TRANSITION PHENOMENA IN THE DIFFUSION SOLDERING / BRAZING

ZJAWISKA PRZEJŚCIOWE W SPAJANIU DYFUZYJNYM

Some morphological observations within the Ni/Al/Ni and Fe/Zn/Fe interconnections were made. The observations allowed to work out a model for some phenomena occurring during diffusion soldering. The model describes dissolution in a connection with solidification and their transition into first from among solid / solid transformations which can occur in the solid. The model explains mechanism of above phenomena. These phenomena precede the final stage of the joining, that is homogenisation resulting from a sequence of the further transformations in the solid. Transition from the liquid filler metal, that is melted foil into its liquid solution as a phenomenon necessary for the formation of sub-layers within the interconnection is explained. Also transition from the initial stable solidification into the final metastable solidification is justified by means of the criterion of maximum temperature of the solid / liquid interface. The connection between period of solidification and first solid / solid transformation is considered. The observation of the birth of coupled phase on the surface of dominant phase of the joint is presented. The dominant phase is distinguished as the phase which has a greater driving force for its formation and coupled phase as the phase which grows in temporary sequence after dominant one. Moreover, the coupled phase is consumed by the dominant phase. The observation of phases birth allows the explanation of the sequence of phases appearance to be delivered. The thermodynamic justification for the mentioned sequence is shown, additionally.

Keywords: metastable solidification, phases birth, sequence of phase appearance

Dokonano obserwacji morfologicznych w złączach Ni/Al/Ni oraz Fe/Zn/Fe. Obserwacje te pozwoliły na opracowanie modelu zjawisk, jakie zachodzą podczas spajania dyfuzyjnego. Model opisuje rozpuszczanie w powiązaniu z krystalizacją i ich przejście w pierwszą fazę transformacji jakie mogą zachodzić w fazie stałej. Model wyjaśnia mechanizm przebiegu tych zjawisk. Zjawiska te poprzedzają końcowe stadium technologii jakim jest homogenizacja, wynikająca z sekwencji dalszych transformacji w fazie stałej. Opisuje się w przejściu ciekłego metalu folii zastosowanej w spajaniu dyfuzyjnym w jej roztwór ciekły, jako zjawisko niezbędne dla formowania podwarsztw w złączu. Również przejście od początkowego stabilnego okresu krystalizacji do końcowego metastabilnego okresu krystalizacji także jest wyjaśnione i uzasadnione poprzez kryterium maksymalnej temperatury frontu krystalizacji. Rozważa się powstawanie między okresem krystalizacji a okresem pierwszej transformacji w fazie stałej. Prezentowane są obserwacje narodzin fazy sprzężonej na powierzchni fazy dominującej. Określa się fazę dominującą jako tę, która ma większą siłę pędną dla jej wzrostu a sprzężoną jako tę, która rośnie jako druga w sekwencji czasowej. Co więcej, po pewnym czasie faza sprzężona zostaje skonsumowana przez fazę dominującą. Obserwacja narodzin pozwala na wyjaśnienie sekwencji pojawiwszy się faz podczas krystalizacji. Dodatkowo, pokazane jest termodynamiczne uzasadnienie dla powstawania wspomnianej sekwencji.

Symbols used in the text

\( h_{\delta C} \) thickness (height) of the \( \delta C \) phase sub-layer

\( h_{\Gamma 1} \) thickness (height) of the \( \Gamma 1 \) phase sub-layer

\( h_{32} \) thickness (height) of the \( \text{Al}_3\text{Ni}_2 \) phase sub-layer

\( k_i \) partition ratio for the \( i \)-th range of solidification, \( i = 1, \ldots n \)

