder}/\text{Cu}_6\text{Sn}_5} = \gamma_{\text{TiO}_2/\text{Cu}_6\text{Sn}_5} + \gamma_{\text{solder}/\text{TiO}_2} \cos\theta \quad (2)$$

where γ represents the interfacial energy per unit square meter area (interfacial tension) between the solution and the particle,. The interfacial energy of $\gamma_{\text{solder}/\text{Cu}_6\text{Sn}_5}$ is decreased due to the adsorption of TiO₂ nanoparticles. The theory of adsorption of surface-active TiO₂ material can be used to explain

Fig. 8 Interfacial Cu_6Sn_5 IMC layer of solder joints after soldering (a) with 2 wt.% TiO_2 nanoparticles in flux (b) energy dispersive X-ray spectroscopy (EDS) spot analysis (point A) on the surface of Cu_6Sn_5 . (C1) Schematic diagram to illustrate the adsorption behavior of TiO_2 on Cu_6Sn_5 IMC; (C2) The RVE of simulation is a cube of Cu_6Sn_5 IMC of side length of 100 nm with a depression on top made by an adsorbed TiO_2 nanoparticle.

its effect on the surface energy of Cu_6Sn_5 IMC. The larger the surface tension, the faster is the plane growth and the more is the adsorption amount of surface-active material [15].

The surface free energy usually used to describe the thermodynamic driving force for adsorption at a surface. K^0 (equilibrium adsorption constant) represents the ability of adsorption. The relationship among K^0 (equilibrium adsorption constant), surface free energy, and the size of adsorbed material can be defined using a classical thermodynamic approach. From the thermodynamic point, the K^0 can be expressed as [16,17]:

$$K^0 = \exp\left(-\frac{\Delta G}{RT}\right) \quad (3)$$

where, the ΔG denotes the free energy change for the adsorption of TiO_2 nanoparticles; R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); and T is the absolute temperature in Kelvin. For constant temperature and standard

pressure, the the ΔG can be described as:

$$\Delta G = \int_{\infty}^C \gamma_{solder/TiO_2} dA \quad (4)$$

where A stands for the molar surface area of the TiO₂ nanoparticles. For spherical particles, the molar surface area $A = \frac{3V_m}{r}$ where V_m is the molar volume of the particle and r is the radius of nanoparticles. If we evaluate the ratio of K^0 for two particles of different size (radius $R_1 < \text{radius } R_2$), Therefore, combining with the relationship with the Eq. 3 and Eq. 4, it can get:

$$\frac{K_{R1}^0}{K_{R2}^0} = \exp \left\{ -\frac{3V_m(\gamma_0^N - \gamma_c^N)}{RT} \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \right\} \quad (5)$$

where γ_c^N is the surface tension of plane N with adsorption of active nanoparticles and γ_0^N is the surface tension of the initial plane N without adsorption. Thus, $\gamma_0^N - \gamma_c^N < 0$ and $R_1 < R_2$. As a result, $K_{R1}^0 > K_{R2}^0$. This means the TiO₂ nanoparticle with small size can be more easily adsorbed by the Cu₆Sn₅ IMC surface than the big size. At the same time, it suggest that surface or interfacial tension of Cu₆Sn₅ can be modified significantly by the size of the adsorbed particles.

All the above relations can be utilized to explain the practical effect of nanoparticles on IMC growth, as sketched in schematic figure in Fig. 9. As the surface area of the 5 nm particles (R_1) per unit volume is larger than 50 nm TiO₂ particles (R_2), the adsorption effect and subsequently suppression effect to IMCs of 5 nm particles will be larger than those for 50 nm particles at a constant weight percentage (e.g. 2.0 wt. % of flux) . However, if Type A NPs are used at 0.2 wt. % and Type B NPs are used at 2 wt. %, the suppression effect is volume dominated , and consequently the latter Type NP, will have larger inhibitory effect on IMC growth. For example, the layer thickness reduction for IMC prepared with 0.2 wt. % of Type A NPs is only 0.04 μm , whereas the reduction for 2.0 wt. % of Type B NPs is about 0.89 μm . For cooling stage, the adsorption of nanoparticle on the surface of IMC also can restrict the process of Cu concentration driven screw dislocation growth of prismatic IMC [1].

3.5 Stress analysis at the Cu₆Sn₅/TiO₂ interface

It is quite known that inert TiO₂ nanoparticles, are adsorbed on the IMC surface and they do not react with it. Thus, as the IMC tries to evolve via the interfacial reaction between Cu and liquid Sn, the TiO₂ nanoparticle will suppress the local growth of the IMC around its vicinity, and thus nano-sized craters or pits are formed at the local interface. A representative volume element(RVE) of an IMC, as shown in Fig. 8 (c2), consists of a cube of Cu₆Sn₅ of length 0.1 μm with a pore of diameter 0.05 μm bored on its top surface. The depth of the pore is equal to its radius and it represents the nanovoid created in the IMC material due to the presence of stable TiO₂ nanoparticle.

