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Physical Chemistry of Ceramic-Metal Interface Formation [†]

Julius C. SCHUSTER*

Abstract

The formation and microstructure of the interface in ceramic-metal systems is discussed. Surface phenomena control wetting in non reactive systems as well as the transitions from non reactive to reactive systems. For reactive systems phase diagrams predict the final equilibrium state. However, the intermediate stage, during which the diffusion path is built up and exists as a series of steady states, is controlled by diffusion kinetics, which are taken into account to understand the details of the morphology of the reaction zone observed in various SiC-metal systems.

KEY WORDS: [Ceramic-metal systems] [Non reactive systems] [Reactive systems] [Interface formation] [Wetting] [Interfacial reactions] [Phase equilibria] [Diffusion path]

1. Introduction

Bonding of dissimilar materials, such as ceramics to metals, require the formation of an interface. Mass transfer must occur in order to achieve the transition from two surfaces in contact at their asperities to a continuous interface. In non reactive ceramic-metal systems mass transfer will be only along the ceramic surface becoming an interface. In reactive systems mass transfer occurs from the ceramic to the metal and vice versa across an interfacial zone being formed by the reaction. The mass transfer mechanisms of solid state joining processes such as friction welding, diffusion bonding, or reaction bonding, are plastic deformation by yield and creep, as well as bulk, surface, and/or interface diffusion. Liquid phase diffusion and spreading are the mass transfer mechanisms in the liquid state joining processes such as (active metal) brazing, eutectic bonding, or fusion welding. The driving forces for these mechanisms of interface formation are (1) the external pressure applied during bonding, (2) the reduction of the total surface and interface energy of the system due to wetting, and (3) the reduction of the bulk Gibbs energy of the system due to chemical reactions. While the external pressure applied is essential in the first stages of interface formation ¹⁾, only the latter two driving forces can cause permanent bonding across the interface. Thus, understanding of the phenomena of

wetting as well as phase formation contributes greatly to predict interface behavior of ceramic-metal joints, coatings, and composites.

2. Wetting in Non Reactive Systems

In non reactive systems the bonding energy, or work of adhesion (W_{ad}), is due to wetting. Thus $W_{ad} = W_{wetting}$. In ceramic-metal systems wetting occurs due to electron transfer from the metal into the valence band of the ceramic ²⁾. This is possible, since even in the undoped, pure ceramic at finite temperatures (T) some electrons are promoted to the conduction band, leaving an equal concentration of holes (c) in the valence band:

$$c = c_0 \cdot \exp(E_g/2kT) \quad (eq.1)$$

(with $c_0 = c$ at $T = 0K$, and E_g the band gap energy)

The amount of electron transfer, and thus W_{ad} , depends on this density of empty states available at the valence band of the ceramic, as well as on the amount of electrons available from the metal, characterized by n_{ws} , the electron density at the Wigner-Seitz cell of the metal. Short of putting forward an equation relating W_{ad} to n_{ws} or E_g , in a series of papers Li showed ²⁻⁴⁾, that indeed W_{ad} scales linearly with n_{ws} of the corresponding metal (systems Al_2O_3 /non reactive metals ²⁾, systems TiC /non reactive

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metals³). Furthermore, Li demonstrated a linear decrease of W_{ad} with increasing E_g of non reactive ceramics (systems ceramic/tin¹, systems ceramic/copper³).

Combining the Dupre equation, which defines the work of adhesion being equal to the surface and interface energy difference occurring upon interface formation,

$$W_{ad} = \gamma_c + \gamma_m - \gamma_{cm} \quad (\text{eq.2})$$

(γ_c surface energy of the ceramic, γ_m surface energy of the metal, γ_{cm} ceramic-metal interface energy)

with the equilibrium condition

$$\gamma_c - \gamma_{cm} = \gamma_m \cdot \cos \theta \quad (\text{eq.3})$$

yields the Young-Dupre equation

$$W_{ad} / \gamma_m = 1 + \cos \theta \quad (\text{eq.4})$$

linking the wetting angle θ to W_{ad} . Wetting ($\theta < 90^\circ$) or non wetting ($\theta > 90^\circ$) in non reactive systems can be predicted from data on W_{ad} accessible from either E_g data of the ceramic or E_g data of the ceramic using the correlations reported by Li, combined with data on γ_m available with reasonable reliability from literature⁵.

