Characteristics of Reactive Ni_3Sn_4 Formation and Growth in Ni-Sn Interlayer Systems

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The near-isothermal growth and formation of Ni_3Sn_4 intermetallic compounds (IMC) in Ni-Sn interlayer systems was studied in the solid state at 473 K (200 °C) and under solid-liquid conditions at 523 and 573 K (250 °C and 300 °C) from an initial state of a few seconds. Scalloped solid-state IMC formation was mainly driven by grain boundary diffusion of Ni through the IMC layer combined with the grain coarsening of the IMC layer. Under solid-liquid conditions, the formation of faceted and needle-shaped Ni_3Sn_4 grains as well as an atypical IMC growth behavior with similar parabolic growth constants for 523 K and 573 K (250 °C and 300 °C) was observed within the first 180 seconds of the holding time, and IMC growth occurred as an isothermal solidification from the Ni-saturated Sn melt. Due to the progressive densification of the IMC layer and the diffusion-controlled growth, the kinetics slowed down by approximately one order of magnitude after 180 seconds of annealing. The final stage was characterized by the formation of IMC islands ahead of the interfacial Ni_3Sn_4 layer. Needle-like IMC growth was effectively suppressed under combined solid-state and solid-liquid conditions. Textured Ni_3Sn_4 IMC formation at the Ni-Sn interface was approved with pole figure measurements. The activation energy Q for solid-liquid IMC formation was calculated as 43.3 kJ/mol, and processing maps for IMC growth and Sn consumption were derived as functions of temperature and time, respectively.

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I. INTRODUCTION

IN recent years, the electronics industry has strived to replace lead-based high-temperature solders in packaging due to legal restrictions on these types of alloys. Simultaneously, the requirements for interconnections have increased as 3D assembly and chip technology are now based on SiC instead of Si, which has led to significantly smaller dimensions and miniaturization.^[1] In these cases, low-volume interconnections are of high interest where the thickness of the solder layer cannot exceed several microns. A promising joining technique to overcome the above-mentioned issues is the so-called transient liquid phase bonding (TLPB) technique, which makes use of a (thin) interlayer arrangement consisting of a low melting point material sandwiched between two layers with higher melting points. Isothermal solidification is accompanied by the formation of intermetallic compounds (IMC) at the interfaces during processing and is completed after the liquid material is fully consumed.^[2]

Interlayers with a X-Sn-X (X = Ni, Cu, Ag, Au) stacking sequence are technically very promising.

Previous scientific studies have focused on different aspects of the kinetics and morphology of IMC formation within various layer systems to develop reliable and optimized processes for TLPB. Cu-Sn and Ni-Sn systems are especially attractive because of their low material costs. While Cu-Sn systems have been extensively studied by many researchers with regard to TLPB, few studies have examined Ni-Sn systems. According to the binary Ni-Sn phase diagram^[3] shown in Figure 1, the first intermetallic target phase within the Ni-Sn system (Ni_3Sn_4) offers the highest re-melting temperature among the above-mentioned systems, that is, 1067.5 K (794.5 °C). Combining this aspect with the excellent corrosion resistance of Ni makes this system an interesting candidate for high-temperature applications in various industrial fields.

In previous studies, different approaches have been developed to assess and analyze the solid-liquid interface reactions in X-Sn systems. Many systems have been developed to study reactions during standard soldering. They are based on the concept that partially considers the reactive features during TLPB when a (near-)eutectic composition of (Ag,Cu,Ni,Pb,Bi)-Sn is deposited on Ni substrates. It has been shown that additional alloying elements in the solder as well as the configuration of the metallization layer can significantly influence the growth kinetics and morphology of IMC formations.^[4–9] A study on Ni-Sn IMC formations using $\text{Sn}_{3.5}\text{Ag}_{0.5}\text{Cu}$ solder and electroless NiP layers at 523 K (250 °C) revealed how the addition of P leads to the embrittlement of the solder joints, resulting in solder

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Fig. 1—Binary Ni-Sn phase diagram.^[3]

delamination and a significant decrease of the shear strength after only 180 min of reflow time.^[10] Shen *et al.*^[7] investigated the IMC formation between Ni plates and Sn3.5Ag0.75Ni solders at 523 K and 553 K (250 °C and 280 °C) for reaction times of up to 10 hours and calculated an activation energy of 11 kJ/mol for Ni_3Sn_4 formation. The well-known scallop-like morphology of IMC, in general, as theoretically described by Schaefer *et al.*,^[11] transformed into a more faceted structure with increasing holding time. Lin *et al.*^[12] interrupted the interfacial reaction between Ni and the Sn3.5Ag solder after 5 seconds at 523 K (250 °C) and identified an amorphous diffusion zone carrying crystalline and metastable NiSn IMC spots. In addition, they observed dissolution channels by TEM analyses, which transport Ni atoms toward the liquid Sn solder. Chen *et al.*^[13] obtained activation energies of 25 and 38 kJ/mol for the Ni_3Sn_4 formation between the eutectic Sn-Ag solder and electroplated Ni and electroless Ni, respectively.

