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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 spośród 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 przejście ciekłego metalu folii zastosowanej w spajaniu dyfuzyjnym w jej roztwór ciekły, jako zjawisko niezbędne dla formowania podwarstw 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 powiązanie 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 pojawiania 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 δC phase sub-layer

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

h_{32} thickness (height) of the Al_3Ni_2 phase sub-layer

k_i partition ratio for the i-th range of solidification, $i = 1,...n$

N solute concentration

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N_0	initial solute concentration for solidification; average solute concentration within formed multi-layer
N_0^F	initial solute concentration for solidification occurring with the presence of flux
N^F	solute concentration in the liquid at the completion of solidification; solute concentration in the liquid solution of the filler metal
N_i	solute concentration in the liquid at the i-th peritectic reaction; initial solute concentration for the $i+1$ range of solidification, $i = 1,...n$
N_L	solute concentration in the liquid (according to *liquidus* line)
N^E	eutectic concentration of the solute
s	saturated zone within the substrate
ss	super-saturated zone within the substrate
t	time
t_M	time of the beginning of the first solid / solid transformation
t_S	time of the completion of solidification
t_{31}^B	time of the birth of the Al_3Ni phase
t_{32}^B	time of the birth of the Al_3Ni_2 phase
t_ζ^B	time of the birth of the ζ phase
$t_{32}^{S/M}$	time of the completion of the transformation of stable solidification into metastable solidification
T	temperature
T_R	real temperature of the solidification imposed in technology
T_0	temperature related to the N_0 – solute concentration
x	amount of the growing solid, dimensionless
ΔT	undercooling of the solid / liquid interface
λ	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, $(Al)_S \rightarrow Al$. 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,

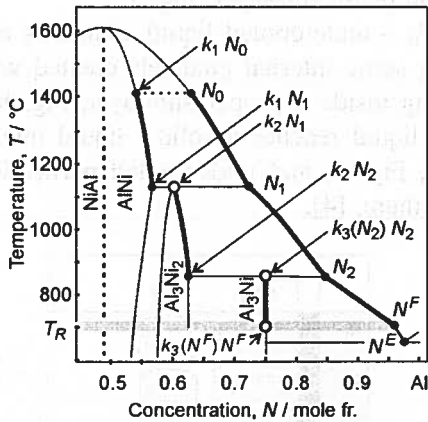this concentration is starting point of the solidification path, Fig. 1.

Fig. 1. Determination of the N^F concentration of the liquid solution of the Al – filler metal being in thermodynamic equilibrium with the coupled peritectic phase Al_3Ni as an intersection of the real temperature for the technology and liquidus line. The N_0 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, $\Gamma 1$). 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.
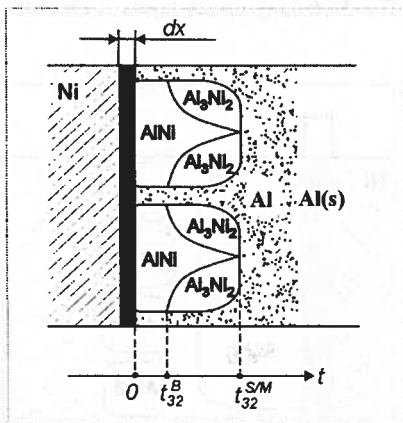
Fig. 2. Transformation of the primary phase AlNi into dominant phase Al3Ni2: $AlNi + liquid(N_1) \rightarrow Al_3Ni_2$. Transformation starts at time t_{32}^B; the completion of primary phase formation at time $t_{32}^{S/M}$. The scheme shown for the Ni/Al/Ni system
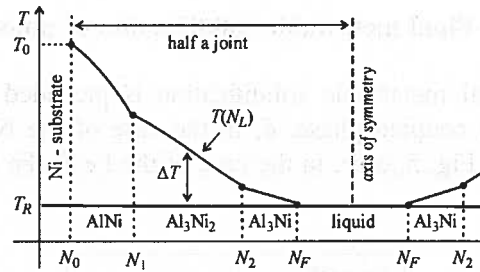

Fig. 3. Driving force for solidification of phases visible in the Ni-Al phase diagram. The driving force is defined as a difference, ΔT, between equilibrium liquidus temperature, $T(N_L)$ and real temperature of technology, T_R. $\Delta T = T(N_L) - T_R$ is undercooling

