

Mechanism of the intermetallic phase / compound growth on the substrate

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co-operating with

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Analysis and modelling

ABSTRACT

Purpose: An analytical model is provided in order to reveal the mechanism of the intermetallic multi-layer formation on a substrate. Thus, formations of the $Al_3Ni_2 - Al_3Ni$ intermetallic multi-layer on the Ni – substrate and $Fe_3Zn_{10} - FeZn_{10} - FeZn_{13}$ intermetallic multi-layer on the Fe (armco) multi-layer are considered.

Design/methodology/approach: The intermetallic multi-layers are the products of the undercooled peritectic reactions as this results from the model. Back-diffusion and partitioning as the phenomena accompanying the peritectic reactions are employed to describe the sub-layers growth.

Research limitations/implications: The model could be modified to describe the multi-layers formation under the metastable conditions.

Practical implications: The modeled descriptions of the mechanism of multi-layer formation seems to be a good tool to control the technologies like: diffusion soldering / brazing or hot dip galvanizing into zinc bath.

Originality/value: This is quite new model revealing the mechanism of the intermetallic multi-layer formation based on the original theory of solute redistribution after back-diffusion.

Keywords: Analysis and modelling; Materials design; Intermetallic phases; Formation multi-layers; Back-diffusion

1. Introduction

A formation of intermetallic multi-layers can be easily observed and studied during the 1D solidification occurring during the diffusion soldering or brazing. In diffusion soldering / brazing a pre-placed filler metal (solute) melts and diffuse into the solid substrates (joining partners/components) to form solid intermetallic phases when heated to the soldering / brazing temperature [1].

The diffusion continues until both physical and mechanical properties of the multi-layer become almost identical to those of joining partners.

In the diffusion soldering the liquid interlayer resolidifies isothermally at a bonding real temperature, T_R . The joint is a result of interaction between a liquid filler metal and solid substrates [1].

Under some circumstances, the bonding process can result in a joint that microstructurally reproduces the sequence of the several intermetallic compounds or phases as visible in a phase diagram.

A microstructural development is assumed to involve three phenomena that occur in a sequence: solute dissolution, isothermal solidification and homogenisation [2]. The solute dissolution is occurring just before solidification or it can also be considered that both analysed phenomena occur at the same time, practically. In the current model, dissolution will be treated only as a process of creation of the final nominal concentration of an alloy subjected to solidification. In the consequence, a local solute concentration changes while dissolution is occurring. At this stage of bonding the solid - liquid system is open.

Eventually, a solidification occurs until complete consumption of the liquid filler metal, (foil).

It can be postulated that diffusion soldering is an element of the TLP bonding. Some applications of the TLP bonding are known, and studied on Ni-Al-Ni or Ti-Al-Ti joints [3-6]. In this paper, an analysis is focused on the formation of the Ni-Al-Ni and Fe-Zn-Fe joints in relation to the diffusion soldering and hot dip galvanizing. A new model for the prediction of both segregation and ratio of thicknesses of the sub-layer is proposed. The model results from the theory of solidification / redistribution both accompanied by back-diffusion [7] and peritectic reactions. The phenomenon of back-diffusion plays an essential role not only in redistribution but in peritectic reactions as well.

2. Role of peritectic reactions in solidification mechanism

The differential equation formulated for the microsegregation with partial back-diffusion is given as:

$$\frac{dN_i^L}{dx} = \frac{(1 - k_i^0) N_i^L}{l_i^0 + \alpha_i^D k_i^0 x - x} \quad (1)$$

$$k_i(N_i^L) = k_i^0 + k_i^L \frac{N_{i-1}^L}{N_i^L} \quad (2)$$

and resultant solute redistribution after back-diffusion:

$$N_i^B(x; \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0) = [1 + \beta_i^{ex}(x; \alpha_i^D, \alpha_i^P, l_i^0, k_i^0) \beta_i^{in}(x; \alpha_i^D, \alpha_i^P, l_i^0, k_i^0)] N_i^S(x; \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0) \quad (3)$$

$$l_i^0 = \begin{cases} L^0, & i = 1; \\ L^0 - \sum_{j=1}^{i-1} x_j^{max}, & i = 2, \dots, n; \end{cases} \quad (4a)$$

$$x_i^0 = \begin{cases} X^0, & i = 1; \\ X^0 - \sum_{j=1}^{i-1} x_j^{max}, & i = 2, \dots, n; \end{cases} \quad (4b)$$

