Tensile testing of metal/metal and ceramic/metal brazed joints
by Shreeram Raj

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering
Montana State University

Abstract:
The current study focused on an increasingly important technological problem: strong and reliable brazed joints between dissimilar metals and between ceramics and metals. The influence of various joint component materials and other relevant variables on the joint strength of these systems was evaluated. The load required to cause separation usually gave clear information about the adhesion of the system of dissimilar materials. Strength data were also useful in ascertaining relative ranking of the adhesion between systems.

Various combinations of ceramics and metals were used to prepare braze coupons with Cusil ABA braze alloy. The evaluation of joint strengths was done using a butt joint geometry in an uni-axial tension test. The tensile tests were conducted on an Instron 8562 testing machine using a self-aligning fixture. This attachment aided in eliminating parasitic bending loads and in accommodating specimen misalignments, both of which are very critical to the tensile testing of brittle joint systems.

The results of these tests have led to a better understanding of the joint strengths of brazed dissimilar materials. Joints with high strengths were produced by an active filler metal process, the most economical of which utilized an active element forming a true alloy with the base filler metal. The results of the study provide an improved basis for material selection and joint design in non-shorting electrodes for use in Magneto-hydro-dynamic channels. This research also contributed to the general database on brazed joint strengths.

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Shreeram Raj

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6/14/91 — Date

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ABSTRACT

The current study focused on an increasingly important technological problem: strong and reliable brazed joints between dissimilar metals and between ceramics and metals. The influence of various joint component materials and other relevant variables on the joint strength of these systems was evaluated. The load required to cause separation usually gave clear information about the adhesion of the system of dissimilar materials. Strength data were also useful in ascertaining relative ranking of the adhesion between systems.

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CHAPTER ONE

INTRODUCTION

The use of ceramic/metal joints has assumed increasing importance in modern technology. One of the key technologies that will enhance or restrict the use of ceramics in high performance structural applications is the ability to reliably join them to metals. The earliest developments in the field of ceramic brazing began in the laboratories of Pulfrich and Vatter in the early 1930's [1]. Like other joining processes, the joining of ceramics was considered more an art than a science. Over the years, extensive research, development and refinement of techniques has improved ceramic/metal and ceramic/ceramic brazing. Efforts of late have been particularly focused on joining ceramics to metals for a wide range of industrial uses. Ceramics are generally brittle, more refractory and less thermally expansive or conductive when compared to metals. There are exceptions to this generalization, and this study dealt with some of those exceptions. Beryllium oxide and aluminum nitride, the ceramics used in this study, have high thermal conductivities. Tungsten and molybdenum, the metals used, are highly refractory. This leads to their use in special applications such as in cold electrodes for MHD channels.

The materials used in this study are metal/metal and ceramic/metal brazed joints for application with copper electrodes. The ceramics are used as high thermal conductivity electrical insulators on the copper electrodes. The metals, in turn, are either used as intermediate layers in ceramic/metal joints or as wear resistant edges to the copper electrodes.

Brazing is a heterogeneous joining process in which materials are joined by a lower-melting material. As far as metals are concerned, brazing is a process of joining similar or dissimilar metals with a nonferrous filler metal that has a melting point below that of the metals being joined. The strength of a brazed joint is attributed to a variety of parameters discussed later. The brazing of ceramics is considerably more difficult than for metals. A major problem in successfully brazing ceramics with metal alloys is the well documented observation that liquid metals generally do not wet ceramic surfaces unless special provisions are made. The active filler metal process is used to overcome this problem in this study. Brazing is a very complex process with a number of different parameters simultaneously affecting the joint. To develop ceramic/metal brazed joints for demanding applications it is necessary to optimize the materials system, including the ceramic, the parent metal, the braze and the intermediate layers, if any. Also, the resistance of the joint materials to thermal shock, which depends heavily on the thermal expansion mismatch at the joint, is one of the more important factors in the formation of a reliable brazed joint.

Initially, to understand the system that was being dealt with here, metal/metal brazed systems were tested for joint strength with different combinations of metals and braze alloys. Then, the ceramic/metal brazed systems were tested. The performance of electrical assemblies using ceramic/metal brazed systems under extreme conditions is directly traceable to the strength of the ceramic/metal joints in the system. Hence, the strength of the brazed joint is an important criterion for the evaluation of the performance of these systems. Systems having ceramic/metal brazed joints behaved in a brittle fashion, and so great care was needed in their testing.

