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An estimate of Si_3N_4 diffusion into Cu based filler metal

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Abstract

The diffusion phenomena occurring at the boundary between Si_3N_4 and active Cu based filler metal during Si_3N_4/metal joining are discussed as a part of the general theory of reaction layer growth. The mechanism of reaction layer formation is explained in the light of wettability, heterogeneous chemical reactions and diffusion in the presence of a moving interface. Observed processes involve diffusion steps in conjunction with chemical reactions at solid/liquid boundary. Illustrative calculation results based on the proposed procedure are presented. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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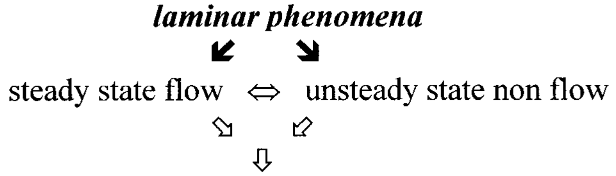
1. Introduction

Metal-ceramic systems, such as structural and electronic materials, increasingly applied in modern technologies. One of the joining techniques, i.e. joining with active filler metal, is of special interest from the view of success and economy. This method relies on the alloying of the filler metal with reactive elements such as Ti and Zr to promote wetting of the ceramic surface necessary for successful joining [1–4]. Joining ceramics to metallic materials is not so easy to carry out without consideration of an interdisciplinary task in which different fields of materials science must participate. The general theory of reaction layer growth [5–8] is an important point for understanding the mechanism of reaction layer formation. In this framework, three steps will be considered: (1) wetting of the ceramic surface, (2) chemical reactions at the interface and (3) diffusion with a moving interface.

2. Theory of reaction layer growth

Two reaction layers between Si_3N_4 and insert metal can be identified, i.e. the layer on the ceramics side in which point-like substances exist, and the layer on the insert metal side in which point-like substances do not exist. The total reaction layer thickness increases simultaneously with temperature and/or time. At higher temperatures and longer times, the growth rate of the reaction layer gradually slackens, and the ultimate thickness of the reaction layer becomes almost constant. Reaction products in a large part of metal-ceramic couples grow following the parabolic law. Assuming that the reaction layer growth is controlled by diffusion of an element through the reaction layer, the growth of the layer can be treated by the simple parabolic law, eventually modified by the Johnson–Mehl or Austin–Rickett type equations [3,5].

However, the phenomena of reaction layer growth gradually deviate from the simple parabolic law, because of different ways of diffusing the element into the layer. The Johnson–Mehl and Austin–Rickett type equations also deviate from the experimental data [3]. In that sense a new approach is proposed. Briefly, the complexity of the fundamental partial differential equation of laminar phenomena, is substituted by an ordinary differential equation [6,7]:



The "simplified" equation:

$$f1\,(N)\zeta^{f2(N)} + \Pi\Theta'' \pm f(m) = 0$$

where $\zeta = y/\delta(t)$ is a dimensionless distance from interface, $\delta(t)$—boundary layer thickness at time (t), Π—relative diffusivity, $\Theta'' = d^2\Theta/d\zeta^2$, $\Theta = Cx/C\max\,(t)$—normalized concentration distribution, Cx—local concentration at the cross-section, $C\max(t)$—local core

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concentration at time (t) and m—characteristic whole number. Solution of this equation, i.e. normalized concentration distribution Θ, is considered in the most general terms with analogous meaning for momentum, mass, heat, chemical reaction, electro-magnetic forces etc. Introducing the relevant boundary conditions the solution of Eq. (1) becomes the polynomial:

$$\Theta = 1 - \theta, \quad \theta = N\zeta + 0.5f(m)\zeta^2 \pm (N-1)\zeta^{[N/\pm(N-1)]^{(\pm1)}} \tag{2}$$

