Modeling of Wetting Phenomena at Grain Boundary Grooves of Metal/Ceramic Joints

Marija Mihailović[1,a], Sinisa Dj. Mesarovic[2,b], Karlo T. Raic[3,c],
Tatjana Volkov-Husović[3,d]

[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, Franchet d'Esperey str. 86, 11000 Belgrade, Serbia,

[2]Sinisa Dj. Mesarovic, School of Mechanical & Materials Engineering, Washington State University, PO Box 642920, Pullman, Washington 99164-2920, USA

[3]Faculty of Technology and Metallurgy, Karnegieva 4, 11000 Belgrade, Serbia

[a]m.mihailovic@itnms.ac.yu, [b]mesarovic@mme.wsu.edu, [c]karlo@tmf.bg.ac.yu, [d]tatjana@tmf.bg.ac.yu

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Abstract. Wetting phenomenon is quite complex in real systems obtained during metal/ceramic joining. Active metal brazing, one of the most effective metal to ceramic joining methods, is strongly influenced by the effect of surface roughness, encompassing several scales of magnitude. The largest surface irregularity (e.g. one micrometer) is grain boundary groove (GBG), which is developed at the surface of polycrystalline material, at the micro-scale level, wherever a boundary intersecting an interface between a solid and another phase. Besides the diffusivity at the interface and into the bulk, the mass transfer around the GBG of the ceramic surface will also be one of the rate controlling mechanisms. GBG diffusion can not be treated separately from the surface kinetics, on the contrary – they enter the rate equation together. In that sense, the effective diffusivity coefficient will be introduced, using Thiele modulus (MT) in determining the complex diffusion mechanism around the grooves. Developing the original model for wetting, a critical stage of joining process, encompassing the surface roughness and wetting properties of the metal braze, will enable rational design of the metal/ceramic joining process.

Introduction

Metal–ceramic joining is the essential step in obtaining materials in which the combined properties of metal and ceramic layers are desired. Among the joining methods, the active metal brazing is one of the most effective. In the process of active metal brazing [1], a quantity of a liquid metallic alloy containing an active component is introduced at the interface between a metal and a ceramic to promote the wetting. Besides the wetting properties of the metal braze, the surface roughness must also be taken into consideration, having in mind it's extending over several length scales. On the micro-scale, the process is controlled by bulk and interface diffusivity, as well as by the mass transfer around the grain boundary grooves of the ceramic surface.

The ensuing chemical reaction creates a bonding layer, e.g. metal oxide or hydride [2-4]. Mechanical properties of the resulting metal-ceramic interface strongly depend on the thickness, uniformity and porosity of the bonding layer [5, 6], which, in turn, is the result of non-homogeneous chemical transformation that starts at the ceramic surface and propagates into the liquid metal. Diffusion and reaction layers mainly grow into metal because atomic diffusion is much easier in metals than in ceramics.

The initial wetting of the ceramic surface by a liquid metal is followed by reactive spreading. This process is characterized by the following:

- Owing to the capillary forces [6], the leading edge of the liquid droplet develops a ridge (Fig. 1b). While these forces are small, the process takes place above the melting temperature of the metal, so that the mobility is high and the diffusive transport through both, the liquid and the interface is fast enough to accommodate creation of ridges [7].

- The reaction rates for creation of the bonding product and the diffusion of the active metal are usually fast enough to enable simultaneous creation of the bonding layer during the spreading process (Fig. 1b) [8].

- Surface roughness complicates the process. Deep grain boundary grooves may result in the final porosity of the interface between ceramic and the bonding layer and certainly affect the rate of the overall joining process (Fig. 1c). Surface roughness and chemical impurities are often cited as the cause of the experimentally observed hysteresis, i.e., different equilibrium contact angles for advancing and retreating fronts.