\( N \) solute concentration

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initial solute concentration for solidification; average solute concentration within formed multi-layer
initial solute concentration for solidification occurring with the presence of flux
solute concentration in the liquid at the completion of solidification; solute concentration in the liquid
solution of the filler metal
solute concentration in the liquid at the \( i \)-th peritectic reaction; initial solute concentration for the \( i+1 \)
range of solidification, \( i = 1, \ldots, n \)
solute concentration in the liquid (according to liquidus line)
eutectic concentration of the solute
saturated zone within the substrate
super-saturated zone within the substrate
time
time of the beginning of the first solid / solid transformation
time of the completion of solidification
time of the birth of the Al\(_2\)Ni phase
time of the birth of the Al\(_2\)Ni\(_2\) phase
time of the birth of the \( \zeta \) phase
time of the completion of the transformation of stable solidification into metastable solidification
temperature
real temperature of the solidification imposed in technology
temperature related to the \( N_0 \) – solute concentration
amount of the growing solid, dimensionless
undercooling of the solid / liquid interface
distance

1. Introduction

A final microstructure of an interconnection is the result of an interaction between a liquid filler metal and
two solid substrates, [1]. Under some circumstances, the bonding process can produce a joint that microstructurally
reproduces a sequence of several intermetallic compounds and phases as they are visible in the adequate
phase diagram.

Furthermore, chemical segregation in both the solid and liquid phases can have a huge effect on surface
and interfacial energies and, hence, wettability as well as mechanical properties of the final joint. It is evident that
knowledge of segregation resulting from solidification during joining process is crucial in the technology.

A microstructural development is assumed to involve three phenomena that occur in a following sequence: solute dissolution, isothermal solidification, and homogenisation, [2]. Solute dissolution occurs just before solidification or it can also be considered that both phenomena occur in the same time. In the current model, dissolution will be treated only as a process for creating a nominal concentration necessary for solidification.

The first solid / solid transformation is created just after the completion of solidification. The present model explains mechanism of dissolution, solidification and first solid / solid transformation. The explanation seems to be useful in the control of technology of diffusion soldering / brazing.

2. Role of dissolution during diffusion soldering or brazing

A solute dissolution, continuously occurring during the joining process makes the solid-liquid system open until the complete consumption of the filler metal. However, at the beginning filler metal (Al, Zn) melts and transforms into the liquid filler metal, (Al)\(_3\) \( \rightarrow \) Al. The liquid filler metal reacts with the substrate (Ni, Fe) to form an undercooled liquid zone, \( dx \), perpetually, just at a surface of a given substrate. The dissolution of a given zone, \( dx \), within a substrate, occurs so long as zone, \( dx \), becomes liquid. This reaction leads to creation of the Al, Zn – solute concentration equal to \( N_0(T_R) \). When the solute concentration reaches the \( N_0 \), concentration within zone, \( dx \), the zone is ready to be solidified. Thus,
this concentration is starting point of the solidification path, Fig. 1.

\[ \text{Fig. 1. Determination of the } N^F \text{ concentration of the liquid solution of the Al – filler metal being in thermodynamic equilibrium with the coupled peritectic phase } \text{Al}_3\text{Ni as at an intersection of the real temperature for the technology and liquidus line. The } N_0 \text{ concentration shown on liquidus line. It is estimated as the average solute concentration measured across the sub-layers formed during solidification within the Ni/Al/Ni system.} \]

3. Initial transient stable solidification of phases

At this stage of the process solidification leads to formation of the primary phase (AlNi, Γ1). Primary phase, however, immediately transforms into dominant phase (Al3Ni2, δ), Fig. 2. The transformation is justified by the criterion of maximum temperature of the solid / liquid interface, [3]. The transformation occurs though the undercooling envisaged for solidification of primary phase (according to phase diagram of stable equilibrium) is greater than undercooling for solidification of dominant phase, Fig. 3.

\[ \text{Fig. 2. Transformation of the primary phase AlNi into dominant phase Al3Ni2: AlNi + liquid(N1) } \rightarrow \text{ Al3Ni2. Transformation starts at } t_{32}; \text{ the completion of primary phase formation at time } t_{52}^M. \]

The scheme shown for the Ni/Al/Ni system.

Finally, the initial transient solidification transforms into metastable solidification due to the criterion of maximum temperature of the solid / liquid interface, and the appearing phase is dominant phase which is formed at the smaller undercooling than undercooling for primary phase.