3. Transition Non Reactive to Reactive System

While earlier models for wetting, based on correlating W_{ad} with the Gibbs energy of compound formation^{6,7}, had great difficulties in accounting for the increase of W_{ad} with temperature, the model of Li²⁻⁴) predicts without ad hoc assumptions, that increasing the temperature will increase W_{ad} due to the increasing number of holes available in the valence band of the ceramic (eq.1). Thus, there must be a temperature, where this increase, and the simultaneous decrease of γ_m ⁵) will result in complete wetting ($\theta=0^\circ$) yielding $W_{ad} = 2\gamma_m$.

On the other hand, as can be seen from eq.2, a positive temperature coefficient of dW_{ad}/dT requires γ_{cm} to decrease more rapidly with increasing temperature than γ_c and γ_m combined. Again, at a certain temperature γ_{cm} will be zero, yielding $W_{ad} = \gamma_c + \gamma_m$. With $\gamma_{cm}=0$, the interface becomes unstable and reaction will occur at this temperature. Unfortunately, at present there is no correlation proposed, to predict accurately the temperature coefficient of the interfacial energy, to anticipate this temperature.

4. Reactive Systems

The occurrence of chemical reactions at the ceramic-metal interface increases bonding beyond the contribution due to wetting:

$$W_{ad} = W_{\text{reaction}} + W_{\text{wetting}}$$

The concomitant breakdown of the original interface and formation of new phases creates an interfacial reaction zone consisting of one or more reaction product layers and the resulting new interfaces confining them. Practical joining processes have a time scale of the same order of magnitude as the kinetics of these reactions. Thus, not only the energetics of the interfacial reactions, but also their mechanisms need to be discussed.

4.1. Thermodynamics of Reactive Systems

Like any other chemical reaction, the reaction at a ceramic-metal interface is driven by the lowering of the Gibbs energy due to formation of (solid) solutions or of new phases. For example, in a system A (a metal) + BC (a ceramic) the reaction $3A + 2BC = AB_2 + 2AC$ will proceed to the right hand side, if (for a given temperature and pressure) the Gibbs energy change is negative:

$$\Delta G = \Delta G_{\text{o}}^{AB_2} + 2\Delta G_{\text{o}}^{AC} - 3\Delta G_{\text{o}}^A - 2\Delta G_{\text{o}}^{BC} + RT \ln \left\{ (a_{AB_2} \cdot a_{AC})^2 / (a_A^3 \cdot a_{BC})^2 \right\} < 0$$

(with ΔG_{o}^i = Standard Gibbs energy of formation of phase i, R = gas constant, T = temperature, a_i = activity of component i)

Reaction will continue until one of the reactants is practically completely consumed and its activity becomes so small, that ΔG of the reaction becomes zero. Alternatively, if one of the reaction products is a gas, its partial pressure (usually taken to be equal with the activity) may become large enough to stop further reaction. Calculation of such equilibria requires not only data on the Gibbs energy of formation for all phases involved, and the variation of ΔG_{o}^i within the temperature and homogeneity range of that phase, but most obvious and still not trivial, knowledge on the existence of it. Having satisfied these requirements, all phase equilibria of a given system can easily be computed. Software automating this procedure using a variety of strategies⁸ is nowadays readily available.

The graphical representation of phase equilibria derived from calculations or observed in experiments indicates

coexisting phases by connecting tie lines. The phases stable upon the completion of the reaction are determined by identifying the phase field of the overall composition of the ceramic-metal couple reacting. The relative amounts of these phases can be calculated using the lever rule. Phase diagrams for systems comprising binary oxide ceramics or non oxide ceramics such as Si_3N_4 , SiC , AlN , Al_4C_3 , BN , or B_4C with metals have been extensively investigated and reported in the literature 9-12).

