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Response to comments on "A numerical method to determine interdiffusion coefficients of Cu_6Sn_5 and Cu_3Sn intermetallic compounds"

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Abstract

Comments have recently been made by Yuan et al. [1] to deny one statement in our paper [2], Eq. (21) in Wagner's paper [3] can be used to accurately calculate the integrated interdiffusion coefficient for an incremental diffusion couple only under the assumption of constant Molar volume for all phases. We respond here to explain how they misunderstood our mathematical deduction, made a mistake in deriving a couple of equations, falsely cited our work and employed unjustifiable assumption. As a result, we believe that their comments are invalid to deny our statement.

*Keywords***:** A. Intermetallics, miscellaneous; B. Diffusion; D. Phase interfaces

Response to comment 1 by Yuan et al. [1]

In comment 1 by Yuan et al [1], they pointed out that we made the composition profile continuous at the interfaces between the different phases, but did not make the change in Molar volume profile at the phase interfaces continuous. What we can see from this comment is that they misunderstood our mathematical deduction expressed in Fig. 9 and Eqs. (23) to (25) in our paper [2]. This is because our mathematical deduction was to prove that only under

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the assumption of constant Molar volume for the different phases, Eq. (21) in Wagner's paper [3] can be used to calculate the exact integrated interdiffusion coefficient of the Cu_3Sn intermetallic (IMC) in the Cu/Cu_6Sn_5 diffusion couple with the profile ABCDEF for the Molar fraction shown in Fig. 9 in our paper [2], without any error. Otherwise, there would be a certain amount of error in the calculated integrated interdiffusion coefficient, no matter how much the error could be. Therefore, it does not matter whether either or both of the composition profile and the Molar volume profile were assumed to be continuous at the interfaces between the different phases.

In comment 1 [1], Yuan et al. also proposed Eq. (3) to replace Eq. [23] in our paper, and claimed that such Eq. (3) was identical to Eq. (16) in Wagner's paper [3]. First, we want to point out their claim is wrong based on the following fact. Eq. (23) in our paper [2], and hence Eq. (3) proposed by Yuan et al. [1] was used to calculate the integrated interdiffusion coefficient on the IJ segment shown in Fig. 9 in our paper [2]. Because the continuous and differentiable curves GHI and JKL in Fig. 9 in our paper [2] were employed like the auxiliary lines in geometric proof to facilitate the mathematic deduction, the integrated interdiffusion coefficient on the IJ segment depends on the selection of the IJ segment on the CD segment. However, Eq. (16) in the Wagner's paper [3] should be applied to the CD segment, and the calculated integrated interdiffusion coefficient on the CD segment is a physical property of the Cu_3Sn phase. Furthermore, we want to say even if Eq. (3) proposed by Yuan et al. [1] is used to replace Eq. (23) in our paper [2], it is still easy to see that only under the assumption of constant Molar volume for the different phases, Eq. (21) in Wagner's paper [3] can be derived to calculate the integrated interdiffusion coefficient of the Cu_3Sn IMC in the Cu/Cu_6Sn_5 diffusion couple with the profile ABCDEF for the Molar fraction, without any error. The detail will be given below, in our comment on **"Corrections considering molar volume change"** proposed by Yuan et al. [1].

Response to comment 2 by Yuan et al. [1]

In comment 2 by Yuan et al. [1], they pointed out that the assumption of GB=CI=JD=EI made in our mathematical deduction [2] imposed a presumption of $V_{Cu}=V_{Cu3Sn}=V_{Cu6Sn5}$. This comment 2 is closely associated with comment 1 made by them [1]. Again, we can see from this comment is that they misunderstood our mathematical deduction expressed in Fig. 9 and Eqs. (23) to (25) in our paper [2]. The reason is extremely simple. Even if the assumption of GB=CI=JD=EI imposed a presumption of $V_{Cu}=V_{Cu3Sn}=V_{Cu6Sn5}$, this should not have any effect on drawing our conclusion. This is because without such assumption/presumption, any other profiles GHI and JKL applied to Eq. (21) in Wagner's paper [3] would lead to a certain amount of error in the calculated integrated interdiffusion coefficient, no matter how much the error could be. Therefore, we can still see that only under the condition of $V_{Cu}=V_{Cu3Sn}=V_{Cu6Sn5}$, Eq. (21) in Wagner's paper [3] can be used to calculate the integrated interdiffusion coefficient for the Cu_3Sn IMC, without any error.