- The formation of the thin bonding layer, results in the intrinsic stresses in the layer and in the substrate [8]. The stresses and inhomogeneities in the layer then drive diffusion, resulting in the non-homogeneous growth.
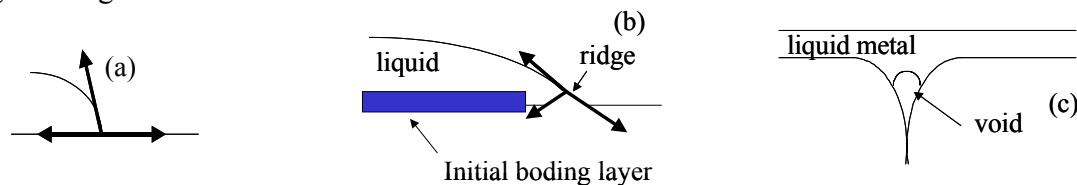

Fig. 1. (a) The vertical component of the liquid-gas surface tension is equilibrated by elastic stresses in the substrate. (b) Capillary forces during reactive spreading with simultaneous formation of the bonding product. The ridge is formed by material diffusion and convection through the liquid and through the interface. (c) Initial void during the wetting of the grain boundary groove.

Subsequent chemical reaction between the ceramic and the active metal takes place under controlled temperature and in the environment with controlled chemistry. The local rate of chemical reaction is controlled by diffusion of the active component. Experiments indicate that the global (average) rate is strongly affected by surface roughness and wetting properties of the liquid metal – ceramic interface (i.e., interface energies) [8, 9]. The former can be controlled by surface finishing methods, while the latter depend on the choice of the brazing alloy and can be, to some extent, modified by controlling the chemistry of the environment.

Surface roughness can be characterized over several orders of magnitude of length. The largest (e.g., one micrometer) surface irregularities are the grain boundary groves, while the smallest are the atomic steps on the surface [10]. Moreover, the nucleation of the bonding product and chemical reaction rates are also dependent of the grain orientation.

Here, the focus is on the effects of surface roughness and wetting properties on the process of non-homogeneous reactive spreading and chemical phase transformation. Chemical properties of the reactants are assumed given. Both, the wetting and subsequent transport-controlled chemical phase transformation with curved propagating interface are complex multiscale phenomena affected by inhomogeneities at different length scales.

Modeling of Phenomena at Grain Boundary Grooves

Liquid metal/ceramic interfaces transport phenomena are of the great importance for metal-ceramics joining techniques. There are three steps usually considered in determining the rate at the interface: wetting of the real ceramic surface, chemical reactions at the interface and diffusion with a moving

interface. The first step will be considered as a micro-wetting process at the grain boundary grooves, and according to the analogy with phenomena on catalytic surfaces [11], here will be presented an original model of this process.

The reaction layer growth is rapid in the first minute, while further increase in the reaction layer growth, after approximately few minutes, is gradual and parabolic with time. Therefore, the growth of product layer can be observed as a two-step process: an initial rapid thickening rate and the second parabolic rate, assumed to be diffusion controlled [12, 13]. Rapid initial layer growth can be related to the substrate surface roughness. On the other hand, slower growth is assisted by capillarity. The capillary mass transport manifests itself by developing a grain boundary groove (GBG) on the surface of a polycrystalline material, wherever a boundary intersects an interface between a solid and another phase. Mass transport can involve several mechanisms: interfacial diffusion, volume diffusion on either side of the interface, and, interfacial reaction (solution-precipitation). Depending on the physical characteristics of the system and the groove size, one of these mechanisms will control the rate, resulting in characteristic groove shapes and growth kinetics [7, 14].

The rate of reaction for the solid ceramic substrate/liquid metal sample may depend on:
(1) Surface kinetics, which may change with developing of the grain boundary grooves,
(2) Grain boundary groove (GBG) resistance, which sets up internal concentration gradients. The effects of volume and surface diffusion on groove development are given in ref. [7, 14],
(3) Interface ΔT or temperature gradient at the liquid metal/solid ceramics interface. This is caused by heat release or absorption during reaction, and,
(4) Film diffusion resistance or concentration gradients across the liquid metal film.

