

From Technology to the Science of Glass/Metal and Ceramic/Metal Sealing

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A tutorial overview of the scientific aspects of our current understanding of the conditions under which two materials (ceramic/ceramic, metal/metal, and ceramic/metal) can be joined to form strong and vacuum-tight seals is presented. Chemical bonding and favorable stress patterns in the interfacial zone are requirements for all joints. The basic principles involved in playing a role to reach this goal are shown to be the same for all joints regardless of their complexity. Discussions are presented on the nature of the chemical requirements and how they are achieved. These include formation of an intimate interface and presence of a stable chemical thermodynamic equilibrium at the interface. The equal need of a science transfer, as well as a technology transfer, is presented.

Through technology we have learned what to do to obtain seals or joints between dissimilar materials that are strong and vacuum tight.^{1,2} Because of many experimental studies we are developing an understanding of what is necessary and why. The present paper is a tutorial overview of the subject of joining of materials based on the current understanding as to how and why materials can be joined, with the exclusion of mechanical joints. The intention is to show that the principles and basic requirements are the same for

all joints regardless of their complexity. Hence, the title. Figure 1 presents the triumvirate of science, technology, and engineering. A great deal has been said about "technology transfer" to engineering but equally important, necessary, and indispensable is the achievement of an appropriate "science transfer" to technology and engineering. In this discussion the understanding of why certain observed events occur from a fundamental viewpoint constitutes the scientific development of the subject.

Requirements for Strong Assemblies

The basic requirements for strong assemblies are chemical bonding and minimal stress differentials at the interfaces with favorable stress gradients in the interfacial zones, as stated in Fig. 2. The importance of matching the coefficients of thermal expansion is well recognized.³⁻⁵ However, the dependence of stress gradients in the interfacial zones on composition gradients and microstructures that form during the making of the seals is not as well recognized.

Let us first explore the general question

of how chemical bonding is achieved at interfaces, as outlined in Fig. 3. It must be emphasized that the conclusions presented are based on deductive analysis of extensive experimental data on many systems with basic thermodynamic reasoning since we do not yet have experimental capabilities of observing electronic structures which characterize chemical bonding, specifically at interfaces. On this basis, it can be generalized and followed as a theme that any two phases can form an acceptable assembly with a chemical bond if they are at stable chemical thermodynamic equilibrium at their interface whether or not the bulk phases are at equilibrium, providing they are also compatible physically.

In joining, the formation of an intimate or true interface is the first requirement. Such an interface is one in which atomic contact exists either with van der Waals attractive forces or an electronic structure across the interface, i.e. chemical bond. Epitaxial compatibility would be expected to play a role in both cases. A solid/solid interface in which at least one of the surfaces is a metal can be formed by pressure at an elevated temperature, resulting in adjustment of irregularities due to localized deformation. An intimate solid/liquid interface can be formed and recognized easily if the liquid wets or spreads, thereby penetrating irregularities at the solid surface. The second, more critical requirement in all cases is the presence of a stable chemical thermodynamic equilibrium at the interface. In

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*It is a pleasure to have an opportunity to present the Arthur L. Friedberg Lecture. Art was a student at University of Illinois during my first years of teaching, a colleague, and a friend. From his viewpoint the subject of the Lecture is appropriate. Art was always interested in the application of science to technology, particularly in the discipline of porcelain enamels which is one of the earliest areas of technological studies on glass/metal interface reactions and bonding.

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FROM TECHNOLOGY TO THE SCIENCE OF
GLASS AND CERAMIC/METAL BONDING

SCIENCE - WHY - UNDERSTANDING

SYSTEMIZING FACTS, PRINCIPLES AND METHODS
ESTABLISHMENT OF VERIFIABLE GENERAL LAWS
DETERMINATION OF PRINCIPLES AND PHENOMENA

TECHNOLOGY - WHAT - APPLICATION

SCIENCE APPLIED TO TECHNICAL METHOD OF
ACHIEVING A PRACTICAL PURPOSE
MEANS EMPLOYED TO DEVELOP OBJECTS NECESSARY
FOR HUMAN SUSTENANCE AND COMFORT

ENGINEERING - HOW - PROCESSING

PRODUCTION IN QUANTITY BY UTILIZATION OF
SCIENCE AND TECHNOLOGY
UTILIZATION OF PRODUCTS OF EARTH.
PROPERTIES OF MATTER FOR SUPPLYING HUMAN
NEEDS

Fig. 1. Relationship and interplay of science, technology, and engineering.

STRONG GLASS/METAL AND CERAMIC/METAL
ASSEMBLIES AS NORMALLY EVALUATED

1) MAXIMUM STRENGTH DEPENDENT ON
DEVELOPMENT OF CHEMICAL BONDING AT ALL
INTERFACES

2) CONSIDERATION OF PHYSICAL FACTORS -
STRESS AND STRESS GRADIENTS - AS
AFFECTED BY PROPERTIES AND CHEMICAL
REACTIONS

- MATCHING OF COEFFICIENTS OF THERMAL
EXPANSIONS
- STRESS GRADIENTS DETERMINED BY
COMPOSITION GRADIENTS AND INTERFACIAL
ZONE MICROSTRUCTURES

Fig. 2. Fundamental requirements for strong and impermeable glass/metal and ceramic/metal assemblies.

HOW IS CHEMICAL BONDING ACHIEVED?