Considering the reliability of assemblies in microelectronics, it is essential to understand solid-state IMC reactions because the service temperatures are below the melting point of Sn or Sn-based solders. IMC formation proceeds even though the growth kinetics are reduced in comparison with the solid-liquid case. Labie *et al.*^[14] studied the long-term annealing behavior of Ni-Sn interlayers up to 1000 hours. The activation energy for the formation of Ni_3Sn_4 due to solid-state diffusion was shown to decrease from 91 to 56 kJ/mol when reducing the temperature from 448 K to 327 K (175 °C to 100 °C). Annealing experiments on electroplated Ni-Sn layers between 423 K and 498 K (150 °C and 225 °C) were conducted by Tang *et al.*^[15] with a lower activation energy of 39 kJ/mol and showed that IMC preferably grew toward the Ni layer. Mita *et al.*^[16] characterized Ni-Sn diffusion couples annealed at 453 K and 473 K (180 °C and 200 °C) between $2 \cdot 10^5$ and $5 \cdot 10^6$ s. Solid-state growth followed a power law with exponents n of 0.459 and 0.405 at 453 K and 473 K (180 °C and 200 °C), respectively, indicating a pronounced contribution from GB diffusion combined with coarsening (compared to volume diffusion) at higher temperatures.

Suh *et al.*^[17] placed a eutectic SnPb solder on a quasi-single crystal Ni and tracked the formation of Ni_3Sn_4 IMC by synchrotron white beam micro-XRD under solid-state conditions at 473 K (200 °C). Two preferred orientation relationships between the Ni substrate and Ni_3Sn_4 were detected, which were formed immediately after nucleation.

Most of the above-mentioned studies focused on holding times of minutes to weeks. When using conventional reflow ovens, experiments are constrained by the limited heating rates of these systems, so the early-stage reactions cannot be precisely examined. Dipping methods, such as submerging a metal substrate into molten Sn baths, can solve this issue of undefined reactions during heating. Dybkov,^[18] for instance, applied this method to monitor IMC formation between Ni and Sn solders that were saturated with Ni or contained no Ni, respectively. After an isothermal holding time of 300 seconds at 623 K (350 °C), the Ni_3Sn_4 layer that was in contact with the saturated solder grew five times thicker because Ni atoms are not needed to diffuse through the IMC layer, but are already dissolved in the solder. Gur and Bamberger^[19] identified a microstructural transition zone, which was explained by the simultaneous and opposite growth of coarse-grained Ni_3Sn_4 IMC toward the Sn side and fine-grained Ni_3Sn_4 toward the Ni substrate. The IMC scallops observed at 773 K (500 °C) were shown to transform into elongated faceted grains at lower temperatures of 673 K and 623 K (400 °C and 350 °C). In a different approach, Görlich *et al.*^[20] assessed early-stage IMC formation by placing molten Sn droplets on a hot Ni plate at 250 °C. They obtained near-isothermal experimental conditions, which were tracked from 30 seconds to 7 days of holding time. These authors proposed that growth kinetics are initially best captured by a cubic growth law (up to 3 minutes), but follow a parabolic function over longer holding times. Bader *et al.*^[21] reached near-isothermal conditions by submerging Ni-Sn and Cu-Sn interlayer combinations protected by Al foils in liquid Pb-Sn baths. The Ni_3Sn_4 reaction kinetics were found to proceed much slower when single crystal Ni or Cu layers were applied compared to polycrystalline materials, which indicated the strong contribution of grain boundary diffusion on IMC formation. Choi *et al.*^[22] and Kim *et al.*^[23] applied the theory posed by Jackson and Hunt^[24] on crystal growth from the melt and morphological differences in X-Sn systems, *i.e.*, whether scallop-like or faceted IMC forms, to the value of the Jackson parameter.

In this work, we mainly targeted the early-stage growth characteristics of Ni_3Sn_4 IMC within Ni-Sn interlayers by applying an experimental setup that enables experiments in the solid-liquid state [523 K, 573 K (250 °C, 300 °C)], solid state [473 K (200 °C)], as well as in a combined solid-state and solid-liquid regime [473 K + 523 K (200 °C + 250 °C)], under identical and near-isothermal conditions. This approach was first introduced in Reference 25 for studying the Ag_3Sn growth characteristics of a Ag-Sn interlayer system. Consequently, the results on the kinetics, morphological features and diffusion mechanisms could be directly

linked to experimental parameters, such as temperature and time.

II. EXPERIMENTAL WORK

A. Experimental Setup and Processing

The experimental setup was inspired by the demand to have near-isothermal conditions with a fast heating rate, to adjust the temperature precisely, and to stabilize the temperature during the experiments. A massive and partially open cavity (1) manufactured from bulk Cu was placed on a temperature-controlled heating plate (2). The experimental accuracy was ensured by installing another thermocouple (3) within the Cu bulk material. The height of the thermocouple, *i.e.*, the distance between the heating plate and measuring point, was chosen to be consistent with the height of the specimen (4). The temperature measurement had an uncertainty of ± 1 K. The same experimental setup was used in our previous study on Ag-Sn interfacial reactions,^[25] where it is described in detail.

Experiments were conducted in the solid-liquid regime with molten Sn at 523 K and 573 K (250 °C and 300 °C), with near-isothermal holding times of 10, 30, 60, 180, 600, and 1500 seconds, and under solid-state conditions below the melting point of Sn at 473 K (200 °C) for 600, 1800, 3600, and 10,800 seconds. Moreover, combined solid-state and solid-liquid reactions were investigated when samples were first annealed at 473 K (200 °C) for 1800 seconds and were subsequently subjected to 523 K (250 °C) with varying holding times of 30, 60, 600, and 1500 seconds. Long-term reactions were marginally captured by performing experiments at 523 K (250 °C) for a holding time of 15 hours. Reactions were interrupted by quenching the samples in cold water.

A 400- μm Cu plate served as the carrier material on which 15 μm Ni and 17 μm Sn were electroplated. The Cu carrier was sufficiently thick to prevent the whole sample from deforming during handling, processing, and the experiments, as well as to enable rapid heat transfer toward the Ni-Sn top layers due to its excellent thermal conductivity. Because the Ni-Sn interface represents a closed system, the experiments were performed under normal atmospheric conditions. According to the binary Ni-Sn phase diagram, interfacial reactions will first initiate the formation of the Ni_3Sn_4 phase, with a melting temperature of 1067.5 K (794.5 °C), as shown in the binary Ni-Sn phase diagram in Figure 1.