The contribution to interfacial bonding due to chemical reaction, W_{reaction} , is equal to the Gibbs energy change upon formation of one monolayer of reaction product at the interface:

$$W_{\text{reaction}} = -n \cdot \Delta G$$

(n= number of moles of reaction product at the interface)

Upon joining, the bonding strength initially increases with increasing bonding area and with the formation of the first monolayer of reaction product. However, the phases formed in ceramic-metal joints are generally brittle, and thus, as the reaction product layers become thicker, residual stresses due to thermal expansion mismatch are not absorbed by ductile deformation, but rather reduce the bonding strength 13). Thus, in order to optimize the bond strength, the thickness of the reaction product zone(s) has to be controlled carefully. To achieve this, and because of practicability of joining processes in general, the interfacial reaction frequently is stopped before either of the two materials joined is completely consumed, and thus before equilibrium, as described by the phase diagram, is reached.

4.2. Kinetics of Phase Formation

For the intermediate stage, after reaction has started and before it is completed by reaching equilibrium, the metal-ceramic system can be viewed as a diffusion couple. The composition, number, and sequence of phases formed during this stage depend on the reaction path the atoms are travelling along. After an initial period (the origin and consequences of it will be discussed below) local equilibrium between each pair of neighboring phases in the diffusion zone is established. Though not truly equilibrium phases of the ceramic-metal system under consideration, these phases form a sequence of steady states and coexist as long as the influx of reactants and the formation of reaction products continues. Thus, like any coexisting phases, each pair of phases sharing an interface must be connected by tie lines on the isotherm of the corresponding equilibrium diagram. The complete sequence of these tie

lines across the isotherm from the pure ceramic to the pure metal, the diffusion path, represents the average composition in planes parallel to the original interface throughout the entire diffusion zone 14).

Thus, knowing from the isotherm the phases occurring, as well as the tie lines connecting or separating them, reduces, together with the requirement of mass conservation (necessitating the diffusion path to cross at least once the straight composition line between the end members of the diffusion couple), the possibilities the diffusion path can take. However, without additional kinetic data, only in special cases can the number of possibilities be reduced to just one and thus predictable diffusion path. Such special cases occur in systems with simple "replacement" type reactions like $\text{A} + \text{BC} = \text{AB} + \text{C}$, if a diffusion layer sequence of A/C/AB/BC can be ruled out, because C is immobile. Then the only possible sequence remaining is A/AB/C/BC . Examples are the systems of SiC with group VIII metals 11), where carbon rests immobilized next to SiC , because otherwise it would have to diffuse up its own activity gradient, which is not allowed by thermodynamics. For more complex ceramic-metal reactive interfaces a helpful guideline seems to be the general rule, that the diffusion path starts in the single phase region of the metallic end member in the direction of the faster diffusing component of the ceramic 14). Assuming carbon to diffuse via an interstitial mechanism, and silicon to diffuse via an vacancy type mechanism, carbon is expected to be the faster diffusing component of SiC . According to the rule, the diffusion path in the more complex systems of SiC with group IV, V, and VI metals is expected to start on the metal end into the direction of the metal carbide. This has been shown to occur for the systems SiC/Ti 15,16), SiC/V 15,17), SiC/Nb 18-21), SiC/Cr 15,17,22), and SiC/Mo 15,23-26). Though this seems to corroborate the above mentioned general rule, the elucidation of the complete diffusion path remains a task to be done from the experimentally observed microstructure of the diffusion zone. Thus, the famous relationship between the diffusion path and the microstructure of the diffusion zone 27) still more often serves to establish the diffusion path, than to predict the microstructure from a known diffusion path.