In the presence of GBG, its resistance must be taken into consideration. Surface kinetics and GBG diffusion cannot be treated as steps in series, they enter the rate equation together. When treating interaction of heat and mass transfer resistances, the rate for surface kinetics will be expressed using first order of reaction. Also, the characteristic size will be chosen based on flat plate example. As a characteristic size, the ratio between the volume of ceramic sample and specimen's exterior surface, L, will be taken. For a flat plate case, the L becomes:

$$L = \text{(volume of sample)/(exterior surface)} = \text{thickness/2}$$

So, for the 1st order reaction on a flat plate specimen, the rate of reaction is expressed through the equation:

$$-r_A''' = k'''C_{As}\varepsilon , \tag{1}$$

Here ε is the effectiveness factor, which value varies between 0 and 1, and which accounts for the GBG diffusion resistance. Effectiveness factor is equal to 1 for the case of no diffusion resistance, while k and C have their usual meaning in kinetics equation.

ε= (actual reaction rate within GBG)/(rate if not slower by GBG diffusion),
The effectiveness factor expression for the flat plate case is:

$$\varepsilon = (\tanh M_T)/M_T \tag{2}$$

where M_T is Thiele modulus, useful for behaviour predicting when kinetic information is known.

$$M_T = L\sqrt{\frac{k'''}{D_{eff}}} \tag{3}$$

D_{eff} is the effective diffusion coefficient in porous solids [m^3 liquid (metal)/$m$solid (ceramic) s], shown in Fig.2. Corresponding measures for δ_1 (~10 μm), l (~50 μm) and L (~950 nm) are taken from [14].
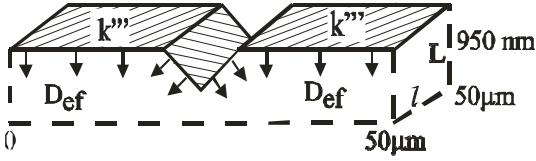
Fig. 2. Unit system of a single GBG

Effectiveness factor, ε is the measure how much the reaction rate is lower because of the resistance to groove diffusion. It is dependent on Thiele modulus, M_T. So, the relationship between the effectiveness factor and Thiele modulus, with corresponding regime limits, are presented in Fig. 3. The "effective diffusivity" must be measured experimentally; it depends generally on concentration of active species, temperature and on the groove structure. The actual mechanism for diffusion in grooves is complex, since the groove dimensions may be smaller than the mean path of diffusing molecules.
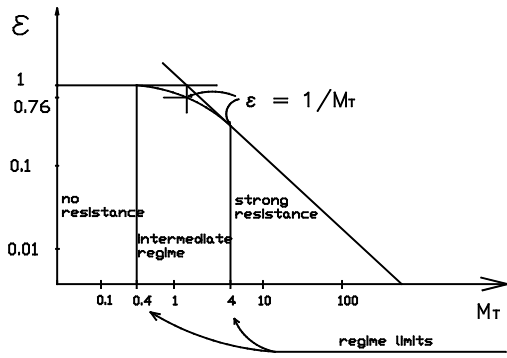

Fig. 3. Schematic presentation of effectiveness factor, ε, dependence on Thiele modulus, M_T
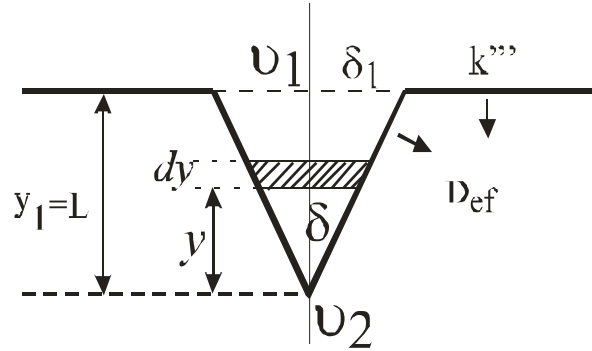

Fig. 4 Schematic detail of a triangular GBG

To evaluate how GBG diffusion influences the rate, the Thiele modulus must be determined, and based on it, ε could be found from the Fig. 3 [11]. Inserting ε into the rate equation (1), it could be determined to what extent the GBG diffusion resistance slows the reaction rate. There is:
- *no GBG resistance* when: $M_T < 0.4$, here: $\varepsilon = 1$ and $-r_A''' = k'''C_{As}$, diffusing liquid metal molecules go through the grain boundary groove with no difficulty;
- *strong GBG diffusion effects* when: $M_T > 4$, the liquid metal molecules concentration at GBG center is equal to zero;
- intermediate regime exists when M_T is between 0.4 and 4. Then: $\varepsilon = 1/M_T$, and

$$-r_A''' = [(k''' \, D_{eff})^{1/2} \, C_{As}]/L \qquad (4)$$

The existence of strong GBG diffusion effects can be determined by calculating M_T if D_{eff} is known.