(1) FORMATION OF AN INTIMATE, ATOMIC
CONTACT INTERFACE

- SOLID/SOLID - PRESSURE, RESULTING IN
PHYSICAL ADJUSTMENT AT INTERFACE BY
LOCALIZED DEFORMATION
- SOLID/LIQUID - WETTING, PENETRATION
OF IRREGULARITIES
SPREADING BY REACTION OR PRESSURE

(2) REACTION TO REACH CHEMICAL EQUILIBRIUM
AT INTERFACE - SATURATION WITH
COMPATIBLE PHASE

- METAL/METAL AND CERAMIC/CERAMIC
SOLUTION REACTIONS AND SATURATION AT
INTERFACE - DIFFUSION BONDING
- GLASS/METAL AND CERAMIC/METAL
SOLUTION OF OXIDE LAYER ON
PREOXIDIZED METAL
REDOX REACTIONS, SATURATION AT
INTERFACE WITH SUBSTRATE OXIDE
PRODUCT REDOX REACTIONS, FORMATION OF
COMPOUND AT INTERFACE COMPATIBLE WITH
BOTH PHASES

Fig. 3. Major requirements for development of chemical bonding at interfaces.

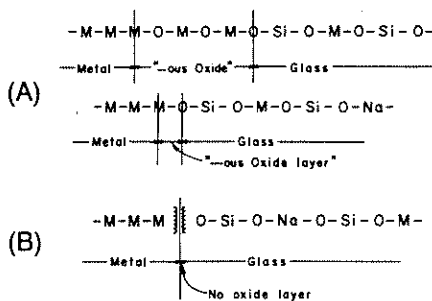


Fig. 4. Schematic of bonding of phases at interfaces: (A) chemical bonding (continuous electronic structure) when glass and metal at interface saturated with metal oxide (MO), and (B) van der Waals bonding (no electronic structure across interface).

practically all cases this requirement is achieved by reactions since invariably they form equilibrium phases. At metal/metal and ceramic/ceramic interfaces either solution or compound formation takes place readily in order to reach the lowest free energy composition because in each case the phases are compatible in the sense that no valence changes occur during reaction. The simplest reaction is the solution of one phase by the other to form an immediate equilibrium saturation at the interface. A continuation of the reaction is associated with diffusion into the bulk. The overall reaction is thus referred to as diffusion bonding.

Glass/metal and ceramic/metal interfaces, however, are not compatible because redox reactions occur at the interface involving an oxidation of the metal and a reduction of a cation in the glass or ceramic.^{1,6} In the case of an oxide phase, the oxygen released by the reduction of the cation forms an oxide with the metal. Saturation of the interface with the oxide and subsequent formation of a molecular or multimolecular layer oxide results in equilibrium and chemical bonding at the interfaces since the oxide layer is compatible with both its metal and the glass or ceramic. Commercially, the necessary compatible oxide layer at the interface is obtained by preoxidizing the metal, which is a redox reaction, before the application of the glass.⁷

These requirements for chemical bonding are schematically shown in Fig. 4. The first line represents a cross section with the presence of an undissolved oxide layer and the adjoining metal and glass interfaces saturated with oxide, resulting in the formation of electronic structures (chemical bonding) across the interfaces. With this structure the assembly would be affected by the physical and thermal properties of the oxide. The second line illustrates a case in which the glass has dissolved all of the oxide except one layer at the interface. The bonding requirements are still fulfilled, but the overall properties of the assembly will not be affected by the presence of a discrete oxide layer but will be by the thicker composition gradient formed by solution/diffusion into the glass. Lastly, the third line

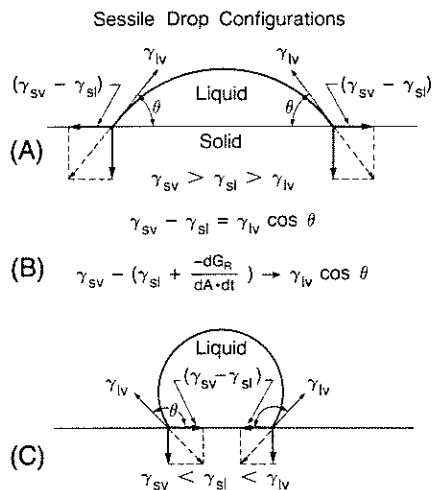


Fig. 5. Sessile drop configurations: (A) wetting and (C) nonwetting. (See text for significance of equations in (B).)

illustrates the case in which the interface is not saturated with the metal oxide. Under this condition the electronic structure across the interface is lost because of a lack of a balance of bond energies with the formation of van der Waals bonding. Separation or cracking along the interface can then occur with the application of stresses.

Wetting and Spreading

Sessile drop experiments with proper interpretation are important because they provide valuable information on the formation of true or intimate interfaces and the existence of reactions which normally may not be recognized and overlooked.⁸ It is thus worthwhile to examine and understand the associated principles.

Sketches of cross-section planes perpendicular to the interfaces and passing through the vertical axes of both wetting and nonwetting sessile drops are shown in Fig. 5. In each case the configuration is determined by the solid rigid phase. Under nonreactive conditions, wetting represented by a steady-state obtuse contact angle, θ , always occurs when $\gamma_{sv} > \gamma_{sl} > \gamma_{lv}$ (γ represents interfacial energy: for solid/vapor as *sv*, solid/liquid as *sl*, and liquid/vapor as *lv*). This configuration is typical of a liquid glass drop on a metal substrate. Also under nonreactive conditions, nonwetting, represented by a steady-state obtuse contact angle, θ , always occurs when $\gamma_{sv} < \gamma_{sl} < \gamma_{lv}$. This configuration is typical of a liquid metal drop on a ceramic or glass substrate. It should be noted that γ_{sl} in both cases is between γ_{sv} and γ_{lv} , i.e., the higher surface energy is reduced in contact with the lower surface energy phase. Wetting is defined as the reduction of γ_{sv} by the liquid, and the driving force for wetting is thus $(\gamma_{sv} - \gamma_{sl})$ which is acting on the periphery of the liquid drop. The resisting force is γ_{lv} since the lowest free energy configuration for the liquid is a sphere. A balance of the horizontal forces gives us a steady-state contact angle and the familiar Young-Dupré equation