A general definition of the peritectic reaction is:

$$x_i + liquid(N_i) \Rightarrow [x_i^{max} - x_i^{min}] \quad (5)$$

It is evident from eqn (5) that problem of two moving boundaries: x_i^{max} and x_i^{min} arises. An analytical form of the problem solution satisfying the mass balance is as follows:

$$x_i^{max}(x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) = x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0) + r_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) / (N_i - k_{i+1}^0 N_i);$$

when $r_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) \leq (N_i - k_{i+1}^0 N_i) \times [x_i^{min}(x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) - x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0)]$

$$\int_0^{x_i^{min}} [N_i^B(x; \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0) - N_i^B(x; \alpha_i^D, l_i^0, N_{i-1}, k_i^0)] dx + \int_{x_i^{min}}^{x_i} [k_{i+1}^0 N_i - N_i^B(x; \alpha_i^D, l_i^0, N_{i-1}, k_i^0)] dx = (N_i - k_{i+1}^0 N_i) [x_i^{max}(x_i^0, \alpha_i^D, \alpha_i^P, l_i^0, N_{i-1}, N_i, k_i^0, k_{i+1}^0) - x_i(\alpha_i^D, l_i^0, N_{i-1}, N_i, k_i^0)] \quad (6b)$$

The model equations are referred to the adequate phase diagram as visible in Fig. 1, plotted for the Ni/Al/Ni interconnection.

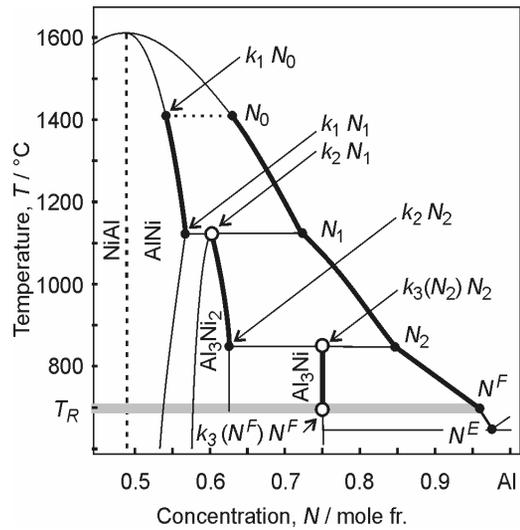


Fig. 1. A solidification path defined for a given technological temperature, $T_R = 700 \text{ }^\circ\text{C}$, (Ni-Al phase diagram)

The N^F concentration is shown in Fig. 1. The adequate reaction for the formation of liquid solution, N^F is explained in Fig. 2.

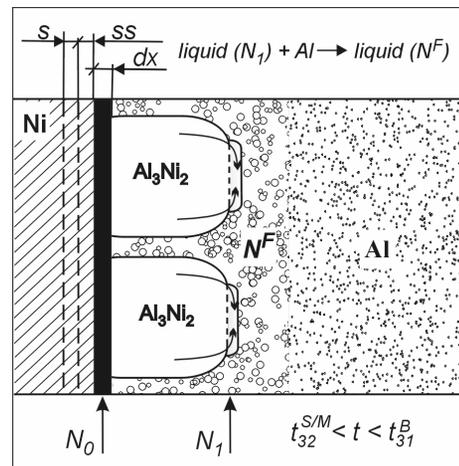


Fig. 2. Transformation of the filler metal into its liquid solution

The peritectic reactions are accompanying the solidification process occurring after complete transformation of the liquid filler metal into its liquid solution. The solidification can be arrested and morphology frozen, Fig. 3.

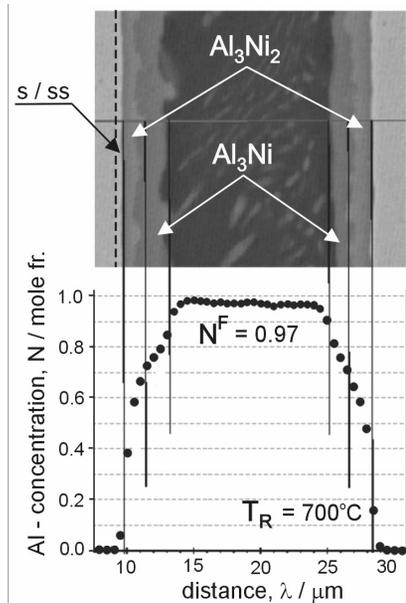


Fig. 3. Morphology of the Ni/Al/Ni interconnection, frozen after 15 s of solidification under a vacuum. The N^F - liquid solution revealed due to EDS measurement of Al – solute concentration

Both products of peritectic reactions: $Al_3Ni_2 - Al_3Ni$ are revealed within the morphology, Fig. 3. Analogously, products of peritectic reactions: Γ_1, δ and ζ are revealed within the morphology of Fe/Zn/Fe system supported solidification, Fig.4.