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 (N_1, N_2) 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: $liquid(N_1) + Al \rightarrow liquid(N^F)$ for the Ni/Al/Ni interconnection, Fig. 4, or in the case of Fe/Zn/Fe interconnection: $liquid(N_2) + Zn \rightarrow liquid(N^F)$.
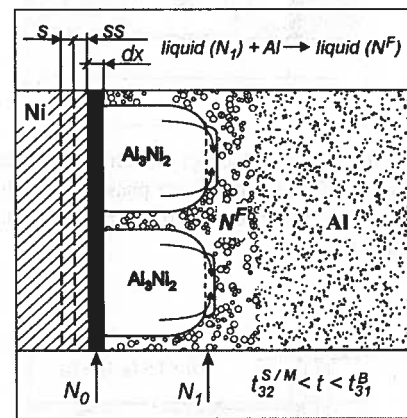

Fig. 4. Transformation of the Al-liquid filler metal into its liquid solution according to the reaction: $liquid(N_1) + Al \rightarrow liquid(N^F)$

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 (Al₃Ni, ς).

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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.
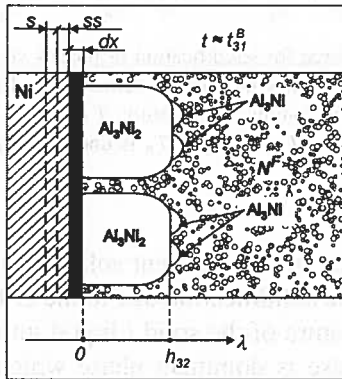

Fig. 5. Birth of the coupled phase Al_3Ni just on the surface of dominant phase Al_3Ni_2 at time t_{31}^B, when the dominant phase has its thickness equal to h_{32}, (λ is the distance)
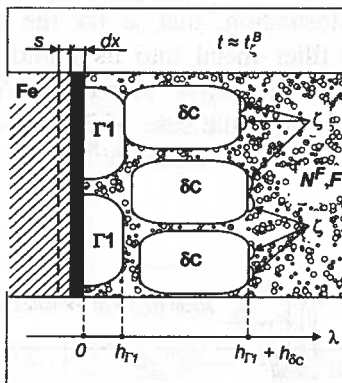

Fig. 6. Birth of the coupled phase ς, just on the surface of dominant phase δ, at time t_ς^B, when the dominant phase has its thickness equal to $h_{\Gamma 1} + h_{\delta C}$, but with presence of both $\Gamma 1$ phase sub-layer and flux, F, (λ is the distance)
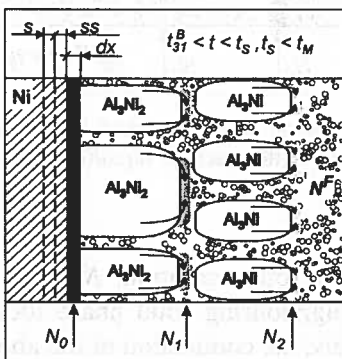
Fig. 7. Final metastable solidification of both phases: Al_3Ni_2 and Al_3Ni due to peritectic reactions occurring in sequence

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

The N_0 – 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].
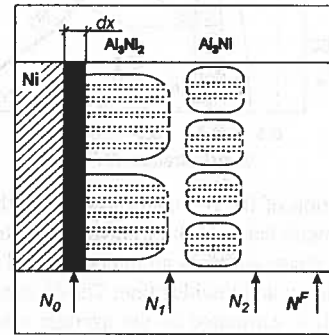

Fig. 8. Channels created along a height of cells. The N_0 undercooled liquid created within the zone dx is ready to flow towards the solid /liquid interface of cells
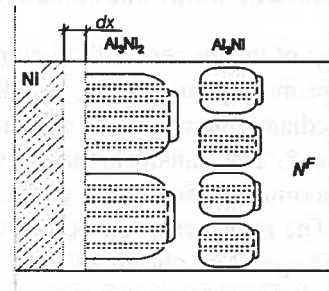

Fig. 9. The zone dx is just abandoned by undercooled liquid, N_0. An undercooled liquid stops at the solid /liquid interface of cells of both phase sub-layers and is subjected to undercooled peritectic reactions, in sequence. The thickening of sub-layers is observed
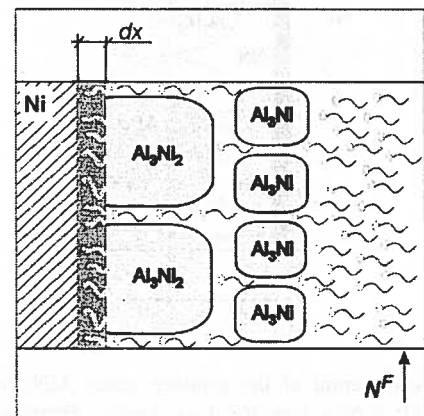

Fig. 10. External channels created between cells used for the flow of liquid metal solution, N^F, which promotes the formation of the dx zone at the surface of substrate

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: $liquid(N^F) + substrate \rightarrow liquid(N_0)$.