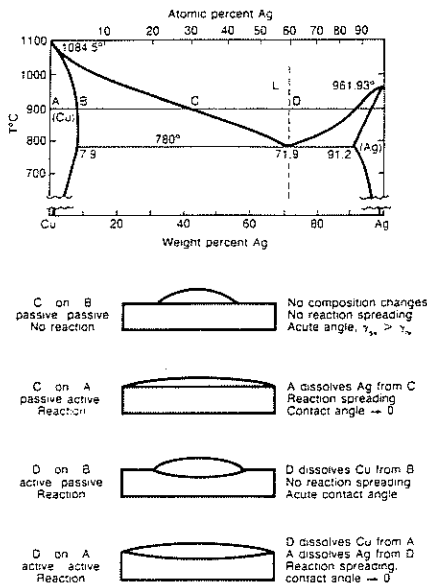


Fig. 6. Stable phase equilibrium diagram for Cu and Ag with sessile drop examples. In all cases $\gamma_{sv} > \gamma_{lv}$. No reaction with C and B. Reaction in other shown cases with B as passive participant and A as active participant. See text.

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (1)$$

In the absence of a reaction, whether stable or metastable chemical equilibrium exists, the driving force for wetting never exceeds γ_{lv} and spreading or extension of the liquid drop does not occur.⁸ Another example of the value of understanding the significance of such relationships follows: if γ_{sv} is known to be greater than γ_{lv} but nonwetting is observed ($\theta > 90^\circ$), then γ_{sl} is greater than γ_{sv} and also γ_{lv} , indicating that a true intimate interface between the solid and liquid in question has not formed due to some unreactive contamination on the solid surface. On the other hand, if γ_{sl} is between γ_{sv} and γ_{lv} , then $\theta < 90^\circ$ and a true interface is present. Furthermore, if $\gamma_{lv} > \gamma_{sv}$ and γ_{sl} is between them, a true interface is also present, but it is technologically unfavorable because the liquid will not wet and penetrate the surface irregularities.

When a reaction occurs, the free energy of reaction per unit interfacial area and unit time enhances the driving force for wetting as indicated by the inequality in Fig. 5 only if the solid is an *active participant*. In a solid-state solution reaction, if only one phase is unsaturated relative to the other, the unsaturated or solvent phase is changing its composition and the solute is not. We can then define the solvent as the active participant and the solute as the passive participant. If both phases are unsaturated relative to each other or they form a compound at the interface, then both phases are active participants. If the driving force for wetting enhanced by a reaction exceeds γ_{lv} , then spreading occurs which can happen either when γ_{sv} is greater or smaller than γ_{lv} . The dynamic stage of movement or

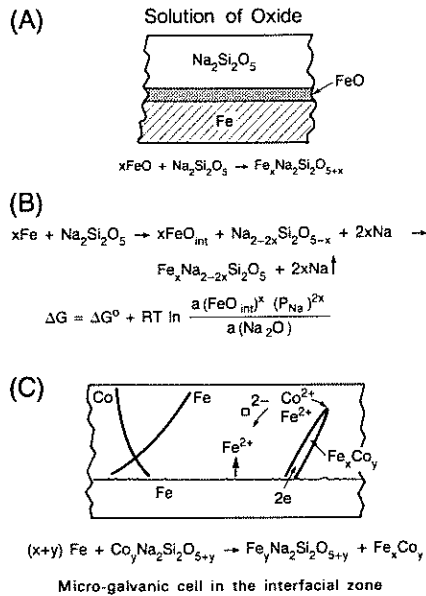


Fig. 7. Schematic cross sections of (A) glass on preoxidized metal with equation representing solution reaction of oxide by glass, (B) two step equation representing redox reaction of glass on metal: formation of metal oxide at interface followed by solution of oxide in glass; and free energy equation for first step, and (C) equation for redox reaction of glass containing CoO with Fe substrate resulting in indicated Co^{2+} and Fe^{2+} gradients—formation of Fe_xCo_y dendrites by microgalvanic cell mechanism with electronic circuit of electrons and negative vacancies. Standard free energies negative except for first step of equation in (B).

spreading stops when the liquid is completely reacted.

It is possible to illustrate the sessile drop behavior under several conditions by use of the phase equilibrium diagram for the Cu-Ag system shown in Fig. 6. If liquid C is placed on solid B at 900°C , an acute angle forms and no reaction occurs since the phases are in stable chemical equilibrium.⁹ However, if liquid C is placed on solid A at 900°C , spreading occurs because the substrate A becomes an active participant in the reaction as it changes its composition toward B. Another example is that of liquid D on solid B at 900°C . Liquid D will dissolve some of the substrate to change to composition C, but no spreading occurs with this reaction because B is a passive participant. However, with liquid D on solid A, spreading occurs since both are active participants as they change to equilibrium compositions C and B. Wetting or spreading occurs in all these cases. An example of diffusion bonding in the solid state is provided by placement of pure Ag in contact with pure Cu below the eutectic temperature under pressure. Stable chemical equilibrium compositions would immediately be attained at the interface by saturation of Cu with Ag and Ag with Cu, and retained since these interface reactions are always faster than

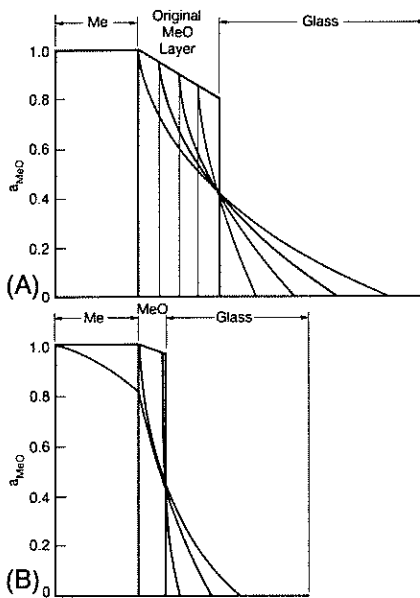


Fig. 8. Schematic showing lengthening activity gradients of MeO in glass with continuing solution of oxide by glass: (A) gradient extension proportional to thickness of oxide; (B) loss of saturation at interface with continued heating beyond complete solution of oxide layer.

the diffusion into the bulk, fulfilling the requirement for chemical bonding at the interface. Similar conditions would be attained at each of the examples described above for this system.