CHAPTER TWO

BACKGROUND

Importance of Joining

Complex structures using structural ceramics which cannot be made in one piece require joining. Joined ceramic components can be made stronger and with shapes and tolerances not easily achieved in a single molding. The most important application of ceramic joining could well be the attachment of ceramic components to structural parts made of metals, where the purpose of the ceramic is to resist high temperature exposure. These assemblies must withstand stress or temperature gradients too great for ceramics alone. Cooling of the metal, and cyclic loading introduce complex stress and temperature gradients into the joints, and hence the design of such systems requires a great deal of information on the materials in the layers of the joint : thermal expansion, annealing effects, viscosity, elastic modulus, strength, fracture toughness, creep and fatigue, all as functions of temperature [1]. The availability of good joining techniques strongly influences the design of such systems.

Ceramic/metal components are joined by one of several primary techniques.

Mechanical Joining

These techniques use mechanical fasteners, hooks or press and shrink fitting to join ceramic to metal. The latter method is usually employed in mass production processes.

Direct Joining

Achieved by pressing very flat mating surfaces at high temperatures to achieve diffusion bonding. Fusion welding using lasers and electron beams is employed for high melting temperature systems.

Indirect Joining

The most common method of achieving high-integrity joints using a wide variety of intermediate bonding materials. Metal intermediates are used as solid-state diffusion bonding agents or as brazes.

Adhesive Joining

In general, polymeric adhesives are not considered for ceramic applications where high temperatures and corrosive environments are present, due to deficiencies in the adhesive properties under these conditions.

Requirements for Strong Joints

Chemical bonding at the interface, low thermal expansion differential, low stress concentrations, and strong component materials are the basic requirements for strong bonded assemblies [1]. It is very difficult to characterize chemical bonding, especially at the interfaces; hence, it is generalized that two phases can form an acceptable assembly with a chemical bond if they are at stable chemical thermodynamic equilibrium at the interface. This is irrespective of the bulk phases, provided they are physically compatible [2].

The formation of an intimate interface is the first requirement in joining. An intimate interface is one where atomic contact exists either as Van der Waals forces or primary bonding. In a solid/liquid combination an intimate interface is formed if the liquid wets or spreads and penetrates irregularities on the solid surface [1].

Stable chemical equilibrium at the interface is the next requirement. At metal/metal interfaces, solution reactions and saturation at the interfaces help achieve chemical equilibrium. At ceramic/metal interfaces, solution of oxide layer on pre-oxidized metal redox reactions, saturation at the interface with substrate oxide product redox reactions and the formation of compounds at the interface which are compatible with both phases help achieve chemical equilibrium [1].

In summary, for ceramic/metal joints the basic requirement is for chemical bonding across the interface and microstructures in the interfacial zone having favorable residual stress patterns [1]. Chemical bonding occurs when chemical reactions occur at the interfaces resulting in stable chemical equilibrium. Hence, the need for a liquid phase and favorable residual stress patterns has been the dominant factor in the design of assemblies that use some intermediate material for joining [1].

Brazing

Despite recent advances in joining technology, brazing is still the foremost method of producing sound joints. Brazing is uniquely suited for the fabrication of ceramic/metal joints, and also lends itself to mass-production operations where small parts must be joined economically or large assemblies must be joined in a single operation.

The primary objective in brazing is to produce a mechanically acceptable bond between two surfaces without fusing the bulk materials. A liquid is made to flow into and to fill the space between the joint faces, and to then solidify. The liquid used has a lower solidification temperature than the bulk phases to be joined. Brazing filler metals are mainly copper, nickel, silver, gold or aluminum alloys. In brazing there exists a degree of intersolubility between the braze alloy and substrate, and hence interdiffusion at the substrate surface should occur [3].

The main factors which govern the effectiveness of joint filling by the braze alloy are the contact angles of the system, joint clearance (separation of joint faces), heating rate, uniformity, and temperature. Uneven heating results in irregular filling, and so circular joints are generally preferred to straight-edged joints in furnace brazing. Optimum joint clearances range from approximately 0.002 in. to 0.005 in. for most brazing materials. However, copper is known to yield strongest joints with an approximately 0.003 in. joint clearance [4].