At time t_S – solidification is completed, Fig. 11. Since applied foil of filler metal is usually of thickness of the order < 50 μm, then $t_S < t_M$, where, t_M, is the time of beginning of the first solid / solid transformation.
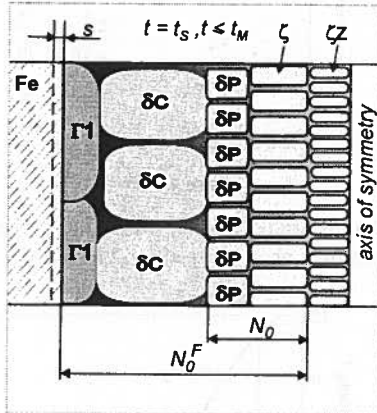

Fig. 11. Completion of solidification. Multi-layer reached the axis of symmetry of joint. All the sub-layers are fully formed. Two morphological types of the δ phase as well as two morphological types of the ς phase are visible within the half a joint

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 ς, is completely consumed by dominant phase, δ.
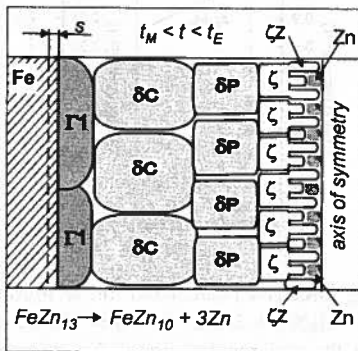

Fig. 12. Scheme of the first solid/solid transformation within Fe/Zn/Fe system. The pure liquid Zn-solute precipitates and is pushed towards the axis of symmetry of interconnection: $FeZn_{13} \rightarrow FeZn_{10} + liquid(3Zn)$

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, $N_0 = const.$
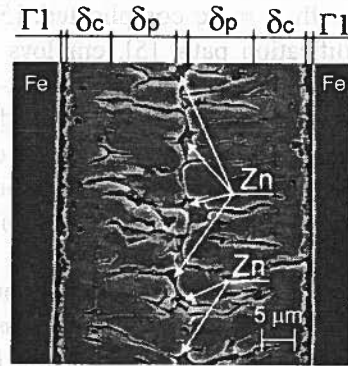

Fig. 13. A pure Zn – solute precipitated just at the axis of symmetry of interconnection (Fe/Zn/Fe system). The coupled phase, ς, is completely consumed by dominant phase, δ. Two types of δ – phase are observed due to the solidification with presence or without presence of a flux: phase δ_C appeared due to presence of flux, δ_P appeared when the flux disappeared in the system

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

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: $k_1 N_0 \rightarrow k_3 \left(N^F\right) N^F$, 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 preceded 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.
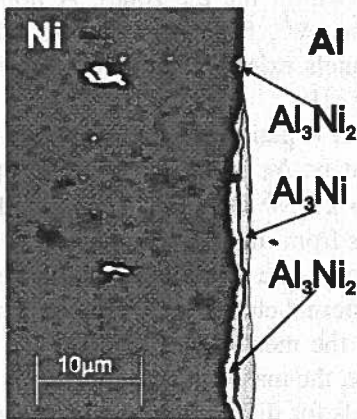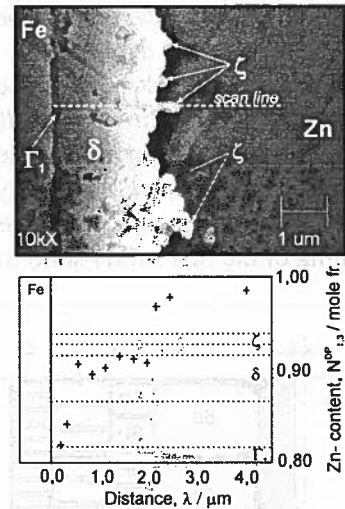