Glass/Metal Sealing

The normal technological procedure of achieving chemical bonding and favorable stress gradients in glass/metal assemblies is to preoxidize the metal and apply the glass as shown in Fig. 7(A). The model system of $\text{Na}_2\text{Si}_2\text{O}_5$ glass and Fe metal is being used to provide examples.¹⁰⁻¹² At temperature the molten glass wets and dissolves the oxide. The glass at the oxide interface immediately becomes saturated because the solution rate of the dissolved oxide into the bulk glass. Chemical bonding is thus realized. The oxide layer also bonds chemically to the metal which is saturated with the oxide, at least at the surfaces. The saturated interfaces and the oxide layer thus have a chemical activity of one for Fe_xO_y , which is a requirement for chemical bonding in this case.

As the dissolved oxide diffuses into the glass a concentration gradient is formed as schematically shown in Fig. 8(A). It can be seen that, as the oxide dissolves, the concentration gradients become more extended, but the equilibrium saturation at the oxide/glass interface and consequently bonding are always maintained because of the faster solution rate. Such an addition of a metal oxide to the glass affects its coefficient of expansion because of an increase of the O/Si ratio and introduction of cations with different de-

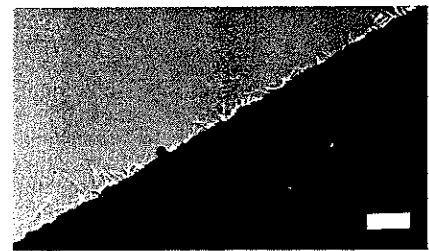


Fig. 9. SEM photograph of cross section of interfacial zone for Cr and glass showing dendritic growth of Cr silicide in the glass at the interface. (bar=50 μm)

grees of covalency. The concentration gradients then are proportional to thermal expansion coefficient gradients which generally result in more favorable stress gradients.¹³ It can be seen that the composition gradients become more extensive with increasing thicknesses of starting oxide. It is thus evident that many, if not most, experiments based on varying thicknesses of oxide which were presumably done to improve chemical bonding were actually strengthening the assembly by realizing more favorable stress gradients, similar to a graded seal.

It is evident that when the oxide is completely dissolved, the oxide saturation at the interface is lost as the diffusion of the dissolved oxide continues into the glass (Fig. 8(B)). At this point because of the loss of chemical equilibrium, redox reactions become possible as represented by the equations in Fig. 7(B) for the model system of $\text{Na}_2\text{Si}_2\text{O}_5$ glass and Fe metal. The net reaction consists of two step reactions: the formation of the metal oxide at the interface followed by its solution by the glass. The first step of this reaction, however, does not take place readily. The standard free energy, ΔG° , is positive because the oxidation potential of the metal substrate is not high enough to reduce any of the oxides in the glass. The reaction can take place if the equilibrium constant is favorably modified to become less than one. This can be achieved by changing the processing conditions so that an adequate vacuum and low enough $p\text{O}_2$ are maintained. The porcelain enamel technologists of many generations ago, however, experimentally found that a small addition of CoO to the enamel glass initiated the redox reaction when all of the surface oxide was dissolved without changing firing conditions. The ΔG° change for this reaction is negative because CoO in the glass is easily reduced by Fe which has a higher oxidation potential than Co. The FeO that is introduced into the glass by either redox reaction maintains the glass/metal interface saturated with the oxide which is necessary to maintain chemical bonding. In addition, the associated formation of Fe_xCo_y dendrites by a microgalvanic cell mechanism in the interfacial zone,^{14,15} as indicated in Fig. 7(C), leads to a composite-type microstructure as shown in Fig. 9 which increases the strength of the assembly.

Instead of modifying the glass composition in order to realize a favorable, i.e., negative, ΔG° for a redox reaction under any firing conditions including 0.1 MPa air, it is possible to use a highly reactive metal as a substrate. Experiments have been made with Cr, Ti and Zr, for example, which have oxidation potentials sufficiently high to reduce even silica in the glass with the formation of an alloy of the metal with Si or a silicide compound as shown in Fig. 9.^{16,17} The released oxygen formed oxides of the substrate metals. Saturation of the interfacial zone with the substrate oxides results in chemical bonding. Because of the high reactivity of the metals, however, side reactions generally occur which complicate the overall analysis of the interrelations and kinetics of the reactions, but the basic principles are still the same.