B. Analytical Methods

Samples were exposed to a defined temperature for a given time and were then embedded into cold mounting resin. The subsequent metallographic preparation consisted of step-wise grinding and polishing with a silica suspension. The cross sections were surface treated by Ar ion beam flat milling (Hitachi IM 4000) to eliminate smearing artifacts caused by the ductile interlayers. A small inclination angle of 5 deg and a reduced

acceleration voltage of 4 kV were chosen to ensure smooth material removal. The ion beam treatment revealed sharp interfaces between the different layers and phases, a slight topography effect between Ni_3Sn_4 and Sn and the grain structure within the single layers. As-coated samples were subjected to XRD measurements on a Bruker D8 diffractometer, with a spectrum recorded between 25 deg and 70 deg and a step time of 1 second. XRD pole figure measurements were conducted on samples after long-term annealing at 523 K (250 °C) for 15 hours. The pole figure measurements were performed for the (111) plane of the Ni_3Sn_4 phase with $2\theta = 30.43$ deg and for the (312) plane with $2\theta = 43.45$ deg. The angle in ψ direction was increased in steps of 5 deg, and the measurement time per spot was defined as 4 seconds.

Imaging was conducted by SEM (Hitachi S3700) with a high-resolution backscattered electron (BSE) contrast detector that amplifies the detector signal and provides better contrast between Cu, Ni, Sn, and Ni_3Sn_4 . The morphology and size of the IMC structures were analyzed by Image J software. The mean intermetallic thickness $z_{\text{IMC,m}}$ was obtained after dividing the total IMC area by the corresponding lateral image length. The irregularity of the observed intermetallic phases was captured by the root mean squared (RMS) interfacial roughness according to

$$z_{\text{RMS}} = \sqrt{\frac{1}{N} \sum_{i=1}^N Z_i^2} = \sqrt{\frac{1}{N} \sum_{i=1}^N (z_i - z_{\text{IMC,m}})^2}, \quad [1]$$

where Z is the distance between the Ni_3Sn_4 -Sn interface and the mean intermetallic thickness. The individual values for Z_i were measured in the BSE images with a lateral step size of 1 μm . Elongated, needle-like IMC observed under solid-liquid conditions were additionally characterized by their aspect ratio, a_r , after dividing the IMC length, l_{IMC} , by its corresponding width, w_{IMC} , and averaging the measurements for each temperature and holding time.

$$a_r = \frac{1}{N} \sum_{i=1}^N \frac{l_{\text{IMC},i}}{w_{\text{IMC},i}}. \quad [2]$$

Each calculated value is based on the analysis of at least seven images.

III. RESULTS

A. Initial Conditions

Before the diffusion experiments at elevated temperatures, the initial state of the Ni-Sn interface was characterized after electroplating and storage. Hence, an Ar ion beam cross section through the Ni-Sn top layers into the Cu substrate was produced. In contrast to the ion beam flat milling option described above, in this case, the ion beam penetrates into the sample perpendicular to the top surface. The Gaussian intensity distribution of the ion beam that came from the top

migrated into the sample by a maximum distance of approximately 70 μm after 1 hour when the beam intensity was highest. Figure 2(a) shows the sharp interface between Ni and Sn, which is characterized by their different contrasts, whereas the Ni and Cu layers can be mainly distinguished by their different grain structures. A higher magnification image (Figure 2(b)) of the Ni-Sn interface does not suggest the formation of IMC in the as-coated conditions. A wedged sample, as shown schematically in Figure 2(c), was used to perform XRD measurements because the top Sn layer absorbs the X-ray beam. The diffraction spectrum clearly confirms the presence of only Ni, Sn, and Cu. No IMC layer was detected between Ni and Sn.

B. Solid-State Reactions

Pronounced reactions at the initial Ni-Sn interface can be observed at a holding temperature of 473 K (200 °C). Figure 3(a) shows a dense IMC layer after a holding time of 30 minutes, and a scallop-like interface divides the Ni_3Sn_4 IMC from the solid Sn. When the

holding time is increased to 180 minutes, uniform thickening of the IMC layer is observed, and the morphology of the IMC layer with its scallops toward the Sn side can be seen in Figure 3(b).

The RMS interfacial roughness was captured by Eq. [1]. The results are listed in Table I. The values of z_{RMS} increase up to 30 minutes of holding time and reach an almost constant value of approximately 0.17 μm at longer holding times, indicating the uniform growth of the IMC layer. Simultaneously, IMC scallops are commonly accepted to indicate the predominant growth and diffusion direction, as shown by Schaefer *et al.*^[11] Ni atoms most likely diffuse through the valleys between neighboring scallops, *i.e.*, along grain boundaries, with the shortest distance to the Sn side. This aspect can be confirmed by fitting the experimental points for $z_{\text{IMC,m}}$ with a power law according to

$$z_{\text{IMC,m}} = a \cdot t^n, \quad [3]$$

where a is the growth proportionality factor and n is the growth exponent. Data points for 473 K (200 °C) can be best fitted by the growth exponent of $n = 0.33$. According to the current literature, this exponent can be assigned to predominant GB diffusion in combination with coarsening.^[11,26]