Fig. 15. *In situ* observation of the birth of the coupled phase $\varsigma\zeta$ on a surface of dominant phase formed for 13 seconds
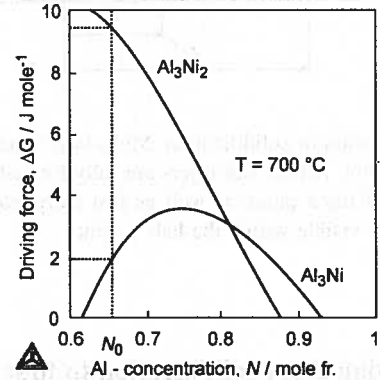

Fig. 16. Driving force (DF) calculated for Al3Ni2-Al3Ni multilayer formation from the undercooled liquid due to stable (virtual) peritectic reactions: *transient primary phase($AlNi$)* + *liquid(N_1)* $\Rightarrow$ Al_3Ni_2 and *transient primary phase(Al_3Ni_2)* + *liquid(N_2)* $\Rightarrow$ Al_3Ni DF(Al_3Ni_2) > DF(Al_3Ni) justifies the sequence of phase appearance during solidification. The Al_3Ni_2 phase appears first

Fig. 14. *In situ* observation of the birth of the coupled phase Al_3Ni on a surface of dominant phase Al_3Ni_2 formed for 9 seconds

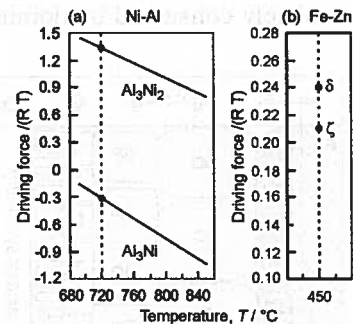

Fig. 17. Driving force (DF) calculated for: a/ solid/solid transformation: $2Al_3Ni \rightarrow Al_3Ni_2 + 3Al$ at the $T_R = 700°C$, b/$\delta - \zeta$ multilayer formation from the undercooled liquid due to stable (virtual) peritectic reactions: *transient primary phase($\Gamma1$)* + *liquid(N_2)* $\Rightarrow$ δ and *transient primary phase(δ)* + *liquid(N_3)* $\Rightarrow$ ζ DF(δ) > DF(ζ) justifies the sequence of phase appearance during solidification. The δ – phase appears first

The following reactions and transformations are considered in the envisaged systems:

1/ for the Ni/Al/Ni system

- melting of the filler metal $(Al)_S \to Al$
- formation of primary phase AlNi with remaining liquid(N_1)
- transformation of the liquid filler metal into its liquid solution: $liquid(Al) + liquid(N_1) \to liquid(N^F)$
- transformation of the primary phase AlNi into dominant phase Al_3Ni_2: $AlNi + liquid(N_1) \to Al_3Ni_2$
- dissolution of the substrate by the liquid solution of the filler metal: $liquid(N^F) + substrate \to liquid(N_0)$
- metastable solidification of peritectic phase Al_3Ni_2 and peritectic compound Al_3Ni, which can be described also with the use of the peritectic reactions for stable thermodynamic equilibrium: $primary(AlNi) + liquid(N_1) \to Al_3Ni_2$, $primary(Al_3Ni_2) + liquid(N_2) \to Al_3Ni$; 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: $2Al_3Ni \to Al_3Ni_2 + liquid(3Al)$

2/ for the Fe/Zn/Fe system

- melting of the filler metal $(Zn)S \to Zn$
- formation of primary phase α and $\Gamma1$ with remaining liquid(N_2) and presence of the flux, F
- transformation of the liquid filler metal into its liquid solution: $liquid(Zn) + liquid(N_2) \to liquid(N^F)$
- transformation of the primary phase α into $\Gamma1$ and $\Gamma1$ into dominant phase δ: $\alpha + liquid(N_1) \to \Gamma1$ and $\Gamma1 + liquid(N_2) \to \delta_C$ with the presence of flux, F
- dissolution of the substrate by the liquid solution of the filler metal: $liquid(N^F) + substrate \to liquid(N_0)$
- 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: $primary(\Gamma1) + liquid(N_2) \to \delta_P$, $primary(\delta_P) + liquid(N_3) \to \zeta$ 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: $\zeta(FeZn_{13}) \to \delta(FeZn_{10}) + liquid(3Zn)$.

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 $t_S \leqslant t_M$ is fulfilled.

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