Another type of glass/metal assembly is one in which the substrate metal is an alloy. Because of the differences in the oxidation potentials or reactivities of the components of the alloys, the redox reactions are not stoichiometric whether the alloy is exposed to atmospheric oxidation, or reacts directly with the glass. Some recent observations on reactions and bonding of a borosilicate glass to several Ni20Cr alloys (one contained parts per million of impurities, and a second had several percent of Si as the principal impurity) provide examples of the complexities encountered.¹⁸ On preoxidation, the purer alloy formed a multilayer oxide scale with a NiO-rich outer layer, whereas the second alloy formed a chromium oxide scale containing in solution a NiO concentration gradient from the alloy interface (Fig. 10). Stable chemical equilibrium exists at all interfaces. Bonding and strength problems related to scale adherence integrity, however, arise because of physical incompatibilities such as specific volume, epitaxial, and coefficient of thermal expansion mismatches. With application of the glass, solution reactions occur as discussed before. The presence of any undissolved oxide, or any penetration of a porous oxide layer by the glass, play a significant role in determining the strength and vacuum tightness of the assembly. If all of the oxide is dissolved or if the glass is placed in contact with unoxidized alloy, then redox reactions take place with the glass to form predominantly chromium oxide at the interface which is initially dissolved by the glass. With saturation of the glass at the interface, a Cr_2O_3 layer forms with the development of chemical bonding. The ultimate acceptability of the assembly will be determined by the physical factors which will be affected by the concentration gradients and microstructures that develop during the chemical reactions that go on in reaching stable chemical equilibrium in the interfacial zone.

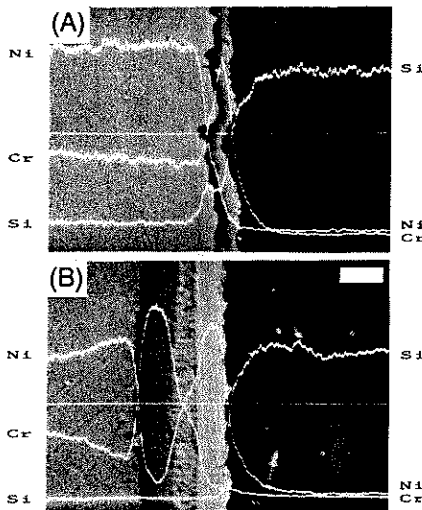


Fig. 10. X-ray line scans for Cr, Ni, and Si across the interfaces of dental procelain glassy phase (A) on 80Ni20Cr type alloy with Si additive preoxidized 60 min at 1000°C in air, and (B) on alloy with no additive preoxidized 1 min at 1000°C in air. (SEM photos at same magnification, bar = 2 μm).

A considerable amount of interest currently exists in glass-ceramic/metal or alloy seals because of the greater strength and toughness of glass-ceramic over normal glass.¹⁹ The bonding principles and requirements already discussed apply because the seal is made with the glass-ceramic when it is in the molten glassy state. On completion of the seal reactions the heat treatment schedule is modified to promote the crystallization of the glass to form the glass-ceramic.

Ceramic/Metal Joining

More complicated technological problems generally arise in joining ceramic and metal solids than in glass/metal sealing wherein the glass itself is in a liquid state during sealing. The same basic requirements, however, exist for an acceptable assembly: chemical bonding across the interfaces and microstructures in the interfacial zones with favorable stress patterns.²⁰ The development of chemical bonding is straightforward and realized when chemical reactions occur at the interfaces resulting in stable chemical equilibrium. The need for a favorable stress pattern and for the presence of a liquid phase at the interface primarily for fabrication reasons has been the dominating factor in the design of various assemblies that use some intermediate material for joining.

Let us first examine the simplest configuration and approach: the direct solid joining of flat specimens.²¹ In the absence of a liquid phase, the seal has to be made at sufficiently high temperatures and pressures, first to realize an intimate contact and second to provide sufficient thermal energy to cause a chemical reaction to obtain equilibrium at the interface. A number of such assemblies have been

studied in detail.^{22,23} The $\alpha\text{-Al}_2\text{O}_3/\text{Nb}$ bonding achieved at $\approx 1700^\circ\text{C}$ has received a great deal of academic attention because of the good match of coefficients of expansion. Cross sections of bonded specimens across the interfacial zone indicated concentration gradients of Al and O into the Nb. Good strength at the interface suggests the formation of stable equilibrium compositions at the interface. Since both phases retain their crystallinity, the role that a possible good epitaxial fit at the interface plays is also a contributing critical factor.

A modification of the preceding configuration would be the joining of two flat surfaces by an intermediate layer or shim of metal if the materials being joined have dissimilar coefficients of thermal expansion.²⁴ A potential benefit of this approach is the use of several shims with different compositions and thermal expansions to reduce stress discontinuities at interfaces. As previously discussed, chemical bonding can readily be achieved at clean metal/metal interfaces because of their reactivity due to electronic compatibility. At ceramic/metal interfaces, development of chemical bonding requires occurrence of equilibrium redox chemical reactions.

A further modification is illustrated by direct bonding of copper to alumina in an inert gas atmosphere with a fractional percentage of oxygen.²⁵ The temperature is between the melting point of Cu and the Cu-O₂ eutectic, causing the formation of a thin film of essentially eutectic liquid on the interfaces of the copper. The liquid spreads on and reacts with the alumina to form a compound CuAlO_2 at the interface which is compatible with both phases.

Another approach is the joining of a ceramic and a metal by an interlayer film of glass. This method is used successfully for bonding alumina to niobium which is utilized for Na vapor lamps.²⁶⁻²⁸ An assembly of a calcium-magnesium-aluminate mixture between the alumina and niobium is heated at $\approx 1400^\circ\text{C}$. The reaction, primarily solution of alumina by the liquid, is extensive and dependent on the temperature and time. The extent of reaction is critical since the degree of crystallization and properties are sensitive to the heating schedule.

To avoid the high bonding temperatures, especially in assemblies that are not exposed to high use temperatures, and to achieve greater reliability, sealing procedures have been technologically developed wherein a metallic interlayer is used in the assembly. These have been arbitrarily divided into two types. Intermediate metals that are used for making the assemblies in the range of 400°C are identified as solders, and those that are used in the range of 900°C are called brazes. The use temperatures in practice would have to be lower than the processing temperature. The principles and requirements of production would be the same except for temperature differences.