Brazing is also important in ceramic to metal joining, allowing complex assemblies to be joined in a stress free state. It also allows for differences in thickness and surface characteristics of joint members. Brazing permits additional members to be joined to a partially completed structure by using brazing filler metals with different melting temperatures. Another advantage here is the need for little or no finishing of the joint [1].

A good brazed joint depends on the braze and its compatibility with the brazing surfaces. The stresses produced in a joint due to geometry and thermal expansion mismatches between components also directly influence the integrity of a brazed joint [1]. The stresses produced in a brazed joint depend on the thermal expansion mismatch between joint components, the relative thickness of the components, the mechanical properties of the components, the geometry of the joint, and the brazing temperature. The strength of the brazed joint also depends on the residual stresses present at the joint, the individual properties of the joint components, and the integrity of the interfaces [1].

Brazing Methods

Brazing can be done by torch, resistance or induction heating, by dipping, or in a furnace. Torch brazing is the common manual technique for brazing, using an oxy-acetylene or oxy-coal gas torch. Resistance or induction brazing is useful for repetitive work in open air conditions, with heating coils being designed for the specific application. Dip brazing is usually applied to sheet products formed to the desired shape, coated with braze alloy and then dipped in a flux bath [5].

Furnace brazing is preferred for batch or continuous processing of a large number of parts, generally at low unit costs. The equipment consists of a furnace that is electric, gas or oil fired with temperature and atmosphere controls. Filler metals are usually used as pre-placed preforms. A major advantage of this method is the ability to braze several joints simultaneously and to control surface oxidation by using a controlled atmosphere (vacuum or gas filled). The limitations of this method include high initial cost, floor space requirements and maintenance costs [6]. Also, the copper which is furnace brazed must be oxygen free or deoxidized, since regular copper is embrittled by hydrogen. Normally, copper, copper alloys and a few other metals are susceptible to intergranular penetration and cracking by the brazing material if residual or applied stresses are present during furnace brazing operation [3]. Hence, such combinations are stress relieved before furnace brazing, or else low-melting silver brazing alloys are used [3].

Brazing Procedure

First, care should be taken in designing the joint assembly so that the molten metal does not touch any part of the brazing fixture. Second, since the metal has a higher thermal conductivity than the ceramic, it heats faster, so that all the filler metal is drawn up by the metal. This effect is even more pronounced when the mass of the metal is small compared to that of the ceramic. Hence, the heating rate has to be controlled to minimize the temperature difference between the ceramic and the metal. This is usually achieved by initially holding the temperature below the solidus temperature of the braze, and then increasing the temperature at a controlled rate to the brazing temperature. Lastly, the rate at which the joint is cooled from the brazing temperature to room temperature is also critical. Slowing the cooling rate allows for the metals to plastically deform and, hence, reduce the thermal expansion mismatch stresses, resulting in a stronger joint [3].

The thermal expansion of both metal and ceramic play a very important role in brazing. A typical brazing cycle is summarized as follows [1]:

1. Heat the assembly to approximately 50 °C below the braze solidus temperature.
2. When melting begins, hold at that temperature for a given time such that all parts reach a uniform temperature.

3. Increase the temperature to about 50 °C above the liquidus temperature for complete braze melting.
4. Hold at this temperature for up to 10 minutes, then cool.

Brazing Ceramics

The major problem with brazing an oxide ceramic is the resistance to wetting caused by oxides on the surface of the ceramic. One way of rectifying this problem is by applying pressure to the braze filler metal to overcome the repelling surface tension forces of the oxides. Results of tests show that joint strength increases with increased applied pressure to a certain extent and then levels off [1]. Purer forms of oxide ceramics also tend to have lower joint strengths. Brazing in a vacuum also tends to yield higher joint strengths [1]. Active metal brazing using active braze alloys (ABA's), like Cusil ABA or Incusil 10 ABA, which contain an active metal to promote a redox reaction with the ceramic, also yield comparable joint strengths to other conventional metallizing-brazing techniques (like the Mo-Mn process) [7].

The braze system is dependent on the condition of the ceramic surface, with lapped surfaces resulting in much higher joint strengths compared to as-ground surfaces [8]. Metal coatings also help considerably in brazing oxide ceramics [1].

As far as ceramic/metal joining by active metal brazing is concerned, furnace brazing is accepted as the best technique. However, vacuum brazing or inert gas brazing are the most economical methods [1].