C. Solid-Liquid Reactions

1. Early-stage reactions

Compared to solid-state reactions, Ni_3Sn_4 IMC forms with an entirely different morphology under solid-liquid conditions. Scallop IMC is replaced by elongated and faceted IMC needles. Figure 4 shows the evolution of Ni_3Sn_4 IMC starting from 10 seconds of holding time and continuing to 60, 180, and 600 seconds, both at 523 K (250 °C) (Figures 4(a) to (d)) and 573 K (300 °C) (Figures 4(e) to (h)). Well-defined IMC needles already exist after 10 seconds of total holding time. At both temperatures, IMC growth proceeds as the initially thin and small needles expand in the length and width direction. It is important to mention that applying Eq. [3] to the experimental values at 523 K and 573 K (250 °C and 300 °C) did not lead to a satisfying fit quality. Therefore, a parabolic growth law was used:

$$z_{\text{IMC,m}} = \sqrt{k \cdot t}, \quad [4]$$

where k is the parabolic growth constant. In this way, it was possible to identify changing growth kinetics over the holding time after plotting the mean IMC thickness over the square root of time, as shown in Figure 5 from our experimental values. The slope of the fitting curve yields the parabolic growth constant at 523 K and 573 K (250 °C and 300 °C). The growth kinetics in the early stages (up to 180 seconds) are similar with those of k , calculated as $1.8 \cdot 10^{-10} \text{ cm}^2/\text{s}$ at 523 K (250 °C) and $1.4 \cdot 10^{-10} \text{ cm}^2/\text{s}$ at 573 K (300 °C), leading to comparable mean IMC thicknesses. However, the growth rate significantly decreases in the second time regime, *i.e.*, for holding times of more than 180 s. The parabolic growth constants within this time regime are determined to be

Fig. 2—(a) Layered specimen with as-coated electroplated Ni and Sn, (b) magnification of the Ni-Sn interface, and (c) X-ray diffraction spectrum of the wedged sample.

Fig. 3—Evolution of Ni_3Sn_4 IMC at 473 K (200 °C) after (a) 1800 s and (b) 10,800 s.

Table I. Summary of Experimental Data

T [K (°C)]	t (s)	$z_{\text{IMC,m}}$ (μm)	SD (μm)	z_{RMS} (μm)	w_{IMC} (μm)	a_r (—)	k ($10^{-10} \text{ cm}^2/\text{s}$)
473 (200)	600	0.66	0.1	0.1	—	—	0.022
	1800	0.87	0.13	0.17	—	—	
	3600	1.2	0.17	0.16	—	—	
	10800	1.66	0.16	0.18	—	—	
523 (250)	10	0.59	0.03	0.23	0.16	4.97	1.8
	30	0.96	0.03	0.71	0.195	8.95	
	60	1.35	0.06	1.08	0.22	10.43	
	180	1.98	0.16	1.38	0.38	7.75	
	600	2.53	0.15	1.1	0.46	7.88	
	1500	3.21	0.23	1.19	0.59	7.5	
573 (300)	10	0.8	0.06	0.53	0.28	4.7	1.4
	60	1.4	0.1	0.8	0.36	6.18	
	180	2.07	0.29	1.01	0.51	5.8	
	600	3.07	0.13	1.53	0.81	5.39	
	1500	3.97	0.2	1.55	0.88	5.7	
	1500	3.97	0.2	1.55	0.88	5.7	
473 (200) + 523 (250)	30	0.346	0.16	0.29	—	—	0.29
	60	0.595	0.1	0.34	—	—	
	600	1.246	0.27	0.62	—	—	
	1500	2.11	0.22	0.97	—	—	

$2.3 \cdot 10^{-11}$ and $5.6 \cdot 10^{-11} \text{ cm}^2/\text{s}$ at 523 K and 573 K (250 °C and 300 °C), respectively. Hence, IMC growth is faster now at higher temperatures.

The aspect ratio a_r of the IMC needles is plotted in Figure 6(a) as a function of time. Similar values of approximately 5 can be obtained after 10 seconds of holding time at 523 K and 573 K (250 °C and 300 °C), respectively. However, as the holding time increases, the curves significantly diverge. At 573 K (300 °C), the aspect ratio remains almost constant over time, approaching a value of approximately 5.7, which indicates a more or less constant growth rate in length and width of the IMC needles. In contrast, the aspect ratio of the IMC needles at 523 K (250 °C) rapidly increases, reaching a peak value of 10.4 after 60 seconds of holding time. Subsequently, it decreases and reaches a plateau after 180 seconds at a value of approximately 7.8. Both graphs in Figures 5 and 6(a) are correlated when assigning the atypically high growth rates at 523 K (250 °C) up to 180 seconds, with preferred growth rates in the length direction.

Once the aspect ratio is stabilized for both temperatures at holding times longer than 180 seconds, the parabolic growth constant is higher at 573 K (300 °C) compared to that at 523 K (250 °C). The evolution of the interfacial roughness z_{RMS} as a function of time is plotted in Figure 6(b) and conforms well to the above-mentioned evolution of the aspect ratio and mean IMC thickness. The preferred growth in the length direction at 523 K (250 °C) and in the early stages is evidently mirrored by the value of z_{RMS} , which is higher at 523 K (250 °C) ($1.31 \mu\text{m}$) than at 573 K (300 °C) ($1.01 \mu\text{m}$) after 180 seconds. However, after reaching a balanced length-to-width thickening of the IMC needles at 600 seconds, z_{RMS} yields a higher value at 573 K (300 °C) ($1.53 \mu\text{m}$), whereas z_{RMS} at 523 K (250 °C) decreases ($1.1 \mu\text{m}$).

2. Long-term reactions

To capture the morphological changes over a longer time regime, additional annealing experiments were performed at 523 K (250 °C) for 15 hours. The

Fig. 4—Evolution of Ni_3Sn_4 IMC after 10, 60, 180, and 600 s at 523 K (250 °C) in (a through d) and at 573 K (300 °C) in (e through h).

corresponding cross section for this sample is shown in Figure 7, where significantly different IMC morphologies can be observed compared to samples that were annealed for up to a few minutes, as shown in Figure 4.