Let assume that the size, δ_1 of a triangular GBG ("fin"), Fig.4, and the excess concentration at the base, $\vartheta_1 = C_{A(lq)} - C_{A(S)}$ are given.

Than, for the change of concentration, the differential equation (5) can be proposed:

$$\frac{d^2\vartheta}{dz^2} + \frac{1}{z}\frac{d\vartheta}{dz} - \frac{1}{z}\vartheta = 0 \qquad (5)$$

where $z = \sqrt{\dfrac{k'''}{D_{ef}}} \dfrac{y}{L\sin\varphi}$ is a new variable, k''' is the surface chemical rate constant that determine the surface mass transport ($k''' \ll k_m$) and k_m is mass transfer coefficient of the fin surface. The boundary

condition (6) for the quantity of mass dissipated to the surrounding grains from the element dy is applied to the Eq. (5).

$$d[D_{ef} f (d\vartheta/dy)] = k_m u \vartheta dy' \qquad (6)$$

Here: $f = 2lytan\varphi$ is the cross-section area of a fin, $u = 2l$ is the perimeter of the fin at the distance y, and, $dy' = dy/cos\varphi$. Finally, the modelling result is the solution of the modified Bessel equation for the current concentration along the groove (7), for the concentration at the tip of the groove (8) and for the net quantity of mass dissipated to the surrounding grains (9) are:

$$\vartheta = \vartheta_1 \left[\frac{I_0(2\sqrt{z})}{I_0(2\sqrt{z_1})} \right] \quad (7), \qquad \vartheta_2 = \vartheta_1 \left[\frac{1}{I_0(2\sqrt{z_1})} \right] \quad (8) \text{ and } \quad m = \sqrt{\frac{k'''D_{ef}}{z_1}} \frac{l\delta_1}{L\sin\varphi} \vartheta_1 \left[\frac{I_1(2\sqrt{z_1})}{I_0(2\sqrt{z_1})} \right] \qquad (9)$$

where I_1 and I_0 are modified Bessel functions.

Diffusion in Liquid Metal at the Interface

In explanation the action of polycrystalline surface, it is thought that molecules of liquid metal are somehow changed, energized, or affected to form intermediates in the region close to the surface. In one theory, the formed intermediate is an association of a reactant molecule with a region of the surface, in another theory molecules are thought to move through liquid metal towards the surface, where surface forces influencing them. In a third theory it is thought that an active complex, a free radical, is formed at the solid surface, than moved back into the liquid metal stream, triggering chain reaction with fresh molecules. In contrast with two theories which consider the reaction to occur in the vicinity of the surface, this theory considers the surface as a generator of free radicals, while the reaction occurs in the main stream of liquid metal [11].
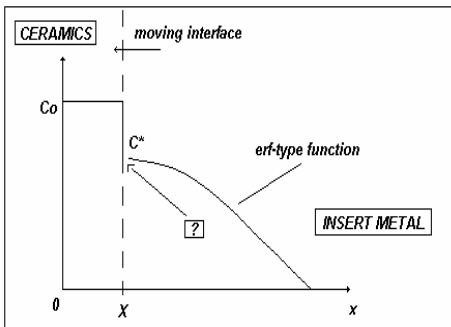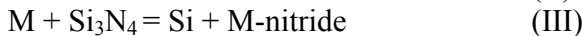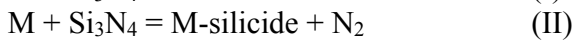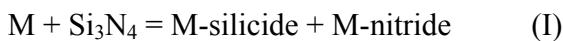

Fig. 5. Diffusion with a moving interface

In order to obtain the knowledge on reactivity, it is very important to respect the changes of the standard free energy for the formation of nitrides, carbides and oxides against temperature. From these thermodynamic data, when metal is placed in contact with nitride, carbide or oxide ceramics, it is possible to predict whether the metal can decompose the ceramics to form its nitride, carbide or oxide.