The criterion $N = \mathrm{d}\theta/\mathrm{d}\zeta_{|\zeta=0}$ defines the state at the cross-section perpendicular to the surface and enables the comparison and classification of (laminar boundary) layers within previously defined reference and boundary distributions. The term $f1(N)\zeta^{f2(N)}$ simulates the partiality of starting fundamental equation. The functions $f1(N)$ and $f2(N)$, for a certain region and chosen criterion N, become constants in the form of a whole number or fraction. The function $f(m) = \mathrm{d}\theta/\mathrm{d}\zeta\,|_{\zeta=1}$ indicates the homogeneous appearances coupled with variable core concentrations $C\max(t)$. This function directly participates in the mass transport. On the other hand, the volume (continuous) homogeneity is incorporated into the basic distribution, through the correctly chosen region change of criterion N. Homogeneous appearances are present inside a phase (i.e. bonding pressure, homogeneous chemical reaction, external heating, electro-magnetic forces, etc.). The heterogeneous appearance that occurred along the interface can be observed as a phenomenon of concentration change with the corresponding distribution. Within borders caused by laminar conditions, heterogeneous appearances are relatively independent. Heterogeneous appearances are present on the interface (i.e. adhesion, wetness, heterogeneous chemical reactions, surface heterogeneities, internal heating etc.).

The total coupling of the whole system is realized by the quantity m, which has a physical meaning of its own. Generally, the m presents the ratio of formation and decomposition processes.

The "simplified" Eq. (1) defines the flux gradient (FG-code) of the concentration change phenomena:

$$FG = \int_0^1 \Theta''\mathrm{d}\zeta = N + f(m); \quad N \in \{0, 2\}, f(m) \in \{0, \pm\infty\} \tag{3}$$

In principle there are laminar layers with: constant local core concentration $C\max(t)$ and constant FG during the time $\{FG = N; f(m) = 0\}$ and variable FG when every stage has its corresponding distribution $C\max(t)$ $\{FG = var; f(m) = var\}$.

The model of reaction layer growth has the same mathematical basis as the steady-state flow model [6]. The boundary layer approach is used in order to obtain information about the behavior in the neighborhood of the interface. Approximate solutions for the concentration profiles in a thin boundary layer near the interface are recommended. Therefore, the general equation of concentration distribution is adapted to the case of one side unsteady-state diffusion in solid which is analogous to flow near a wall suddenly set in motion. The integral method, based on setting mass balances for the control volume, is used. The model considers the boundary layer development as a function of time. The following assumptions are made: (i) at any time t, there is a boundary-layer thickness $\delta(t)$ beyond which there is no diffusion, so the concentration change effects are confined to the region $0 \leqslant \zeta \leqslant 1$ and (ii) the dimensionless concentration profiles, Θ remain similar as time proceeds. We can develop the expression for $\delta(t)$ in terms of any "reasonable" function Θ taking the values for $N, f(m)$ and M from data [5]. Generally, the boundary layer thickness increases through the stages as square root of the time.

The total heterogeneity: $FG_H = FG_{\text{wetness}} + FG_{\text{heterogeneous reaction}} + FG_{\text{interface diffusion}}$ participates in the mass transport process and its inflection is evident after some time t′ or t″. The simulated system is shown in Fig. 1.

The total heterogeneity FG_H participates in the mass transport process and its inflection is evident after some time t^* (t' or t″, Fig. 1). So, at time t^* one obtains:

$$M\delta\mathrm{d}\delta = D(FG_D + FG_H)^{\text{stage(i)}}\mathrm{d}t \tag{4}$$

where $M = \int_0^1 \Theta_D \mathrm{d}\zeta$ is the total amount, D—the diffusion coefficient throughout the reaction layer, $FD_D = \Theta'_D\,|_0^1$—the diffusion flux, $FG_H = \Theta'_H\,|_0^1$—the total heterogeneity flux, $\Theta_D = (1 - \theta_D)$—dimensionless concentration ratio of diffusion and $\Theta_H = (1 - \theta_H)$—dimensionless concentration ratio of total heterogeneity.

Integration of Eq. (4) gives:

$$\begin{aligned} &\delta(t)^{\text{stage(i)}} = a^{\text{stage(i)}}t^{1/2} + \delta\mathrm{o}^{\text{stage(i)}}; \\ &a^{\text{stage(i)}} = [2(FG_D + FG_H)^{\text{stage(i)}}D/M] \end{aligned} \tag{5}$$

Also, in "critical time" t^* at "critical thickness" δ^* one obtains the ratio:

$$\begin{aligned} &(FG_D + FG_H)^{\text{stage(i)}}/(FG_D + FG_H)^{\text{stage(i+1)}} \\ &= 1 - [a^{\text{stage(i+1)}}/a^{\text{stage(i)}}]^2 \end{aligned} \tag{6}$$

that indicates the "power" change of total heterogeneity.