Ni_3Sn_4 IMC islands form within the whole volume of liquid Sn. Considering the shape of the IMC spots, it can be concluded that they form independently. The holding time was apparently not sufficient to consume

Fig. 5—Mean IMC thickness vs square root of time for 523 K (250 °C), 573 K (300 °C), and 523 K + 573 K (200 °C + 250 °C) with corresponding growth constants.

Fig. 6—Evolution of (a) aspect ratio and (b) root mean squared interfacial roughness.

the whole Sn layer. Faceted IMC needles, as observed during the short-term annealing process, can no longer be found.

3. IMC grain orientation

Figure 8(a) shows the atomic arrangement within the Ni_3Sn_4 monoclinic unit cell with $\alpha = \gamma = 90^\circ$ and $\beta = 105^\circ$, which belongs to the $C 12/m$ space group. The unit cell includes the (111) plane in red and the (312) plane in green, both subjected to pole figure measurements. To assess the dense IMC layer after long-term annealing for 15 hours, as shown in Figure 7, the sample was grinded down to remove the top layer with its IMC islands and Sn channels. Figure 8(b) shows the cross-sectional view of the sample where only the dense layer of IMC is shown with an average thickness of 3 to

Fig. 7— Ni_3Sn_4 IMC growth after 15 h at 523 K (250 °C).

4 μm . A pronounced out-of-plane texture could be identified for both planes when (111) demonstrated a ring-shaped intensity maximum in red at an angle ψ between 30 deg and 40 deg, as shown in Figure 8(c), whereas the intensity maximum for (312) was found to be normal to the sample surface, with $\psi = 0^\circ$, as shown in Figure 8(d).

Dendritic cells are known to grow with a preferred grain orientation that is dependent on the crystal structure of the material, *e.g.*, in the (100) direction for fcc and bcc unit cells.^[24] Generally, loose packed planes are expected to grow fastest after nucleation at a solid–liquid interface because larger spacing between the crystal atoms leads to the easier attachment of additional atoms from the liquid phase. The angle between the (111) and (312) planes was calculated as 87.2 deg, which indicates that both directions represent separate grain orientations. This suggests that an individual IMC grain that has the measured (111) orientation should not provide the measured texture for (312). However, because the monoclinic unit cell contains equivalent crystallographic planes, both pole signals shown in Figures 8(c) and (d) are diffracted from the same IMC grain family. Further calculations provided an angular distance of 43 deg between (111) and (010), which correlates well to the measured intensity maximum for (111) at an angle ψ of approximately 40 deg. Consequently, (010) can be claimed to be the normal orientation toward the surface ($\psi = 0^\circ$) within IMC needles oriented according to the ring-shaped intensity pattern for (111).

D. Combined Solid-State/Solid–Liquid Reactions

After the samples were exposed to solid-state conditions at 473 K (200 °C) for 1800 seconds, a Ni_3Sn_4 IMC layer, as shown in Figure 3(a), forms. During the subsequent solid–liquid reaction at 523 K (250 °C), the IMC layer continues to grow with its scallop-like contour. However, the scallops become more faceted, as seen in Figure 9(a), over a near-isothermal holding time of 60 seconds at 523 K (250 °C). When the solid–liquid holding time is increased to 1500 seconds, further growth of the dense IMC layer is observed,

Fig. 8—(a) Atomic arrangement in monoclinic Ni_3Sn_4 unit cell including (111) and $(31\bar{2})$ planes, (b) cross section of the specially prepared sample subjected to pole figure measurement, (c) pole figure of the Ni_3Sn_4 layer for the (111) plane, (d) pole figure of the Ni_3Sn_4 layer for the $(31\bar{2})$ plane.

whereas detached Ni_3Sn_4 IMC particles evolve in the vicinity of the interface between the dense IMC and the liquid Sn according to Figure 9(b). The kinetics of the solid–liquid reactions in the dense IMC layer formed under solid-state conditions are captured by a parabolic growth constant of $k_{250^*} = 2.9 \cdot 10^{-11} \text{ cm}^2/\text{s}$. This value corresponds well to that obtained in the second reaction regime for continuous solid–liquid conditions at 523 K (250 °C) in Section III-C-1. In contrast to pure solid–liquid reactions, the reaction kinetics of the combined solid-state and solid–liquid reactions do not change over time.

IV. DISCUSSION

A. Morphological Evolution of Ni_3Sn_4 IMC

Based on the experimental results in our study, a morphological model for early-stage Ni_3Sn_4 formation from nucleation until a holding time of minutes is proposed, which combines and links the above-mentioned aspects and suggests the predominant growth mechanisms.

Immediately after exceeding the melting point of Sn, Ni atoms can easily dissolve in liquid Sn at intimate contact points. The diffusion coefficient for Ni in liquid Sn, $D_{\text{Ni/liqSn}}$, at 523 K (250 °C) was given in the work of

Ma and Swalin^[27] as $10^{-2} \text{ cm}^2/\text{s}$. Applying this value to our experimental configuration with a Sn layer of 17 μm demonstrates that Ni atoms can diffuse through the whole liquid Sn layer within milliseconds. Additional Calphad calculations of the Sn-rich side of the binary Ni–Sn phase diagram provided a maximum solubility of Ni in Sn of 0.095 and 0.171 mol pct at 523 K and 573 K (250 °C and 300 °C), respectively, which in combination indicates that the Sn layer will be quickly saturated with Ni.