For example, the chemical reaction occurring between silicon nitride and metal (M), follows one of the formulas:

$M + Si_3N_4 = M\text{-silicide} + M\text{-nitride}$ (I)
$M + Si_3N_4 = M\text{-silicide} + N_2$ (II)
$M + Si_3N_4 = Si + M\text{-nitride}$ (III)

Free Si and N atoms diffuse in the reaction layer towards the melted inserted layer (e.g. Cu and Ag-Cu based alloys) and react with active metals (Ti, Cr). Finally, the rest of free Si and N atoms form Si_3N_4.

So, it may be concluded that the reaction layer growth from the melted inserted layer is diffusion controlled by Si_3N_4 [9]

This process involve diffusion steps in conjunction with chemical reactions at solid/liquid boundary The consequence 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.5 . The moving phase boundary is at x=X, and at this boundary the Co and $C^*=C(X, t)$, represents the equilibrium Si_3N_4 concentration, that coexists in ceramics and inserted metal, respectively, at the temperature under consideration.

In inserted metal phase, the Fick's second law applies: $dC/dt = D \, d^2C/dx^2$, x > X, where C is the Si_3N_4 concentration during transient diffusion, D is the diffusion coefficient of Si_3N_4 in inserted melted metal , assumed to be independent of composition. The following condition is that the concentration on either side of the interface is related by an equilibrium expression of the form: Co = KC*, where K is partition ratio between the phases. The material balance at the interface takes the form:

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

Eq. 10 describes the locus of X with time. Relationship between Co and C*:

$$\pi^{0.5}[C^*/(C^*-Co)] = \beta \, \exp\beta^2 \, erf\beta \quad (11) \qquad \text{when } X = 2\beta(2D)^{0.5} \qquad (12)$$

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

Summary

The wetting phenomena at metal/ceramic interface during active metal brazing and reaction layer formation are presented as an original model, in the light of surface kinetics affected by the grain boundary groove (GBG) diffusion. Chemical reactions at the interface and diffusion with a moving interface are considered as a part of the original theory of reaction layer growth. Based on it, the diffusion coefficient of the rate controlling molecules can be determined.

References

[1] Pask, J.A. (1987) Am. Ceram. Soc. Bull. 66, p. 1587.
[2] Klomp, J.T. (1989) In Designing interfaces for Technological Applications. Ed. By Peteves, S.D., Elsevier, London, p. 77.
[3] Mattox, D.M. & Smith, H.D. (1985) Role of manganese in the metallization of high alumina ceramics. Am. Ceram. Soc. Bull. 64, p. 1363.
[4] Bondley, R.J. (1947) Electronics 20, p. 97.
[5] G. Elssner and G. Petzow: ISIJ Int., Vo.l 30 (1990) p.1011
[6] Spaepen, F. (2000) Interfaces and stresses in thin films. Acta mater. 48, p. 31
[7] E. Saiz, R.M. Cannon and A.P.Tomsia: Acta mater. Vol.47 (1999)p.4209
[8] E. Saiz, R.M. Cannon and A.P.Tomsia: Acta mater. 48 (2000), p.4449-4462
[9] Y. Nakao, K. Nishimoto and K. Saida: ISIJ Int., Vol. 30 (1990) p.1142
[10] M. Mihailovic, T. Volkov-Husovic, K.T. Raic, Advances in Science and Technology, Vol.45, (2006) pp.1526-1531
[11] O.Levenspiel: Chemical Reaction Engineering, ed. John Wiley&Sons, Inc. 1972
[12] K.T.Raic, Advances in Science and Technology, 32, 2003, Part C, Section H: Ceramics Joining, 725-733, Techna, Faenza
[13] K.T. Raic: Ceramics International, Vol. 26 (2000) p.19
[14] J. Schöllhammer et al.: Z.Metallkd. 90 (1999) 9, p.687