Wetting and Adherence

The shape of a drop of molten braze metal on a solid ceramic surface (Figure 1) is determined by gravity and by the interacting forces of solid-liquid interfacial energy (γ_{SL}), solid-vapor interfacial energy (γ_{SV}) and liquid surface tension (γ_{LV}) [1]. Young's equation gives the relationship between these interfacial tensions as

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos\theta \qquad (2.1)$$

The contact angle (θ) may vary from 0° to 180°. If γ_{SL} is high, the drop tends to form a ball with very small interface area, and if γ_{SV} is high then the drop tends to spread. Also, if only the liquid surface energy is decreased, the contact angle decreases for initially wetting drops ($\theta<90^{\circ}$) but increases for initially non-wetting drops ($\theta>90^{\circ}$) [1].

The contact angle is greater than 90 degrees when γ_{SL} is larger than γ_{SV}, and the liquid drop tends to spheroidize. Similarly, θ is less than 90 degrees when γ_{SV} is larger than γ_{SL}, and the liquid drop tends to flatten out and wet the solid surface.

Brazing filler metal should wet the solid in order to form a joint. The contact angle should be less than 90 degrees, i.e., γ_{SV} must be greater than γ_{SL}. From practical considerations a contact angle of about 70 degrees is found to be satisfactory [3]. Dupre [1] showed that the free energy