Response to comment 3 by Yuan et al. [1]

In comment 3 by Yuan et al. [1], they derived Eq. (4) from Eq. (24) in our paper [2]. It is obvious that they made a mistake in deriving such Eq. (4) because the equation which can be derived should be Eq. (1):

$$\frac{D_{Int,CD}}{\Delta x_{CD}} = \frac{D_{Int,IJ}}{\Delta x_{IJ}} \tag{1}$$

It is also obvious that Eq. (5) derived from the wrong Eq. (4) by Yuan et al. [1] is incorrect. As mentioned in our response to comment1, the integrated interdiffusion coefficient $D_{Int,IJ}$ is dependent on the selection of IJ segment on the CD segment, and only the $D_{Int,CD}$ is a physical property of the Cu_3Sn phase. Therefore, all the arguments which were made based on

3

the wrong Eqs. (4) and (5) in this comment [1] are meaningless.

Response to comment 4 by Yuan et al. [1]

In comment 4 by Yuan et al. [1], they pointed out that "we stated that the prediction that the interfaces between the different phases move towards the Cu side during the growth of Cu_3Sn and Cu_6Sn_5 in annealed Cu-Sn diffusion couple is not correct." It is clear that they falsely cited the sentences in or paper [2]. In fact, what we said should be that all the interfaces of the different phases simulated with the integrated interdiffusion coefficients calculated using the Wagner method [3] are moved towards the Cu side when compared with those simulated with the integrated interdiffusion coefficients determined with the numerical method [2]. If we have a look at Fig. 10 (b) in our paper [2], all the interfaces of the different phases simulated with the latter integrated interdiffusion coefficients were still at the original Cu side. Therefore, it is easy to see what we said in our paper [2] were different from what they pointed out in this comment [1].

Comment on the "Corrections considering molar volume change" by Yuan et al. [1]

Yuan et al. [1] also proposed an assumption expressed by Eq. (6) and the derived Eqs. (7) and (8) from Eq. (3) to verify the validity of Eq. (21) in the Wagner's paper [3]. In their derivation from Eqs. (7) to (8) [1], they ignored the contribution from the integral part in Eq. (7) based on the so called assumption that "the thickness of the interface is usually several orders of magnitude smaller than the length of the phase layer in the diffusion zone" [1]. However, given the fact that the thicknesses of the phase layers reported in the literature [4-7] were in the range of a few to tens of micrometres, it is hard to say that the micro-scaled thicknesses of the interface zones are several orders of magnitude thinner than the length of the phase layer in the diffusion zone. For example, as reported in Ref. [7], the thickness of

4

Cu$_3$Sn IMC was approximately 15 μm, and those of the interface zones were 2 to 3 μm for the growth of Cu$_3$Sn IMC in the Cu/Cu$_6$Sn$_5$ diffusion couple. Therefore, it cannot be justified to simply ignore the contribution from the integral part in Eq. (7) [1].

It should be emphasised that Eq. (21) in Wagner's paper is supposed to calculate the integrated interdiffusion coefficient of the Cu$_3$Sn IMC in the Cu/Cu$_6$Sn$_5$ diffusion couple with Molar fraction profile ABCDEF, rather than the Molar fraction profile AGHIJKLF as shown in Fig. 9 in our paper [2]. If the Molar volume is a constant for the different phases, we can assume that in the auxiliary continuous and differentiable curves GHI and JKL, GH and HI are symmetrical relative to H, JK and KL are symmetrical relative to K, and GB=CI=JD=EI=δx, as done in our paper [2]. Then, from Eq. (7) proposed by Yuan et al. [1], we can obtain Eq. (2):

$$D_{Int,IJ} = \frac{(N_2 - N_1)(N_3 - N_2)}{(N_3 - N_1)} \frac{(\Delta x_{IJ}^2 + 2\delta x \Delta x_{IJ})}{2t} \qquad (2)$$

Making use of Eqs. (24) and (25) in our paper [2], we can further obtain an equation the same as Eq. (21) in Wagner's paper [3] to calculate the integrated interdiffusion coefficient of the Cu$_3$Sn IMC. It should be noted that the assumptions made here are not physically realistic. However, they can be employed to demonstrate that under a constant Molar volume for the different phases, Eq. (7) proposed by Yuan et al. [1] is mathematically consistent with Eq. (21) in Wagner's paper [3], and there would be no error in the integrated interdiffusion coefficient calculated with the latter equation. If the Molar volume for the different phases is not a constant, there would be a certain amount of error in the interdiffusion coefficient calculated with latter equation because neither the integral part in Eq. (7) proposed by Yuan et al. [1] could exactly become zero nor this equation could be mathematically equivalent to Eq. (21) in Wagner's paper [3]. Therefore, Eqs. (3), (6) and (7) proposed by Yuan et al. [1] actually support our statement that Eq. (21) in the Wagner's paper [3] can be used to accurately

calculate the integrated interdiffusion coefficient for an incremental diffusion couple only under the assumption of constant molar volume for all phases.