In the initiation phase, IMC nuclei form at the Ni–Sn interface. It can be strongly assumed that these nuclei are textured, as claimed by van Beek *et al.*^[28] Only a fraction of the IMC nuclei that coincidentally have a preferred orientation toward the liquid Sn will continue growing (fast) as elongated needles. This is probably related to the minimization of the interfacial energy and is consistent with the work of Suh *et al.*^[17] However, a direct verification of the orientation relationship is difficult due to the rather complex structure of Ni_3Sn_4 and would require a detailed ab-initio study, which is beyond the scope of the present work. This configuration is visualized in Figure 10(a), indicating that the direct contact points between Ni and liquid Sn allow for the dissolution of Ni atoms into liquid Sn. This is strongly consistent with the experimental results shown in Figures 4(a) and (e), which show deep valleys down to

Fig. 9—Evolution of the Ni_3Sn_4 IMC after 1800 s at 200 °C, and subsequent annealing at 523 K (250 °C) for (a) 60 s and (b) 1500 s.

the Ni-coating gap between the individual IMC needles after very early reaction times of 10 seconds. The resulting IMC layer is therefore not dense and Ni is continuously dissolved in liquid Sn during this first stage. Ni_3Sn_4 IMC needles clearly grow toward the liquid Sn side.

Many studies have demonstrated that IMC growth in the solid–liquid regime can be described by the flux-driven-ripening model,^[29] in which atomic transport occurs through liquid channels between single IMC grains. This transporting mechanism leads to the well-known scallop-like IMC morphology observed in Ag–Sn or Cu–Sn systems.^[11,25,26] By contrast, the formation of faceted Ni_3Sn_4 IMC has been monitored in various studies.^[19,20,22,23] Generally, a phase facets when it is difficult for atoms to attach from the liquid state to a nucleated solid layer. Jackson and Hunt^[24] developed a theory on the solidification from the melt, in which they introduced the Jackson parameter α as

$$\alpha = \frac{\Delta H_f}{RT_s} \cdot \xi, \quad [5]$$

where ΔH_f is the enthalpy of formation, R is the gas constant, T_s is the soldering temperature, and ξ describes the fraction of the total number of nearest neighbors in a plane parallel to the interface (usually

$\xi = 0.5$). The equation claims to predict faceted solidification for α larger than 2 and smooth, scalloped growth for α smaller than 2. Choi *et al.*^[22] and Kim *et al.*^[23] validated the model of Jackson and Hunt for the reactive solid–liquid formation of faceted Ni_3Sn_4 IMC ($\alpha > 2$) and scallop-like Cu_6Sn_5 IMC ($\alpha < 2$). Thus, the enthalpy of formation mainly governs the morphology of IMC when Ni_3Sn_4 IMC formation is accompanied by a much larger release of heat, *i.e.*, approximately 24 kJ/mol, compared to Cu_6Sn_5 and Ag_3Sn formation (6.1 and 4.2 kJ/mol,^[30] respectively), leading to more pronounced local supersaturation of the Sn melt and growth anisotropy.

As a consequence, IMC growth is governed by the crystal growth rates of Ni_3Sn_4 from the Ni-saturated Sn melt, and therefore, the parabolic growth constants are almost identical for near-isothermal annealing at 523 K and 573 K (250 °C and 300 °C), respectively. Differences in the length-to-width growth of the IMC needles at 523 K and 573 K (250 °C and 300 °C) and during early reaction stages can be derived from the plot of the aspect ratio over time, as shown in Figure 6(a). The explanation for this phenomenon might be given by the solubility of Ni in liquid Sn, which differs by a factor of almost 2 comparing both experimental temperatures. Because the growth of IMC needles from the saturated Sn certainly depletes the matrix in its vicinity, needles might preferably grow more in the length direction in which a sufficient reservoir of Ni atoms is available. This stage of IMC formation is schematically shown in Figure 10(b).

In the subsequent characteristic step, the IMC needles grow in the length and width directions, which finally leads to densification of the IMC layer and sealing of the Ni dissolution points and fast diffusion paths between the Ni substrate and liquid Sn. This effect was experimentally observed after a holding time of approximately 180 seconds, as shown in Figures 4(c) and (g), for a mean IMC thickness of approximately 2 μm . The elimination of the direct diffusion paths further influences the growth kinetics, as seen in Figure 5, where the densification of the IMC layer is correlated to the decrease of the parabolic growth constants at both 523 K and 573 K (250 °C and 300 °C) by approximately one order of magnitude. Further dissolution of Ni atoms into liquid Sn is strongly reduced because a solid IMC barrier separates the initial interlayers. The diffusion coefficient of Ni through the IMC layer was given in the work of Wang *et al.*^[31] as $1.36 \cdot 10^{-17} \text{ cm}^2/\text{s}$ at 443 K (170 °C), *i.e.*, many orders of magnitude lower compared to the value for Ni in liquid Sn.^[27] Rapid growth of IMC needles proceeds as long as the Ni atoms are dissolved within liquid Sn. Once Ni is completely consumed, IMC needle growth within this characteristic stage is limited by the diffusion of Ni atoms through the IMC layer, as depicted in Figure 10(c). The diffusion-controlled supply of Ni atoms through the IMC layer will certainly proceed faster at 573 K (300 °C) compared to 523 K (250 °C), which is reflected by the faster kinetics observed at 300 °C for annealing times longer than 3 minutes. The kinetic observations in the present study are consistent with the work of Görlich

Fig. 10—Characteristic morphological regimes during growth of Ni_3Sn_4 IMC schematically divided into representative reaction times of (a) ms, (b) s, and (c) min.

et al.,^[20] in which a transition toward slower growth kinetics was also identified after a 3-min near-isothermal holding time. Van Beek *et al.*^[28] claimed that Sn is the faster diffusing element through Ni_3Sn_4 IMC, whereas Reference 31 determined a diffusion coefficient for Ni into Ni_3Sn_4 that was twice as high as that for Sn into Ni_3Sn_4 . Although the present study did not aim to quantify the diffusion rates of Ni and Sn into Ni_3Sn_4 , it must be stated that considerable Ni diffusion through the IMC layer and most likely along the IMC grain boundaries must occur to keep the IMC needles growing toward the liquid Sn side, as was observed in the second kinetic regime (from 3 until 25 minutes). In fact, interdiffusion of Ni from the electroplated layer and Sn from the liquid layer through the IMC layer will affect IMC growth, as is schematically shown in Figure 10(c). Consequently, IMC growth will also occur at the Ni- Ni_3Sn_4 interface.