2.1. Wettability of the ceramic surface

The so called active metal brazing materials, which are in the forms of foils and wires of alloys or powder

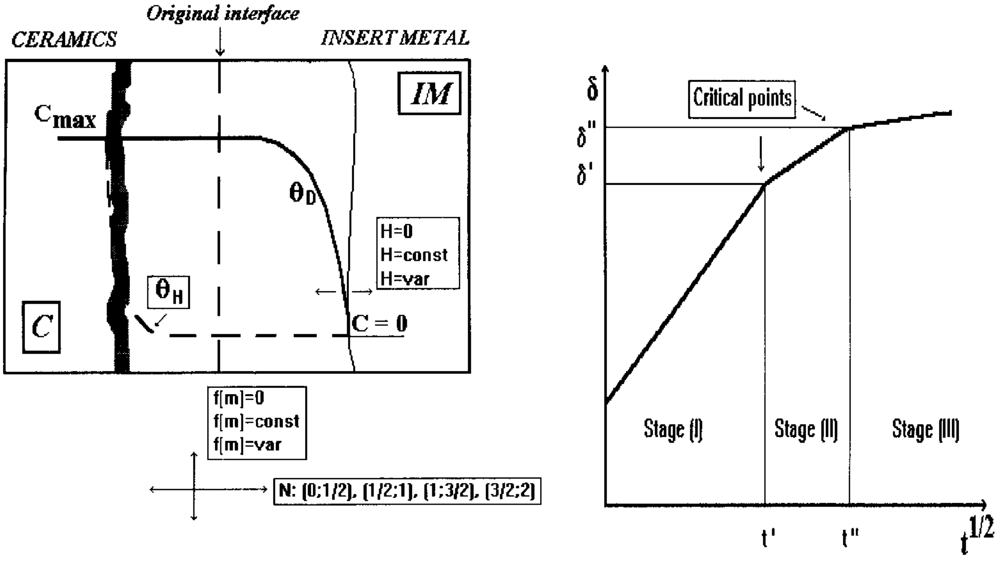

Fig. 1. The simulation system of reaction (laminar boundary) layer during the chosen stage (I, II or III).

mixture of metal hydrides, contain a few weight per cent of active elements. Typical examples are Ag–Cu eutectic alloys with a few weight percent (1–10 wt%) addition of Ti or Zr and Cu–Ti eutectic alloy. The active component can be added in three different ways: (i) included as an alloying element, (ii) as a thin film added separately to the braze and (iii) as a sputtered thin film deposited on the substrate prior to addition of the braze. The wetting behavior for the three different ways of adding varies from non-wetting to wetting. The reason is believed to be the chemical composition and state of the reaction layer formed between the ceramic substrate and the braze. On the other hand, the initial characteristics of ceramics, such as impurity content and grain boundaries, must affect the condition of the metal–ceramic interface zones as well as the contact angle.

It is difficult to estimate the extent of wetting because interfacial reactions change the wetting characteristics as time elapses. On the other hand, the relationship between wetting and interfacial reactions is not well understood, i.e. molten copper shows high contact angle and low wettability against ceramics such as Si_3N_4, SiC and ZrO_2, though molten aluminum exhibits low contact angle and high wettability against ceramics.

Reactivity and wetting data for nitrides are not as clearly established as for carbides and oxides but fit the same general pattern. It is well known that the wetting of nitride ceramics by Cu–Ti alloys is good, while the wetting by commercial Ag–28%Cu–2%Ti is excellent [1]. As an example, the typical equilibrium contact angles of 90° were measured at 1200°C for Cu–x%Cr (x = 1,3,7) alloys on Si_3N_4 [4].