As a result, the dominant phase sub-layer is formed, only, and some portions of the undercooled liquid phase (N1, N2) remain. A remaining liquid is necessary for another transformation, that is for the transformation of the liquid filler metal into its liquid solution, \( N^F \): liquid(N1) + Al \rightarrow liquid(N^F) for the Ni/Al/Ni interconnection, Fig. 4, or in the case of Fe/Zn/Fe interconnection: liquid(N2) + Zn \rightarrow liquid(N^F).

\[ \text{Fig. 4. Transformation of the Al-liquid filler metal into its liquid solution according to the reaction: liquid(N1) + Al } \rightarrow \text{ liquid(N^F).} \]

The liquid solute solution, \( N^F \), is not in equilibrium with neighbouring solid phase (dominant phase), Fig. 1. Scarcely, the completion of the above transformation involves the final stage of the solidification that is, metastable solidification of two phases: dominant phase (Al3Ni2, δ) and coupled phase (Al3Ni5).
4. Final metastable solidification of phases

Final metastable solidification is preceded by the birth of coupled phase, δ, in the case of the Ni/Al/Ni system, Fig. 5, or ς, in the case of the Fe/Zn/Fe system, Fig. 6.

![Diagram](image1)

**Fig. 5.** Birth of the coupled phase Al₂Ni just on the surface of dominant phase Al₂Ni₂ at time t₁^p₁, when the dominant phase has its thickness equal to h₃₂₂ (λ is the distance)

![Diagram](image2)

**Fig. 6.** Birth of the coupled phase ς just on the surface of dominant phase δ at time t₁^p₂, when the dominant phase has its thickness equal to h₁₁ + h₃₂, but with presence of both Π' phase sub-layer and flux F (λ is the distance).

![Diagram](image3)

**Fig. 7.** Final metastable solidification of both phases: Al₂Ni₂ and Al₃Ni due to peritectic reactions occurring in sequence

Scarcely, the final metastable solidification involves two peritectic reactions at the solid / liquid interface of an adequate phase sub-layer, Fig. 7.

The N₀ - undercooled liquid abandons zone dx to flow along some internal channels created within each cell existing inside a proper sub-layer, Fig. 8. The undercooled liquid reaches a solid / liquid interface of a given cell, Fig. 9, and undercooled peritectic reaction can occur there, [4].

![Diagram](image4)

**Fig. 8.** Channels created along a height of cells. The N₀ undercooled liquid created within the zone dx is ready to flow towards the solid / liquid interface of cells

![Diagram](image5)

**Fig. 9.** The zone dx is just abandoned by undercooled liquid, N₀. An undercooled liquid stops at the solid / liquid interface of cells of both phase sub-layers and is subjected to undercooled peritectic reactions, in sequence. The thickening of sub-layers is observed

![Diagram](image6)

**Fig. 10.** External channels created between cells used for the flow of liquid metal solution, N^F¹, which promotes the formation of the dx zone at the surface of substrate
At the same time, the dissolution operates in such a way to create subsequent \(dx\) – zones, Fig. 10. The dissolution of the substrate takes place according to the reaction: \(\text{liquid}(N^F) + \text{substrate} \rightarrow \text{liquid}(N_0)\).

At time \(t_s\) – solidification is completed, Fig. 11. Since applied foil of filler metal is usually of thickness of the order < 50 \(\mu m\), then \(t_s < t_M\), where, \(t_M\) is the time of beginning of the first solid / solid transformation.

![Fig. 11. Completion of solidification. Multi-layer reached the axis of symmetry of joint. All the sub-layers are fully formed. Two morphological types of the \(\delta\) phase as well as two morphological types of the \(\gamma\) phase are visible within the half a joint.](image)

It is to be noticed that average solute concentration measured across the sub-layers and precipitated pure solute does not change during first solid/solid transformation, \(N_0 = \text{const}\).

![Fig. 13. A pure Zn – solute precipitated just at the axis of symmetry of interconnection (FeZn/Fe system). The coupled phase, \(\gamma\), is completely consumed by dominant phase, \(\delta\). Two types of \(\delta – \) phase are observed due to the solidification with presence or without presence of a flux: phase \(\delta_c\) appeared due to presence of flux, \(\delta_p\) appeared when the flux disappeared in the system.](image)

Moreover, the average solute concentration during transformation, \(N_0\), is equal to average solute concentration, \(N_0\), measured across a multi-layer during solidification.