A braze that is used extensively and will be used as a model in this discussion is the noble metal braze $\text{Cu}\cdot x\text{Ag}^\dagger$ which corresponds approximately to the eutec-

[†]Cusil, GTE Products Corp., Wesgo Div., Belmont, CA.

[‡]Cusil ABA with 1.5 wt% Ti and Ticusil with 4.5 wt% Ti, GTE Products Corp., Wesgo Div., Belmont, CA.

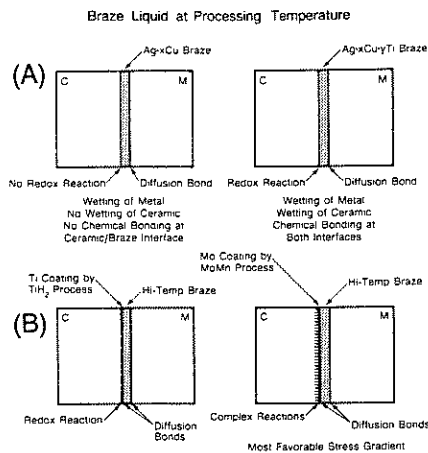


Fig. 11. Schematic illustrating several conditions under which brazes are utilized: (A) braze in contact with unmetallized ceramic, and (B) braze in contact with metallized ceramic.

tic composition in the Ag-Cu system (Fig. 6). A braze must react and reach chemical equilibrium at the interfaces with both the metal and ceramic components. Metal systems are generally compatible, resulting in wetting and solution/diffusion bonding of the braze with the metal component. The braze, however, since it has a higher γ_{lv} , does not wet the ceramic, e.g. Al_2O_3 . It also does not react since the oxidation potentials of Cu and Ag are less than that of Al. Without stable chemical equilibrium, bonding does not occur at the braze/ceramic interface. Consequently, Cu-xAg brazes to be used directly with ceramics generally have a small percentage of a reactive metal, e.g. Ti, added.²⁹ The high oxidation potential of the Ti causes it to undergo a redox reaction with the ceramic (Al_2O_3) which results in the spreading of the braze and formation of an oxide compound at the interface that is compatible with both phases, producing a chemical bond at the interfaces. The wetting and solution/diffusion bonding with the metal component are unaffected. Figure 11(A) schematically illustrates these two cases.

An example of the effectiveness of small amounts of a reactive metal in a braze is indicated by actual experimental sessile drop data of several brazes on Si_3N_4 , as shown in Fig. 12.³⁰ Cu-xAg braze and Sn on Si_3N_4 show constant high contact angles with time, indicating no wetting, probably with no formation of an intimate interface, and no reactions; these sessile drops had no adherence. Cu-xAg brazes with additions of active metal Ti²⁺ reacted with the Si_3N_4 surface, which was an active participant, to form Ti nitride and silicide. Spreading and strong chemical bonding resulted. In this case the reaction compounds are compatible and in equilibrium with both the substrate and the liquid.

Another example of the effectiveness of small amounts of additives was provided by sessile drop experiments of Cu on

sapphire substrates.³¹ With increasing additions of oxygen to the Cu as CuO, the contact angles decreased, e.g. 0 wt% and 6.7 wt% showed contact angles of 163° and 27°, respectively. Bonding strength developed with the formation of $CuAlO_2$ at the interface.

Instead of having an active metal as part of the braze in order to realize redox reactions necessary for spreading and an equilibrium chemical reaction, an extensively used procedure is to first metallize the surface of the ceramic to be bonded to the metal or another metallized ceramic component. The braze is then used to join two metal surfaces with which it is compatible, wets, and undergoes a solution/diffusion reaction. Two metallizing processes most commonly used are schematically illustrated in Fig. 11(A). In the first type the chemical bond is achieved by a redox reaction between the metallic coating and the ceramic. In the second type the assembly is obtained through an intermediate glass phase that bonds to the metallizing and the ceramic grains.

An example of the first type is the TiH_2 (Ref. 32) process which consists of painting a slurry of TiH_2 onto the ceramic, drying, and firing at a reduced pressure. The hydride decomposes, and the Ti undergoes a redox reaction with the ceramic at the interface to form a bond, and the bulk Ti powder sinters to form a coating. Chemical vapor deposition and other metallizing techniques are also being used and developed for this purpose.

The second type is referred to as the Mo/Mn process and results in the formation of a Mo coating. A paint of Mo and Mn, or their oxides, powder is applied to the ceramic, generally Al_2O_3 or BeO, and fired in H_2 with a controlled dew point so that Mn is present as MnO and Mo as a metal. The MnO reacts with the ceramic grains and the liquid glassy phase to form a controlled amount of glassy phase with the proper viscosity.³³ The Mo sinters to form a porous coating into which the glassy phase permeates and interlocks mechanically. In addition the glass at the interface reacts with the Mo and becomes saturated with MoO, thus forming a chemical bond with Mo. The glass also wets and bonds to the ceramic grains since they are compatible. The Mo coating is generally electroplated with Ni to provide a clean and continuous surface as well as one on which the braze spreads easily. A similar process is also followed for a W metallizing with an appropriate bonding glass composition.

The second type of metallization process is generally more reliable and used more extensively. Although it is not normally recognized, the increased reliability is suggested to be most likely due to a more favorable stress pattern across the interface because of the formation of a thicker interfacial zone with a more extended and graded microstructure.