The physico-chemical principles underlying the wetting action are to be found in standard texts [9]. If the liquid metal is (or not) under pressure it will come to rest on a real (porous and/or rough) ceramic surface in some position, determined by the advancing smooth surface–liquid metal contact angle and the shape of the pores in the surface. The surfaces of practical importance are usually grids formed of roughly spherical atom positions and/or grain boundaries One can start from the well known Young–Dupré equation:

$$W_{ad} = \gamma_M(1 + \cos\varphi) \tag{7}$$

and the relationship given by Cassie and Baxter, modified with two coefficients (h^{LS} and h^{SA}) [7]:

$$\cos\varphi = h^{LS} f_1 \cos\alpha - h^{SA} f_2 \tag{8}$$

where W_{ad} is work of adhesion, γ_M is surface energy of the metal, φ is apparent contact angle, α is advancing (receding) contact angle, f_1 is the total area of the solid–liquid interface, f_2 is the total area of the liquid–air (or furnace atmosphere) interface, h^{LS} is the coefficient of the net liquid–solid heterogeneity influence and h^{SA} is the coefficient of the net liquid–air (furnace atmosphere) heterogeneity influence.

The general tendency of the heterogeneity influence can be presented through the action of the coefficients as follows:

(1a) $h^{LS} > 1 \Rightarrow f_1 \uparrow \Rightarrow \cos\varphi \uparrow$		(1b) $h^{LS} < 1 \Rightarrow f_1 \downarrow \Rightarrow \cos\varphi \downarrow$
(2a) $h^{SA} > 1 \Rightarrow f_2 \uparrow \Rightarrow \cos\varphi \downarrow$		(2b) $h^{SA} < 1 \Rightarrow f_2 \downarrow \Rightarrow \cos\varphi \uparrow$
Wetting: without heterogeneous appearances		Wetting: with heterogeneous appearances
$\cos\varphi = f_1 \cos\alpha - f_2$	porous surface	$\cos\varphi = h^{LS} f_1 \cos\alpha - h^{SA} f_2$
$\cos\varphi = f_1 \cos\alpha$	rough surface	$\cos\varphi = h^{LS} f_1 \cos\alpha$
$\cos\varphi = \cos\alpha$	smooth surface	$\cos\varphi = h^{LS} \cos\alpha$

The microstructural parameters that may have an influence on the properties of the metal/ceramic interface (reflected on h^{LS} and h^{SA}) are: structure of the heterophase boundary; characteristic defects such as steps, faces and dislocations at or to the interfaces, possible chemical reactions; reaction products; chemical gradients and segregation of impurities at the interface [10].

2.2. Chemical reactions at the interface

Briefly, the chemical reaction occurring between silicon nitride and metal (M) can be described by one of the three formulas:

$$M + Si_3N_4 = M\text{-silicide} + M\text{-nitride}$$
$$M + Si_3N_4 = M\text{-silicide} + N_2$$
$$M + Si_3N_4 = Si + M\text{-nitride}$$

Free Si and N atoms diffuse in the reaction layer towards the melted insert layer (i.e. Cu and Ag–Cu based alloys) and react with active metals (i.e. Ti, Zr, Cr). Finally, the rest of free Si and N atoms form Si_3N_4. So, it may be deduced that the reaction layer growth from the melted insert layer is diffusion controlled by Si_3N_4 [3].

2.3. Diffusion with a moving interface

The problem of predicting, correlating and extrapolating diffusion data in liquids is very difficult because of our lack of understanding of the structure of liquids. The difficulties of making accurate experimental determinations of diffusion coefficients in liquids due to the homogeneous and/or heterogeneous appearances, and the problems of sampling, further complicate the diffusion problem. Various theories of liquid state (i.e. Hydrodynamical, Hole, Eyring and Fluctuation theory) related to diffusion may be confusing. Thus, no critical tests of these models will really be possible until more accurate data over much wider ranges of experimental conditions are available. Therefore, in the present approach a simplified routine will be discussed.

The observed process involves diffusion steps in conjunction with chemical reactions at the solid/liquid boundary. One result of these transient processes is the motion of the boundary between the phases. In the general situation , two phases are in contact as in Fig. 2. The moving phase boundary is at $x = X$, and at this boundary Co and $C^* = C(X, t)$ represents the equilibrium concentration of Si_3N_4 that coexist in ceramics and insert metal, respectively, at the temperature under consideration.