5. Transition from solidification to first solid/solid transformation

At time, \(t_M\), the beginning of the first solid/solid transformation is expected, Fig. 12. The experimental confirmation for the first solid/solid transformation is shown in Fig. 13. According to the reaction connected with the first solid/solid transformation the coupled phase \(\gamma\), is completely consumed by dominant phase, \(\delta\).

![Fig. 12. Scheme of the first solid/solid transformation within FeZn/Fe system. The pure liquid Zn-solute precipitates and is pushed towards the axis of symmetry of interconnection: \(\text{FeZn}_{13} \rightarrow \text{FeZn}_{10} + \text{liquid}(3\text{Zn})\).](image)

6. Concluding remarks

Transition phenomena play essential role in understanding further solid/solid transformations within the interconnection leading to thermodynamic equilibrium of a given system. It allows the conscious control of technology to be possible.

So, the current model delivers explanation for dissolution path: \(N^F \rightarrow N_0\). Dissolution occurs at the surface of substrate (within the \(dx\) zone). A non-undercooled liquid solution, \(N^F\), flows towards the substrate along external channels existing between cells within a given sub-layer, Fig. 10.

The model explains also the existence of solidification path, that is: \(N_0 \rightarrow N^F\), with solid/liquid interface path: \(k_1 N_0 \rightarrow k_3 (N^F) N^F\), Fig. 1. The undercooled liquid, \(N_0\), flows from the \(dx\) – zone towards a solid/liquid interfaces to take part in undercooled peritectic reaction, Fig. 7. The internal channels existing within the cells are employed for the mentioned convection.

Therefore, the mass transport occurs by means of external channels for dissolution and by means of internal channels for solidification, according to present model assumptions. However, a mixed mechanism should be observed, in real processes.
The solidification path can be determined after the preceding measurement of the average solute concentration, \( N_0 \), within the phase sub-layers formed during different stages of solidification. In the case of systems containing more than two elements, the calculation of solidification path is more complicated, [5]. The calculation of solidification path, [5], employs a concept of back-diffusion, [6]. The concept of back-diffusion has successfully been applied in cellular solidification, [7]. Therefore, an application of the mode of calculation of solidification path, [5], is justified, all the more so as cellular morphology is observed within joint sub-layers, Fig. 13.

Generally, the metastable solidification occurs during diffusion soldering/brazing. But, the initial transient stable formation of phases precedes the final stage of metastable solidification, Fig. 2.

The liquid filler metal cannot be observed during metastable solidification. It transforms into its non-undercooled liquid solution, \( N^F \), just at the beginning of the process under investigation, Fig. 4.

The solidification begins at \( N_0 \) – concentration of the solute created by dissolution within \( dx \) zone. It is evident that dissolution and solidification are complementary phenomena during both initial transient stable formation of phases and final metastable formation of phases within a given joint sub-layers.

The value of the \( N_0 \) – concentration of the solute depends on the real temperature, \( T_R \), imposed in the process under investigation.

The birth of phases do not appear at the same time. A delay between birth of coupled phase and birth of dominant phase is to be observed, Fig. 14, Fig. 15. The delay is explained schematically in Fig. 5, Fig. 6.

The sequence of the phase appearance discussed in Fig. 3, shown schematically in Fig. 7, Fig. 9 can be confirmed thermodynamically, Fig. 16, Fig. 17b.