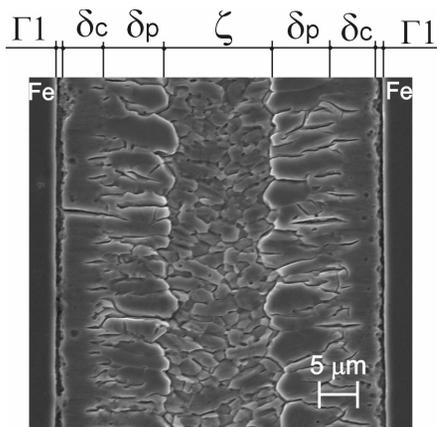


Fig. 4. Morphology of the Fe/Zn/Fe interconnection, frozen just after completion of solidification

Two peritectic reactions are observed during formation of intermetallic multi-layer under metastable condition within the Ni/Al/Ni system, Fig. 3. But, three peritectic reactions occur during formation of intermetallic multi-layer within the Fe/Zn/Fe

system, within which the presence of a flux is necessary, Fig. 4. The third peritectic reaction is a result of the presence of flux [8].

3. Mechanism of peritectic reactions at the solid / liquid interface

An explanation of the mechanism of peritectic reaction at the solid / liquid interface and required reactive diffusion involves the necessity of delivering of model of a zone – dx. The model assumes that liquid solution of the filler metal, N^F , diffuses towards the substrate, Fe to form a zone denoted as dx. The substrate is dissolved until it became liquid but undercooled within the zone. This state is reached when dissolved area, dx, has a proper content of the Zn – solute, equal to N_0 , Fig. 5.

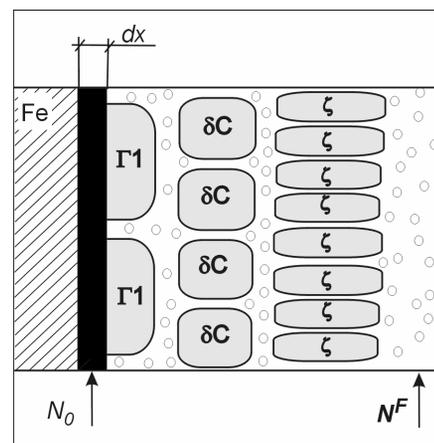


Fig. 5. Zone – dx formed just at the surface of substrate due to its dissolution caused by liquid solution of the filler metal. The multi-layer formation for Fe/Zn/Fe system with presence flux

It is evident that two diffusive flows are to be observed: flow of the liquid solution of the filler metal, N^F , towards the substrate to promote the dissolution, Fig. 6a and flow of the undercooled liquid, N_0 , created within the zone, dx, towards the solid / liquid interfaces of growing cells within adequate sub-layers, Fig. 6b. However, the flow of the undercooled liquid, N_0 , stops at each solid / liquid interface to involve a proper peritectic reaction, as shown schematically in Fig. 6b. The undercooled liquid changes its solute concentration: $N_0 \rightarrow N_1 \rightarrow N_2 \rightarrow N_3$ due to the sequential peritectic reactions. The thickening of sub-layers is a result of peritectic reactions accompanied by reactive diffusion.

The discussed model assumes the existence of canals between cells as well as along cells, inside, Fig. 6a. It can be assumed that external canals are destined to the flow of undercooled liquid N_0 along cells boundary. In this case kinetic law of thickening requires $m -$ exponent equal to 1.0. It is associated with boundary diffusion necessary for peritectic reactions. Internal canals as well as bulk material could be destined to flow of the liquid solution of filler metal, N^F . In the case of volume diffusion $m -$ exponent is equal to 0.5. Boundary and volume diffusion are observed simultaneously because the exponent satisfies inequality: $0.5 < m < 1$ for a period of dissolution / solidification [8].

The present model of dissolution / solidification corresponds to another approaches [9]- [12] in which reactive diffusion is considered. However, the current model defines precisely a type of reaction as an undercooled peritectic reaction.

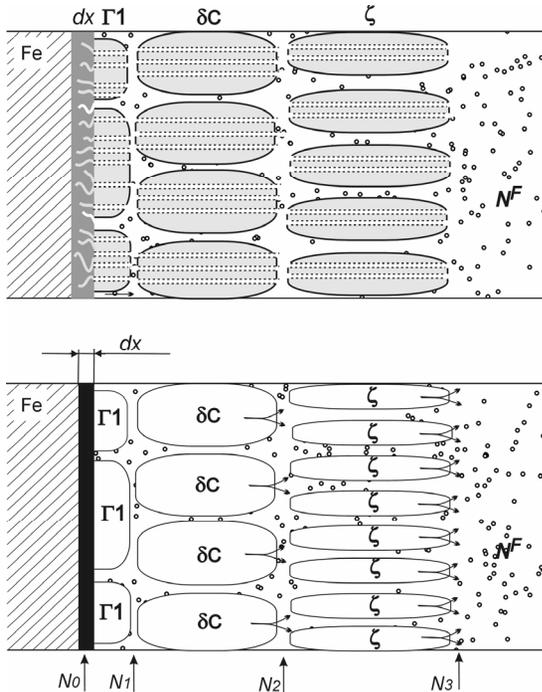


Fig. 6. Model for dissolution and solidification accompanied by peritectic reactions; a/ diffusive flow of the liquid solution of filler metal, N^F to create the zone – dx at the surface of substrate, b/ diffusive flow of undercooled liquid, N_0 to promote peritectic reactions at each solid / liquid interface, sequentially, (arrows indicate a place of peritectic reaction and thickening of sub-layer)