In the insert metal phase, Fick's second law applies:

$$dC/dt = D\, d^2C/dx^2,\ x > X \tag{9}$$

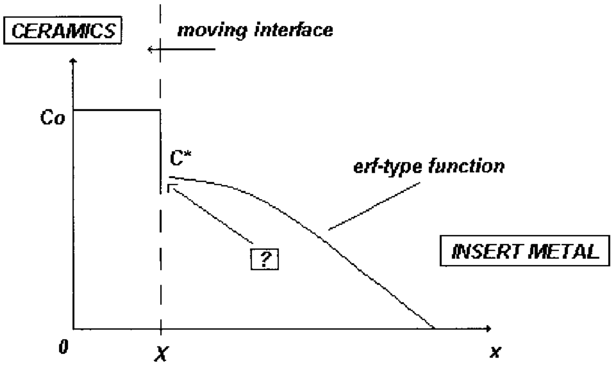

Fig. 2. The concentration profile during transient diffusion.

where C is the Si_3N_4 concentration during transient diffusion, D the diffusion coefficient of the Si_3N_4 in melted insert metal, assumed to be independent of composition. The next condition is that the concentration on either side of the interface are related by an equilibrium expression of the form: $Co = KC^*$, where K is the partition ratio between the phases. The material balance at the interface takes the form:

$$-D(dC/dx)_{x=X} = (C^* - Co)dX/dt \tag{10}$$

Eq. (4) describes the locus of X with time. Relationship between Co and C^*:

$$\pi^{-0.5}[C^*/(C^* - Co)] = \beta \exp \beta^2 \text{erf} \beta \tag{11}$$

when

$$X = 2\beta(tD)^{0.5} \tag{12}$$

is well known. The function of β, $\beta \exp \beta^2 \text{erf} \beta$ may be evaluated from [11]. So, the D can be calculated if Co, C^*, X and t are measured.

3. Calculation results

Experiments used as valuable data for mathematical analysis have been the Si_3N_4-W joint bonded using Cu-based insert metals [3]. The estimate of Si_3N_4 diffusion coefficients according to Eqs. (10), (11) and (12) for various joints and conditions is presented in Table 1. Appropriate distribution values and curves are presented in Figs. 3–6.

The departures from the ideal erf type curves for Cu–5%Cr and Cu–3% filler metals are probably due to experimental errors (it is difficult to avoid the homogeneous and/or heterogeneous appearances completely) and to a variation of D with composition. Also, the influence of alloying elements on "pure" diffusion is not always clear. According to the calculated data it seems that the characteristic value of C^* is about 0.85. But for

Table 1
Bonding conditions (*T*,*t*), reaction products, relative concentration of Si_3N_4 in molten Cu based alloy (C^*), depth of reaction layer (M) and calculated diffusion coefficient (D)

Metal–ceramics joint	T, [K]	t, [s]	Reaction products	C*, I/I_{max}	M, [μm]	$D(\times 10^{-12}$, cm^2/s)
W//Cu–5%Cr//Si_3N_4	1573	1800	$CrSi_2$, Cr_2N, CrN	86	30	0.103
W//Cu–3%V//Si_3N_4	1573	1800	V_6Si_5, VN	85	30	0.105
W//Cu–5%Ti//Si_3N_4	1373	1800	Ti_5Si_3, TiN, (?)	84	40	0.197 (?)
W//Cu–10%Zr//Si_3N_4	1423	1800	Zr_5Si_3, ZrN, (?)	85	16.6	0.032 (?)

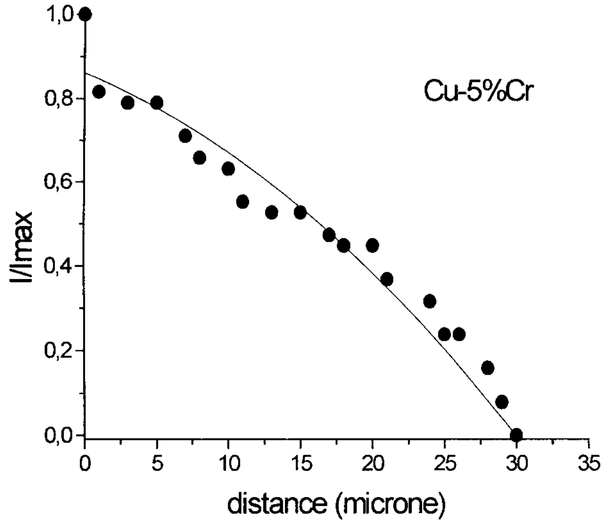

Fig. 3. Distribution of Si_3N_4 perpendicular to the bonding layer of Si_3N_4-W joint bonded using Cu–5%Cr insert metal [3].