![Fig. 15. In situ observation of the birth of the coupled phase \( \gamma \) on a surface of dominant phase formed for 13 seconds](image)

![Fig. 16. Driving force (DF) calculated for Al3Ni2-Al3Ni multilayer formation from the undercooled liquid due to stable (virtual) peritectic reactions: transient primary phase (AlNi) + liquid (N1) \( \Rightarrow \) Al3Ni2 and transient primary phase (Al3Ni2) + liquid (N2) \( \Rightarrow \) Al3Ni DF (Al3Ni2) > DF (Al3Ni) justifies the sequence of phase appearance during solidification. The Al3Ni2 phase appears first](image)

![Fig. 17. Driving force (DF) calculated for: a) solid/solid transformation: 2Al3Ni \( \Rightarrow \) Al3Ni2 + 3Al at the \( T_p = 700^\circ C \), b) \( \delta \) – \( \gamma \) multilayer formation from the undercooled liquid due to stable (virtual) peritectic reactions: transient primary phase (\( \Gamma \)) + liquid (N1) \( \Rightarrow \) \( \delta \) and transient primary phase (\( \delta \)) + liquid (N2) \( \Rightarrow \) \( \gamma \). DF (\( \delta \)) > DF (\( \gamma \)) justifies the sequence of phase appearance during solidification. The \( \delta \) – phase appears first](image)
The following reactions and transformations are considered in the envisaged systems:

1/ for the Ni/Al/Ni system:
- melting of the filler metal (Al)$_3$ → Al
- formation of primary phase AlNi with remaining liquid(N$_1$)
- transformation of the liquid filler metal into its liquid solution: liquid(Al) + liquid(N$_1$) → liquid(N$^F$)
- transformation of the primary phase AlNi into dominant phase Al$_3$Ni$_2$: AlNi + liquid(N$_1$) → Al$_3$Ni$_2$
- dissolution of the substrate by the liquid solution of the filler metal: liquid(N$^F$) + substrate → liquid(N$_0$)
- metastable solidification of peritectic phase Al$_3$Ni$_2$ and peritectic compound Al$_3$Ni, which can be described also with the use of the peritectic reactions for stable thermodynamic equilibrium: primary(AlNi) + liquid(N$_1$) → Al$_3$Ni$_2$, primary(Al$_3$Ni$_2$) + liquid(N$_2$) → Al$_3$Ni; the products of stable peritectic reactions are the same as for the metastable solidification of peritectic phases/compounds, but stable reactions are included into the model for their simplicity in description; fundamentals of the model are already known, [6]
- first solid/solid transformation: 2Al$_3$Ni → Al$_3$Ni$_2$ + liquid(3Al)
- for the Fe/Fe/Fe system:
- melting of the filler metal (Zn)S → Zn
- formation of primary phase α and Γ1 with remaining liquid(N$_2$) and presence of the flux, F
- transformation of the liquid filler metal into its liquid solution: liquid(Zn) + liquid(N$_2$) → liquid(N$^F$)
- transformation of the primary phase α into Γ1 and Γ1 into dominant phase δ: α + liquid(N$_1$) → Γ1 and Γ1 + liquid(N$_2$) → δC with the presence of flux, F
- dissolution of the substrate by the liquid solution of the filler metal: liquid(N$^F$) + substrate → liquid(N$_0$)
- metastable solidification of peritectic phase δ$_p$ and peritectic compound ζ, which can be described also with the use of the peritectic reactions for stable thermodynamic equilibrium: primary(Γ1) + liquid(N$_2$) → δ$_p$, primary(δ$_p$) + liquid(N$_3$) → ζ without the presence of flux, F; the products of stable peritectic reactions are the same as for the metastable solidification of peritectic phases/compounds, but stable reactions are included into the model for their simplicity in description
- first solid/solid transformation: ζ(FeZn$_{13}$) → δ(FeZn$_{10}$) + liquid(3Zn).

It is to be noticed that $N_0$ – concentration of the solute observed during solidification is conserved during the first solid/solid transformation. The first solid/solid transformation is connected with solidification through the $N_0$ – concentration of the solute. However, the time for completion of solidification should be less than time for the beginning of first solid/solid transformation: $t_S < t_M$. Usually, this condition is satisfied because the thickness of foil used in experiment is less than 50 μm.

Time $t_M$ seems to be typical for the first solid/solid transformation in a given joint, while time $t_S$ depends on the thickness of foil applied in technology.

Solidification and first solid/solid transformation are independent phenomena if the condition $t_S \leq t_M$ is fulfilled.

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