Conclusions

Strong seal assemblies of any two materials are dependent on both chemical and physical factors: development of chemical equilibrium bonding at all in-

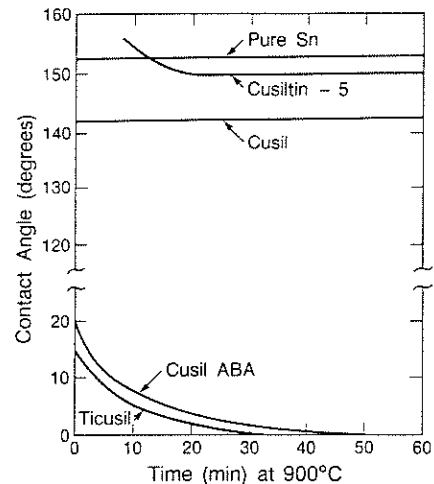


Fig. 12. Contact angles vs time at 900°C showing wetting behavior of braze alloys determined by reactive metal contents (unreactive alloys and Sn—nonwetting, Ti-containing alloys—zero contact angle.)

terfaces, and development of acceptable stress patterns and gradients across the interfacial zones. The latter is dependent on relative coefficients of expansion of the materials being joined and the changes of the coefficients due to composition gradients and microstructures that form because of the reactions at the interfaces. Thus, the physical factors introduced in design and by reactions play a significant role, knowingly or unknowingly, in the development of a sealing process or assembly. Chemical or electronic bonding in itself is not a problem since the required chemical equilibrium generally forms at the interface and is retained by continuing reaction because the reaction rate is faster than the diffusion rate. Identification of the mechanisms and kinetics of the reactions themselves, however, is generally difficult because of their complexity, particularly when highly reactive metals are necessarily utilized. The identification and development of an understanding of such reactions in which at least one solid is participating constitutes the development of the discipline of solid state chemistry.

Sessile drop experiments properly interpreted provide information as to whether solid-state reactions are taking place at the interfaces. Continuing reactions in which the substrate is taking part actively, i.e. its composition changes during the reaction, contribute to the driving force for wetting. When the driving force exceeds the surface energy of the liquid, the liquid spreads dynamically. This is indicative that an intimate interface has formed and that the liquid would be properly distributed throughout the interface. The sessile drop configuration is also convenient for cross-sectioning in order to characterize the reactions and developed microstructures.

Technology transfer to engineering or processing is critical, but equally important is a science transfer both to tech-

nology and engineering. This objective develops an understanding of the significance of processing procedures and resulting microstructures which permit a refinement, an improvement, or better control of seals in development and production. Such an understanding also permits better utilization of published data and its transfer to improvement of sealing processes; it also provides a basis upon which quantitative experiments, calculations, and designs can be effectively performed. Our understanding of ceramic/metal systems is in the development stage with principles and generalities being formulated by continuing studies on relatively simple systems, followed by studies on more and more complex systems.

Acknowledgment

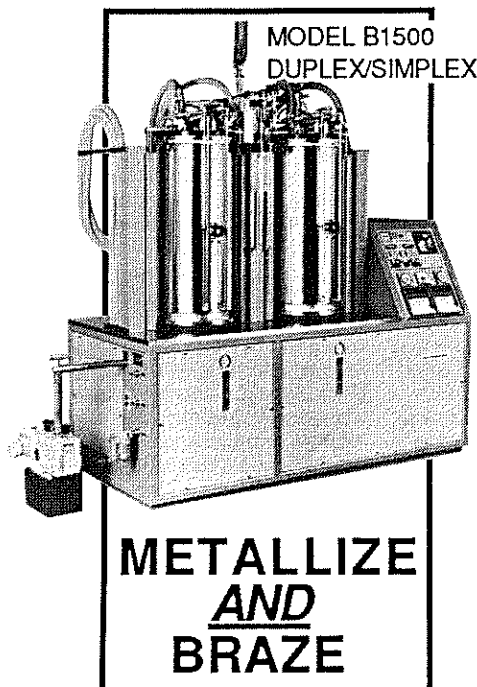
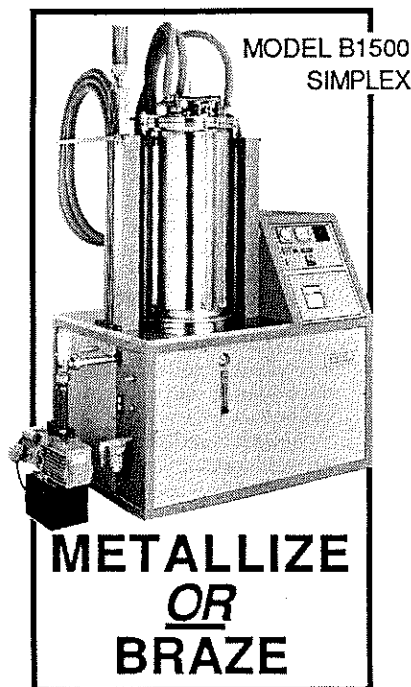
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References

- ¹A. P. Tomsia and J. A. Pask, "Chemical Reactions and Adherence at Glass/Metal Interfaces: An Analysis," *Dent. Mater.*, **1** [2] 10-16 (1986).
- ²M. G. Nicholas and D. A. Mortimer, "Ceramic/Metal Joining for Structural Applications," *Mater. Sci. Technol.*, **1** [9] 657-65 (1985).
- ³S. M. Rekhson, "Annealing of Glass-to-Metal and Glass-to-Ceramic Seals. Part 1. Theory," *Glass Technol.*, **20** [1] 27-34 (1979).
- ⁴S. M. Rekhson, "Annealing of Glass-to-Metal and Glass-to-Ceramic Seals. Part 2. Experimental," *ibid.*, **20** [4] 132-43 (1979).
- ⁵A. K. Varshneya, "Stresses in Glass-to-Metal Seals";