Three peritectic phases are visible in Fig. 6b. The phases appear in sequence [13]. The $\Gamma 1$ - phase appears first at the substrate surface. It grows until disappearing of the flux [8]. The growth of the $\Gamma 1$ phase is followed by an appearance of δC phase during existence of the flux [8]. Then, the δP phase is expected. The ζ phase appears in two forms: as a sub-layer due to oriented growth or as some dendrites due to free growth in the liquid.

4. Conclusions

The mechanism governing the solidification during diffusion soldering or hot dip galvanizing is cleared.

Two opposite flows have been distinguished to explain the common occurrence of both dissolution of the substrate by liquid solution of a filler metal, N^F and solidification of the undercooled liquid of the N_0 concentration of solute, the last accompanied by the undercooled peritectic reactions.

A sequence of phase sub-layers appearance is suggested. This sequence is the same as a localization of peritectic reactions in the

considered phase diagram. Thus, the highest is the localization of peritectic reaction in the phase diagram the first this peritectic phase appears within a multilayer.

Back-diffusion parameters α_D and α_P are differentiated to formulate independent descriptions for primary phase formation and peritectic reaction itself.

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References

- [1] D. Duvall, W. Owczarski, D. Paulonis, TLP Bonding, A New Method for Joining Heat Resistant Alloys, *Welding Journal* 53 (1974) 203-214.
- [2] I. Tuah-Poku, M. Dollar, T. Massalski, A Study of the Transient Liquid Phase Bonding Process Applied to a Ag/Cu/Ag Sandwich Joint *Metallurgical Transactions* 19A, (1988) 575-586.
- [3] W. Wołczyński, E. Guzik, D. Kopyciński, T. Himemiya, J. Janczak-Rusch, Mass Transport during Diffusion Soldering or Brazing at the Constant Temperature, *Proceedings of the 13th International Heat Transfer Conference, Sydney - 2006, MST-11, (CD-ROM)*.
- [4] S. Corbin, P. Lucier, Thermal Analysis of Isothermal Solidification Kinetics during TLP Sintering, *Metallurgical and Materials Transactions* 32 (2001) 971-978.
- [5] T. Studnitzky, R. Schmid-Fetzer, Phase Formation and Diffusion Soldering in Pt/In, Pd/In, Zr/Sn Thin Film System, *Journal of Electronic Materials* 23 (2003) 362-369.
- [6] G. Lopez, S. Sommadossi, W. Gust, E. Mittemeijer, P. Zięba, Kinetic Behavior in Diffusion Soldered Ni/Al Interconnection, *Interface Science* 10 (2002) 13-19.
- [7] W. Wołczyński, Back-diffusion Phenomenon during Crystal Growth by the Bridgman Method, Chapter 2., in, *Modelling of Transport Phenomena in Crystal Growth*, eds J.S.Szmyd, K.Suzuki, WIT Press, Southampton / Boston, 2000, 19-59.
- [8] D. Kopyciński, Solidification of Intermetallic Phases on the Iron and its Low- and High-carbon Alloys during Hot Dip Galvanizing. *Monographs-AGH* 149 (2006) 131 (in Polish).
- [9] H. Woźnica, M. Michalik, Kinetics of Growth of the Zinc Coating on a Cast Iron during Hot Dip Galvanizing, *Corrosion Protection* 11 (2002) 157-162 (in Polish).
- [10] S. Divinski, F. Hisker, C. Herzig, R. Filipek, M. Danielewski, Self- and Interdiffusion in Ternary Cu-Fe-Ni Alloys, *Defect and Diffusion Forum* 237-240 (2005) 50-61.
- [11] I. Belova, G. Murch, R. Filipek, M. Danielewski, Theoretical Analysis of Experimental Tracer and Interdiffusion Data in Cu-Ni-Fe Alloys, *Acta Materialia* 53 (2005) 4613-4622.
- [12] R. Filipek, Modeling of Inter-diffusion and Reactions at the Boundary, Initial-value Problem of Inter-diffusion in the Open System, *Defect and Diffusion Forum* 237-240 (2005) 250-260.
- [13] W. Wołczyński, T. Wierzchoń, Formation Sequence of the Intermetallic Phases within Multi-layer Coatings, *Materials Engineering* 153 (2006) 1268-1271.