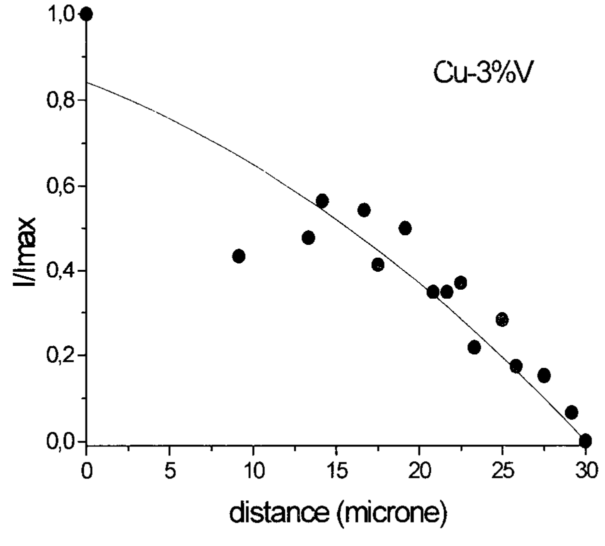

Fig. 4. Distribution of Si_3N_4 perpendicular to the bonding layer of Si_3N_4-W joint bonded using Cu-3%V insert metal [3].

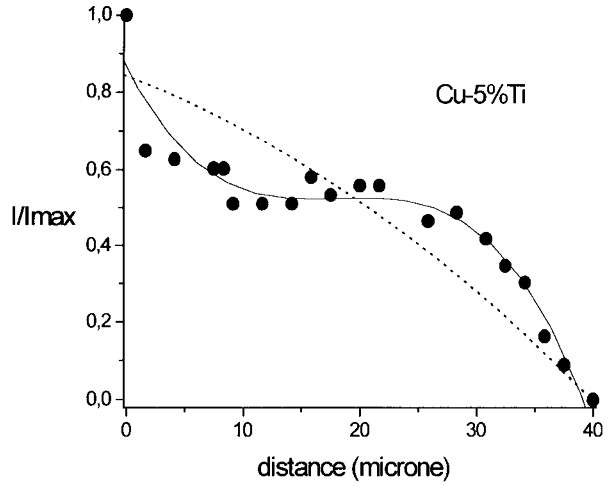

Fig. 5. Distribution of Si_3N_4 perpendicular to the bonding layer of Si_3N_4-W joint bonded using Cu–5%Ti insert metal [3].

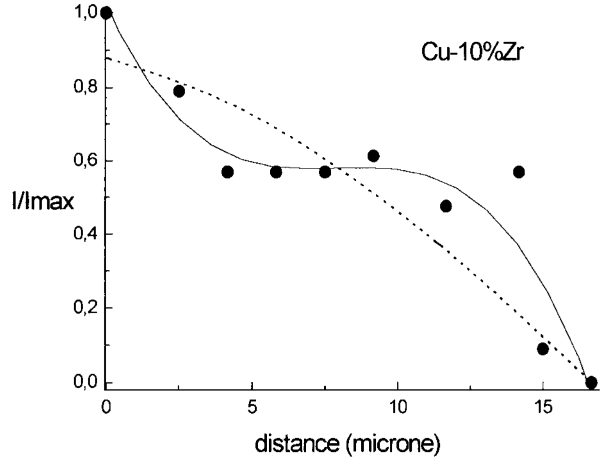

Fig. 6. Distribution of Si_3N_4 perpendicular to the bonding layer of Si_3N_4-W joint bonded using Cu–10%Zr insert metal [3]

Cu–5%Ti and Cu–10%Zr filler metals there also exists an plateau in concentration distribution at 0.5 and 0.55 respectively. Therefore, one may conclude that some uncovered reactions and/or products exist or that a multi phase problem is involved. Because of that, in the last two cases another mathematical routine must be applied.

4. Conclusions

Diffusion phenomena occurring at liquid filler metal/nitride ceramics interfaces are of great importance for metal–ceramics joining techniques. So, in this paper the basic equations are given, and the approaches necessary to treat laminar diffusion phenomena are carefully explained. The attention is confined to typical examples taken from the literature.

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