- pp. 241-306 in *Treatise on Materials Science and Technology*, Vol. 22. Academic Press, New York, 1982.
- ⁶J. T. Klomp, "Ceramic-Metal Reactions and Their Effect on the Interface Microstructure," pp. 307-17 in *Ceramic Microstructures '86: Role of Interfaces*. Edited by J. A. Pask and A. G. Evans. Plenum, New York, 1987.
 - ⁷J. A. Pask, "New Techniques in Glass-to-Metal Sealing," *Proc. IRE.*, **36** [2] 286-89 (1948).
 - ⁸I. A. Aksay, C. E. Hoge, and J. A. Pask, "Wetting Under Chemical Equilibrium Conditions," *J. Phys. Chem.*, **12** [78] 1178-83 (1974).
 - ⁹P. R. Sharps, A. P. Tomsia, and J. A. Pask, "Wetting and Spreading in the Cu-Ag System," *Acta Metall.*, **29** [7] 855-65 (1981).
 - ¹⁰A. P. Tomsia and J. A. Pask, "Kinetics of Iron-Sodium Disilicate Reactions and Wetting," *J. Am. Ceram. Soc.*, **64** [9] 523-28 (1981).
 - ¹¹J. J. Brennan and J. A. Pask, "Effect of Composition on Glass-Metal Interface Reactions and Adherence," *ibid.*, **56** [2] 58-62 (1973).
 - ¹²C. E. Hoge, J. J. Brennan, and J. A. Pask, "Interfacial Reactions and Wetting Behavior of Glass-Iron Systems," *ibid.*, **56** [2] 51-54 (1973).
 - ¹³P. Mayer, J. A. Topping, and M. K. Murthy, "Correlation Between Thermal Expansion of Glass and Glass-to-Metal Adherence," *J. Can. Ceram. Soc.*, **43**, 43-46 (1974).
 - ¹⁴M. P. Borom and J. A. Pask, "Role of 'Adherence Oxides' in the Development of Chemical Bonding at Glass-Metal Interfaces," *J. Am. Ceram. Soc.*, **49** [1] 1-6 (1966).
 - ¹⁵M. P. Borom, J. A. Longwell, and J. A. Pask, "Reactions Between Metallic Iron and Cobalt Oxide-Bearing Sodium Disilicate Glass," *ibid.*, **2** [50] 61-66 (1967).
 - ¹⁶J. A. Pask and A. P. Tomsia, "Wetting, Spreading and Reactions at Solid/Liquid Interfaces," pp. 411-19 in *Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems*. Edited by J. A. Pask and A. G. Evans. Plenum, New York, 1981.
 - ¹⁷A. P. Tomsia, F. Zhang, and J. A. Pask, "Reactions and Bonding of Sodium Disilicate Glass with Chromium," *J. Am. Ceram. Soc.*, **68** [1] 20-24 (1985).
 - ¹⁸A. P. Tomsia and J. A. Pask, "Bonding of Dental Glass to Nickel-Chromium Alloys," *ibid.*, **69** [10] C-239-C-240 (1986).

- ¹⁹R. D. Watkins and R. E. Loehman, "Interfacial Reactions Between a Complex Lithium Silicate Glass-Ceramic and Inconel 718," *Adv. Ceram. Mater.*, **1** [1] 77-80 (1986).
- ²⁰M. G. Nicholas, "Bonding Ceramic-Metal Interfaces and Joints"; pp. 349-57 in Ref. 6.
- ²¹K. Suganuma, T. Okamoto, M. Koizumi, and M. Shimada, "Effect of Thickness on Direct Bonding of Silicon Nitride to Steel," *J. Am. Ceram. Soc.*, **68** [12] C-334-C-335 (1985).
- ²²J. T. Klomp, "Bonding of Metals to Ceramics and Glasses," *Am. Ceram. Soc. Bull.*, **51** [9] 683-88 (1972).
- ²³M. Rühle, K. Burger, and W. Mader, "Structure and Chemistry of Grain Boundaries in Ceramics and of Metal/Ceramic Interfaces," *J. Microsc. Spectrosc. Electron.*, **11**, 163-77 (1986).
- ²⁴M. Shimada, K. Suganuma, T. Okamoto, and M. Koizumi, "Solid State Bonding of Alumina and Steel by Hipping"; pp. 409-14 in Ref. 6.
- ²⁵J. F. Burgess, C. A. Neugebauer, and G. Flanagan, "The Direct Bonding of Metals to Ceramics by the Gas-Metal Eutectic Method," *J. Electrochem. Soc.*, **122** [5] 688-90 (1975).
- ²⁶C. I. McVey, "High-Pressure Sodium Lamp Seals and Recent Improvements," *J. IES.*, **8** [1] 72-77 (1979).
- ²⁷J. F. Ross, "Ceramic Bonding," U.S. Pat. No. 3,281,309, October 25, 1966.
- ²⁸Kenneth W. Lay, R&D Center, General Electric Co., Schenectady, NY; private communication.
- ²⁹H. Mitzuhara and E. Huebel, "Joining Ceramic to Metal with Ductile Active Filler Metal," *Weld. J.*, **65** [10] 43-51 (1986).
- ³⁰R. E. Loehman, A. P. Tomsia, J. A. Pask, and S. M. Johnson, "Why Metals Adhere to Si₃N₄"; submitted to *J. Am. Ceram. Soc.*
- ³¹A. C. D. Chaklader, A. M. Armstrong, and S. K. Misra, "Interface Reactions Between Metals and Ceramics: IV, Wetting of Sapphire by Liquid Copper-Oxygen Alloys," *J. Am. Ceram. Soc.*, **51** [11] 630-33 (1968).
- ³²R. J. Bondley, "Metal-Ceramic Brazed Seals," *Electronics*, **20** [7] 97-99 (1947).
- ³³D. M. Mattox and H. D. Smith, "Role of Manganese in the Metallization of High Alumina Ceramics," *Am. Ceram. Soc. Bull.*, **64** [10] 1363-67 (1985).



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