Size of TiO ₂ NPs	specific surface area	Content of TiO ₂ NPs	Relative shielding effect
$2R_1 = 5 \text{ nm}$	$\frac{S}{V} = \frac{3}{R_1}$	0.2 %
		2 %

$2R_2 = 50 \text{ nm}$	$\frac{S}{V} = \frac{3}{R_2}$	2 %

Fig. 9 Schematic sketch for the influence of content and size of TiO₂ nanoparticles on IMC growth morphology. IN the figure, S and V imply surface area and volume respectively.

The equation of linear elasticity for deformation of Cu₆Sn₅ IMC cube is defined by the following partial differential equation:

$$\rho \frac{\partial^2 \vec{d}}{\partial t^2} - \nabla \cdot \tau = \vec{f} \quad (6)$$

where, $\vec{f}$ denotes the body force vector; the stress (τ) and strains (ϵ) are represented as following functions of displacement vector ($\vec{d}$) :

$$\tau = 2\nu\epsilon + \lambda \nabla \cdot \vec{d} I - \beta(T - T_0) \quad (7)$$

$$\epsilon = \frac{1}{2}(\nabla \vec{d} + (\nabla \vec{d})^T) \quad (8)$$

In Eq. 7, ν and λ are Lamé's parameters (related to poisson's ratio (μ) and Young's modulus of Elasticity (E) for isotropic IMC material), β is heat expansion coefficient and I is unit tensor. During isothermal reflow and even at cooling for smaller sized solders, Biot number is smaller than 0.1 and effects of thermal gradients on effective value of stress in IMCs are neglected for the present study. Thus, the second term in right hand side of Eq. 7 vanishes. For steady state condition, the first term in left hand side of Eq. 6 is zero, and thus equation becomes:

$$\nabla \cdot \tau + \vec{f} = 0 \quad (9)$$

For Cu₆Sn₅ IMC material, μ and E are taken as 0.31 and 112.3 GPa respectively [18,19,20,21]. During the growth of IMC during interfacial reaction, there is the development of stress and so volumetric body stress of 306.5 MPa per unit volume is exerted on the RVE. The solution of Eq. 9 obtained by using finite element method in Elmer multiphysics software [22], gives the von

Fig. 10 The von Mises stress distribution on the RVE of Cu_6Sn_5 IMC.

Mises stress distribution as shown in Fig. 10. The magnitude of simulation results are in agreement with those of [23].

From the numerical simulation results it is observed that the stress in the depression region is maximum and is of magnitude 22.95 GPa. However, in the bulk part of element of IMC at several nanometer away from this pore, the stress is very low and is in the order of 0.3 GPa. This inference is very important in terms of the experimental results of IMC with finger like projections at the topmost portion of the layer or disappearance of whiskers due to TiO_2 addition at sufficiently larger weight percentage for a given particle size, as discussed in Section 3.1. The adsorption of nanoparticles at the top surface, creates a region of larger stress concentration and causes the breaking off of brittle IMC material. The breakage of Cu_6Sn_5 compound, during its growth stage can be a causative factor for "suppression effect" on the IMC layer thickness and grain diameter. So, the occurrence of stress concentration regime in context of TiO_2 constituting specimen, is the major cause which explains the distinct morphology of IMCs in these joints and growth-suppression effect on Cu_6Sn_5 as compared to those of undoped specimens.

4 Conclusions

The following conclusions can be drawn from this study:

1. Sn/Cu joints were prepared by using flux doped with different content (0.0-2.0 wt. % of flux) and particle size (5 nm and 50 nm) of TiO_2 nanoparticles, and their influence on Cu_6Sn_5 IMC growth was investigated.

2. For the Sn/Cu solder joints reflowed at 250 °C for 10, 20 and 120 s, and then subjected to air cooling, the increase in reflow duration was characterized with an increment in IMC layer thickness and grain size.
3. The increase in content of TiO₂ nanoparticles in flux was observed to suppress the growth of IMC layer and grain size. The suppression effect was more pronounced, when the particle diameter of nanoparticles is smaller. Thus, particle diameter and mass/weight proportion of TiO₂ nanoparticles are important material design parameters. TiO₂ nanoparticles, adsorbed on IMC plane inhibit the growth of the latter.
4. Presence of sufficient volume of a given sized TiO₂ nanoparticles among IMCs, will increase the effective stress at the localized interfaces; and thus cause the breaking of brittle Cu₆Sn₅ during growth stage. This explains the disappearance of IMC whiskers and decrement of IMC size in TiO₂ containing samples, as compared to solder joints prepared with undoped flux.

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