Furthermore, in another paper [8], we developed the following Eq. (3) to replace Eq. (14) in Wagner's paper [3]:

$$D^* = \frac{1}{2t[\partial(N_2^*/V^*)/\partial x]}\left[\begin{array}{l} \dfrac{N_2^R/V^R - N_2^*/V^*}{N_2^R/V^R - N_2^L/V^L}\displaystyle\int_{x_L}^{x^*}(\dfrac{N_2}{V} - \dfrac{N_2^L}{V^L})dx \\[4mm] + \dfrac{N_2^*/V^* - N_2^L/V^L}{N_2^R/V^R - N_2^L/V^L}\displaystyle\int_{x^*}^{x_R}(\dfrac{N_2^R}{V^R} - \dfrac{N_2}{V})dx \end{array}\right]$$

(3)

Where D is the interdiffusion coefficient, V is the Molar volume, N_2 is the Molar fraction of component 2 in a binary system, t is time, x is position coordinate, x_L and x_R are the left and right boundaries of the diffusion couple, respectively. Both the subscripts L and R and the superscripts L and R specify the corresponding values at the left and right boundaries, respectively.

From Eq. (3), we can derive the following Eq. (4) for the formation of phase i from phase $i-1$ and $i+1$ coexisting with phase i where the three phases all have narrow homogeneity ranges:

$$D_{Int}^i = \frac{(N_2^{i+1}/V^{i+1} - N_2^i/V^i)(N_2^i/V^i - N_2^{i-1}/V^{i-1})}{N_2^{i+1}/V^{i+1} - N_2^{i-1}/V^{i-1}}\frac{(\Delta x^i)^2}{2t}$$

(4)

The detailed deduction was reported in our paper [8], and is not repeated here. The integrated interdiffusion coefficient calculated with Eq. (4) was in excellent agreement with that determined with the numerical method to solve the governing equation based on Fick's second law for the Cu_3Sn IMC formed in the Cu/Cu_6Sn_5 diffusion couple [4]. It can also be seen that Eq. (4) will be exactly the same as Eq. (21) in Wagner's paper [3] if the Molar volume is a constant for all the three phases. Therefore, we believe that Eq. (4) is different from, but more accurate than Eq. (21) in Wagner's paper [3] to calculate the integrated

interdiffusion coefficient for an incremental diffusion couple where all the three phases have narrow homogeneity ranges.

In addition, as explained in our paper [8], let us consider two special cases for the formation of phase i from phase $i-1$ and $i+1$ coexisting with phase i, where the three phases all have narrow homogeneity ranges. In case 1, the thickness of phase i is Δx^i, the Molar fractions of the phases $i-1$, i, and $i+1$ are N_2^{i-1}, N_2^i and N_2^{i+1}, and the Molar volumes of the three phases are equal to each other, i.e. $V^{i-1}=V^i=V^{i+1}=V^m$. In case 2, the thickness of phase i and the Molar fractions of the phases $i-1$, i, and $i+1$ are exactly the same as those in case 1, i.e. Δx^i, N_2^{i-1}, N_2^i and N_2^{i+1}. However, the Molar volumes of the three phases are not equal to each other, e.g. $V^{i-1}=2V^i=2V^{i+1}=2V^m$. Such two cases are obviously mathematically different from each other. However, according to Eq. (21) in Wagner's paper [3], exactly the same integrated interdiffusion coefficient for the phase i is obtained for both cases. This is mathematically absurd, and hence there must be an inequality of diffusion fluxes at the interfaces, leading to considerable errors when the Wagner method is used to calculate the interdiffusion coefficients and/or integrated interdiffusion coefficients. If any reader still doubts the mathematical deduction and the relevant conclusion in our papers [2,8], he or she is kindly asked to think about the following question: how the mathematic absurdity associated with the two special cases could be explained and overcome with Eq. (21) in Wagner's paper [3].

Summary

From the above detailed response, it can be seen that Yuan et al. misunderstood our mathematical deduction in their comments 1 and 2, made a fundamental mistake in their comment 3, falsely cited our work in their comment 4, and employed unjustifiable assumption in their proposed corrections considering Molar volume change. Therefore, it can readily be concluded that their comments and proposal are invalid to deny the relevant statement in our paper.

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