With a time delay of minutes to hours counting from growth initiation, faceted IMC islands that are disconnected from the dense IMC layer form in the last characteristic step of the morphological evolution. While setting Sn as the faster diffusion element along the grain boundaries, Görlich *et al.*^[20] suggested that Sn penetrates the IMC layer along the grain boundaries and continuously forms new IMC grains at the Ni- Ni_3Sn_4 interface. The ongoing formation and growth of these interfacial IMC grains pushes the adjacent IMC grains toward the liquid Sn, which results in detached IMC islands within the liquid Sn. However, it must be noted that diffusion coefficients for Ni or Sn along the grain boundaries of Ni_3Sn_4 IMC are not available in the current literature. Thus, the assumption in Reference 20 that Sn is the fastest diffusion species is vague and even controversial considering Reference 31, which might not have fully captured the rather complex growth mechanisms of Ni_3Sn_4 IMC over time.

Although the transition toward island-like IMC growth was not the focus of this work, it is important to mention that there is a pronounced supply of Ni atoms through the IMC layer (most likely along grain boundaries). Based on this observation,

- (1) Detached Ni_3Sn_4 IMC particles might nucleate due to Ni diffusion through the IMC layer into liquid Sn, and Ni saturation of liquid Sn may occur ahead of the IMC reaction front line.
- (2) Diffusion of Ni atoms into liquid Sn can promote the more or less equiaxial growth of the detached IMC particles.

These aspects are difficult to verify and would require in-situ observations or marker experiments of the IMC growth from the early stages to the formation of the detached IMC particles.

The characteristic morphological steps according to Figure 10(a) through (c) are supported by the combined solid-state and solid-liquid experiments. When a dense IMC layer between Ni and Sn exists after solid-state formation at 473 K (200 °C), needle-like IMC growth is fully suppressed in the subsequent near-isothermal annealing under solid-liquid conditions at 523 K (250 °C). Direct contact points between Ni and liquid Sn do not exist, and the liquid Sn layer is prevented from saturating with Ni. Consequently, needle-like IMC formation out of a saturated matrix is disabled, and hence, the first two characteristic reaction stages are shown in Figures 10(a) and (b). In this configuration, IMC formation starts in the stage shown in Figure 10(c), when diffusion of Sn and Ni is required for the further growth of the IMC layer. These growth mechanisms are consistent with the kinetics for the combined reaction type shown in Figure 5 when the parabolic growth constant of $2.9 \cdot 10^{-11} \text{ cm}^2/\text{s}$ is comparable to that of $2.3 \cdot 10^{-11} \text{ cm}^2/\text{s}$ obtained under pure solid-liquid conditions at 523 K (250 °C) after the needle-like IMC layer is densified and the IMC growth is governed by diffusion.

Independent from the transport mechanism, by pole figure measurements, for instance, (010) textured IMC

growth has been found to normally be oriented to the Ni-Sn interface. Chan *et al.*^[32] noted rapid crystal growth in the direction of smallest lattice spacing. This is consistent with the orientation of (010) because the lattice spacing of the *b*-axis is given as 4.061 Å, whereas the lattice spacings of the *a*- and *c*-axes are larger, that is, 12.199 Å and 5.224 Å, respectively.

B. Derivation of Processing Maps

The data obtained in the present work allow for the derivation of processing maps in accordance to those obtained in our previous paper on IMC formation in layered Ag/Sn systems.^[25]

The growth kinetics for 523 K and 573 K (250 °C and 300 °C) diverge in the second characteristic time regime ($t_{\text{tot}} > 180$ seconds). The parabolic growth constants can be described by an Arrhenius relationship:

$$k = k_0 \cdot \left(-\frac{Q}{RT} \right), \quad [6]$$

where k_0 is a proportionality constant, Q is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. The present study provides three parabolic growth constants for the calculation of Q , *i.e.*, from the experiments at 523 K, 573 K (250 °C, 300 °C), and combined 473 K/523 K (200 °C/250 °C). When $\ln(k)$ is plotted versus the reciprocal temperature, the activation energy for solid-liquid Ni_3Sn_4 IMC formation can be determined from the slope of the graph to be 43.3 kJ/mol. The proportionality constant is calculated to be $4.93 \cdot 10^{-7} \text{ cm}^2/\text{s}$. After identifying these parameters and inserting Eq. [6] in Eq. [4], the Ni_3Sn_4 thickness can be calculated as a function of temperature and time according to

$$z_{\text{IMC,m}}(T, t) = \sqrt{k_0 \cdot \exp\left(-\frac{Q}{RT}\right) \cdot t + z_{0,\text{off}}} \quad [7]$$