One of the most notable phenomena in ceramic-metal reaction zones is the occurrence of duplex phase layers, consisting of one phase with precipitates of another, or of a zone with a corrugated interface between two phases. This can occur because metal-ceramic diffusion couples are ternary or higher order systems. While the Gibbs phase rule limits binary diffusion couples to single phase zones

and flat interfaces, the additional freedom due to the third component allows in ternary systems the occurrence of two phase zones and corrugated interfaces. For simple displacement reactions of the type $A + BC = AB + C$, yielding an interface structure $A/AB/C/BC$, a kinetic argument, based on the relative fluxes of A through AB (J_A) and B through C (J_B), predicts the formation of a flat or corrugated interface between AB and C layers²⁸. A presupposed wavy interface between these two phases will develop into a flat interface for $J_B > J_A$, because the supply of A will be rate limiting, and thus protruding tips of AB will be leveled out. If however $J_A > J_B$, the waviness will be magnified by even accelerated growth of the protruding AB tips and a corrugated interface develops, which eventually cannot be treated as one-dimensional diffusion problem anymore. Precipitates may occur due to local fluctuations such as grain boundaries, grain orientations, and grain sizes causing local supersaturation. In SiC-metal systems two phase zones occur, if due to the mass balance requirement, carbon has to interdiffuse uphill, and thus for that section of the diffusion path the metal becomes the faster diffusing species. Best investigated examples are the systems SiC/Ti^{15,16} and SiC/Mo^{15,23-26}. Kao and Chang²⁹ have extended this argument to the case $J_A \gg J_B$. For this case local fluctuations are all leveled out, and the flux of B is insufficient to react with all incoming A. Thus, the remaining A diffuses through the layer of C, where it again starts to react with B to form a new band of AB creating newly a (B depleted) zone C. The original zone AB stops growing because no fresh B arrives anymore. Ongoing diffusion of A generates thus multiple, flat interface bands of equal thickness. With time only the number of these bands increase. Such bands have been observed in the systems SiC/Fe³⁰, SiC/Ni³⁰, and SiC/Pt³¹, where carbon is completely immobilized and thus $J_{\text{metal}} \gg J_{\text{carbon}}$.

While the discussion of kinetics up to now has centered on diffusion, it should be kept in mind, that layer growth, defined as the advance of the interface normal to the interfacial plane, consists not only of material transport from the interior of each phase to the interface, but also of the actual reaction steps occurring at the interface. Thus the growth rate (k) might be interpreted as "total growth impedance"

$$1/k = \delta/D + 1/k_i$$

(with δ the diffusion layer thickness, D the diffusion coefficient, k_i the reaction rate of the interfacial reaction steps)

At steady state, $\delta/D \gg 1/k_i$, and diffusion should be rate limiting. However at the very beginning of the reaction, when δ is very small, still close to zero, we have $\delta/D \ll 1/k_i$ and thus the interface reaction steps will be rate limiting. Integration of the interface reaction controlled growth rate law yields growth proportional to time (t), while integration of diffusion controlled growth rate yields growth proportional to $t^{1/2}$. Thus initial growth control by interface reaction has two consequences: (1) Growth kinetics follow linear-parabolic rather than simple $t^{1/2}$ laws. (2) The formation of phases is sequential, that is new phases appear only after other phases have reached a critical thickness. Both phenomena are observed in carefully executed experiments such as recently done in the system SiC/Ti³². The same experiments also reveal the change of growth rate upon the formation of an additional reaction layer. The abrupt change of slope in a thickness² versus time plot observed³² indicate contributions to growth control by both, the original as well as the newly formed layer¹³.

5. Conclusions

The physicochemical aspects of the initial step (wetting) as well as final state (equilibrium) of interface formation in ceramic-metal systems are well understood. With the aid of existing material data such as n_{ws} and E_g , or phase diagrams respectively, the behavior of the ceramic-metal system in these two regimes can be accurately predicted. For the intermediate stage, which is diffusion controlled, the principles are clear, but more data on individual systems are needed for accurate predictions.

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