The transformation factor ϕ can be used in combination with Eq. [7] to obtain the consumed thickness of Sn $z_{\text{Sn,con}}$ as a function of temperature and time:

$$z_{\text{Sn,con}}(T, t) = \left(\frac{\phi}{1 + \phi} \right) \cdot \left[\sqrt{k_0 \cdot \exp\left(-\frac{Q}{RT}\right) \cdot t + z_{0,\text{off}}} \right] \quad [8]$$

with

$$\phi = \frac{4}{3} \cdot \frac{M(\text{Sn})/\rho(\text{Sn})}{M(\text{Ni})/\rho(\text{Ni})}, \quad [9]$$

where M is the molar mass and ρ is the density of Ni and Sn, respectively. The solutions of Eq. [7] and [8] are illustrated by the three-dimensional contour plots shown in Figures 11(a) and (b), respectively, for a temperature interval between 505 K and 620 K (232 °C and 347 °C) and a time interval from 180 to 3600 seconds. In the very early stages, that is, up to 180 seconds, the activation energy could not be calculated

Fig. 11—Processing maps as a function of time and temperature for (a) Ni_3Sn_4 thickness and (b) Sn consumption.

due to almost identical parabolic growth constants. This was addressed by adding an IMC offset thickness $z_{0,\text{off}}$ of 2 μm , which corresponds to the IMC thickness after 180 seconds for both 523 K and 573 K (250 °C and 300 °C). The influences of temperature and time are evident in Figure 11(a), as, for instance, at 505 K (232 °C) and 3600 seconds, an IMC thickness of approximately 4.5 μm can be predicted, whereas at 620 K (347 °C) with the same holding time, the IMC thickness approximately doubles to 8.3 μm . The plot in Figure 11(b) can be directly implemented into TLPB applications where an optimized set of parameters for the time-temperature-Sn consumption relation can be derived. The formation of a 1- μm thick Ni_3Sn_4 layer requires initial Ni and Sn layers with thicknesses of 0.235 and 0.765 μm , respectively. Interestingly, Görlich *et al.*^[20] observed faster thickening at 523 K (250 °C) and near-isothermal conditions with molten Sn droplets on a hot Ni plate. They measured a mean IMC thickness of 7.6 μm after 480 seconds, whereas our analysis measured 2.53 μm after 600 seconds. This may be related to the larger volume of the Sn droplets compared to our thin Sn layer. When the whole volume of the Sn droplet becomes saturated with Ni in the early stages, IMC formation can proceed for longer without being dependent on Ni diffusion through the IMC barrier. IMC growth from saturated liquid Sn is fastest, as shown in the present study and in Dybkov.^[18] In Chen *et al.*,^[13] a mean IMC thickness of 2.42 μm was measured at 513 K (240 °C) after 1500 seconds for electroplated Ni in combination with a eutectic Sn-3.5Ag solder, which resulted in an activation energy of 25 kJ/mol. Our study provides a value of 3.08 μm for an identical holding time and

temperature, which shows strong agreement considering that reactions are generally slowed with eutectic solders compared to pure Sn layers. Equation [7] can also consider heating or cooling rates during TLPB:

$$z_{\text{IMC,m}}(T, t) = \sum_{\substack{j=n \\ i=n-1 \\ i=0 \\ j=1}}^j \left[k_0 \cdot e^{\frac{-Q}{R \left(\frac{1}{T-t_i} \right) \int_{t_i}^{t_j} \frac{1}{T(t)} dt}} \sqrt{t_j - t_i} \right] \quad [10]$$

The current work can finally be compared to our previous study on Ag-Sn interfacial reactions^[25] because identical experimental proceedings and analytical methods were applied. Significantly faster growth kinetics of Ag₃Sn IMC were identified; for example, at 620 K (347 °C) and after a holding time of 3600 seconds, a mean IMC thickness of approximately 17 μm was calculated. However, the consumption of Sn was similar for the Ni-Sn system because the formation of Ag₃Sn requires much less Sn. The thickness ratio between Ag and Sn to form Ag₃Sn IMC can be calculated as 0.654 to 0.346.

V. CONCLUSIONS

We conducted near-isothermal experiments on application-oriented Ni-Sn interlayers, for which undefined reactions during heating were minimized. Consequently, the observed reaction features of Ni₃Sn₄ IMC in solid-state and solid-liquid regimes could be directly linked to defined holding times and temperatures. Our study clarifies the following scientific aspects:

1. Ni₃Sn₄ IMC grows with a scallop-like morphology under solid-state conditions at 473 K (200 °C). Pronounced contributions from grain boundary diffusion of Ni through the IMC layer and grain coarsening of IMC scallops were deduced from the growth exponent of $n = 0.33$.
2. Detailed analysis on the IMC growth kinetics at early stages of up to 180 seconds revealed an unexpected thickening behavior with almost identical IMC growth rates at 523 K and 573 K (250 °C and 300 °C). Due to the rapid supply of Ni atoms to Sn through direct contact points between both interlayers, saturation of the liquid Sn layer with Ni is reached and the kinetics in the early time regime are governed by the crystal growth rate of the saturated Sn matrix.
3. The pronounced grain orientation in the dense IMC layer at the Ni interface was found when the (111) and (31 $\bar{2}$) planes showed clear texturing in the pole figure measurements.
4. The IMC growth kinetics remarkably slow down at both 523 K and 575 K (250 °C and 300 °C) after 180 seconds of holding time and after reaching a mean IMC thickness of approximately 2 μm. Microstructural investigations demonstrate that the needle-like IMC layer continuously densifies at the Ni-Ni₃Sn₄ interface so that a diffusion barrier forms and direct contacts point between Ni and

liquid Sn vanish. Kinetics are controlled by diffusion.

5. Representative reaction parameters, such as the activation energy Q or the proportionality constant, were determined from the parabolic growth constants, which allowed for the establishment of processing maps for Ni₃Sn₄ formation and the corresponding Sn consumption.

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