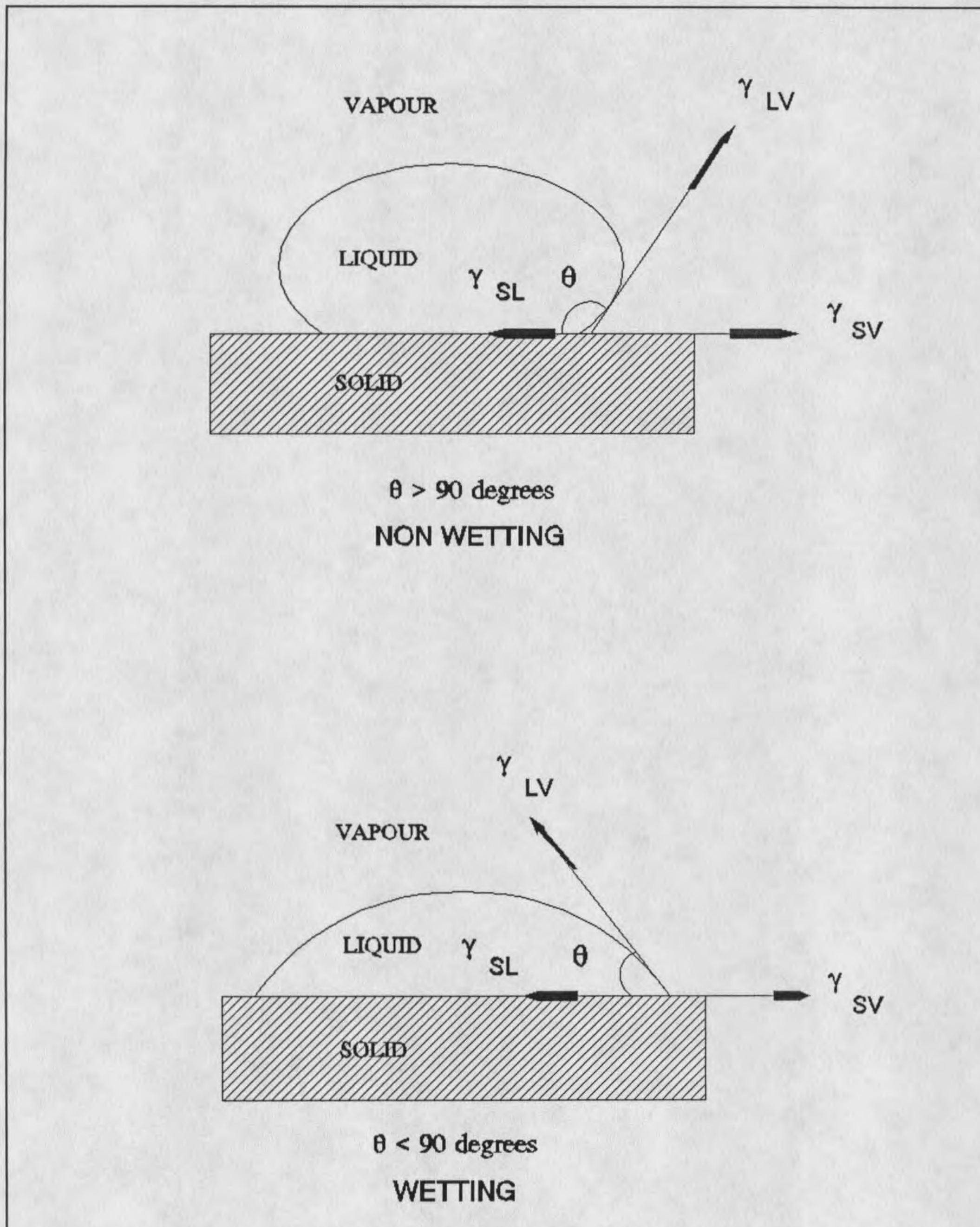

Figure 1. Wetting and contact angles.

change when solid and liquid are joined, combined with Young's equation, can be given in terms of the work of adhesion (W_A) as

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \qquad (2.2)$$

This relates the adherence of the drop to the substrate, but not necessarily the adherence of the solidified drop. However, these equations assume the absence of any diffusion or reaction at the contact interface, which is not generally true, particularly with the use of active metals in braze filler metals [1].

It is important to analyze the factors that make wetting effective, including the effect surface cleanliness has on wetting. The effects of surface roughness versus smoothness and other methods to improve wetting are equally important. The contact angle should be such that the braze filler metal wets the ceramic but does not flow. However, if a low contact angle or flow on the ceramic is necessary, this can be achieved by using a high active metal content brazing alloy. Most high titanium content brazing alloys are very hard and brittle, thereby limiting their use in joining ceramic/metal systems with mismatched thermal expansions [1].

In general, the molten filler metal contact angle to the base metal ranges from 0 degrees, where the filler metal blushes or flows over the metal substrate surface, to 90 degrees (1.6 radians), where the molten metal stays where it melts [1].

The braze filler metal may alloy with the substrate to form a lower melting temperature alloy, which results in deep erosion followed by severe blushing of the newly formed composition. The opposite may also happen, with the braze filler metal readily alloying with base metal to form a higher melting temperature alloy, which then results in sluggish braze formation and no flow [1].

The joining of two materials with different brazing filler metal contact angles can be more difficult than that with same contact angles. In ceramic/metal systems this is due to the fact that in most cases the ceramic member mass is much greater than that of the metal member, and, hence, the metal becomes much hotter than ceramic at short times. This causes most of the braze filler metal to spread over the metal, leaving insufficient braze filler metal to wet the ceramic.

Braze Filler Metal

A braze filler metal works by melting, reacting and reaching chemical equilibrium at the interfaces with both the ceramic and metal components [1]. Unlike metal systems, the ceramic systems are not usually compatible, and wetting and subsequent bonding of the braze with the ceramic component becomes a problem. This is because the braze has a higher γ_{LV} and does not wet the ceramic. In joining AlN or BeO using a silver-copper eutectic braze alloy, no reaction occurs since the oxidation potentials of Cu and Ag are less than that of Al or Be. Without stable chemical equilibrium, bonding does not occur at the braze/ceramic interface. Hence, Cu_xAg brazes usually have a small percentage of reactive metal, like Ti, added [9]. The high oxidation potential of Ti causes it to undergo a redox reaction with the ceramic, which causes spreading of the braze, and oxide formation at the interface compatible with both phases, resulting in bonding at the interface. Figure 2 shows the two cases of brazing with and without active metal additions. Table 1 compares a few silver-copper braze alloys.

Table 1. Some silver-copper braze alloys and their compositions [1].

	BRAZE ALLOY	COMPOSITION (wt %)
1	Cusil	72 Ag, 28 Cu
2	Ticusil	68.6 Ag, 26.7 Cu, 4.5 Ti
3	Cusil ABA	65 Ag, 33.5 Cu, 1.5 Ti
4	Cusiltin - 5	65 Ag, 30 Cu, 5 Sn

Most metal alloys used in brazing as braze filler metals do not wet ceramics easily unless their surfaces have been treated to promote wetting. Oxide ceramics (Al_2O_3 and BeO) are the most important of such structural ceramics. Even the slightest amount of Al of Ti present in a super-alloy can cause wetting problems due to the formation of oxides during heating (unless vacuum brazing is employed). Brazing of metals

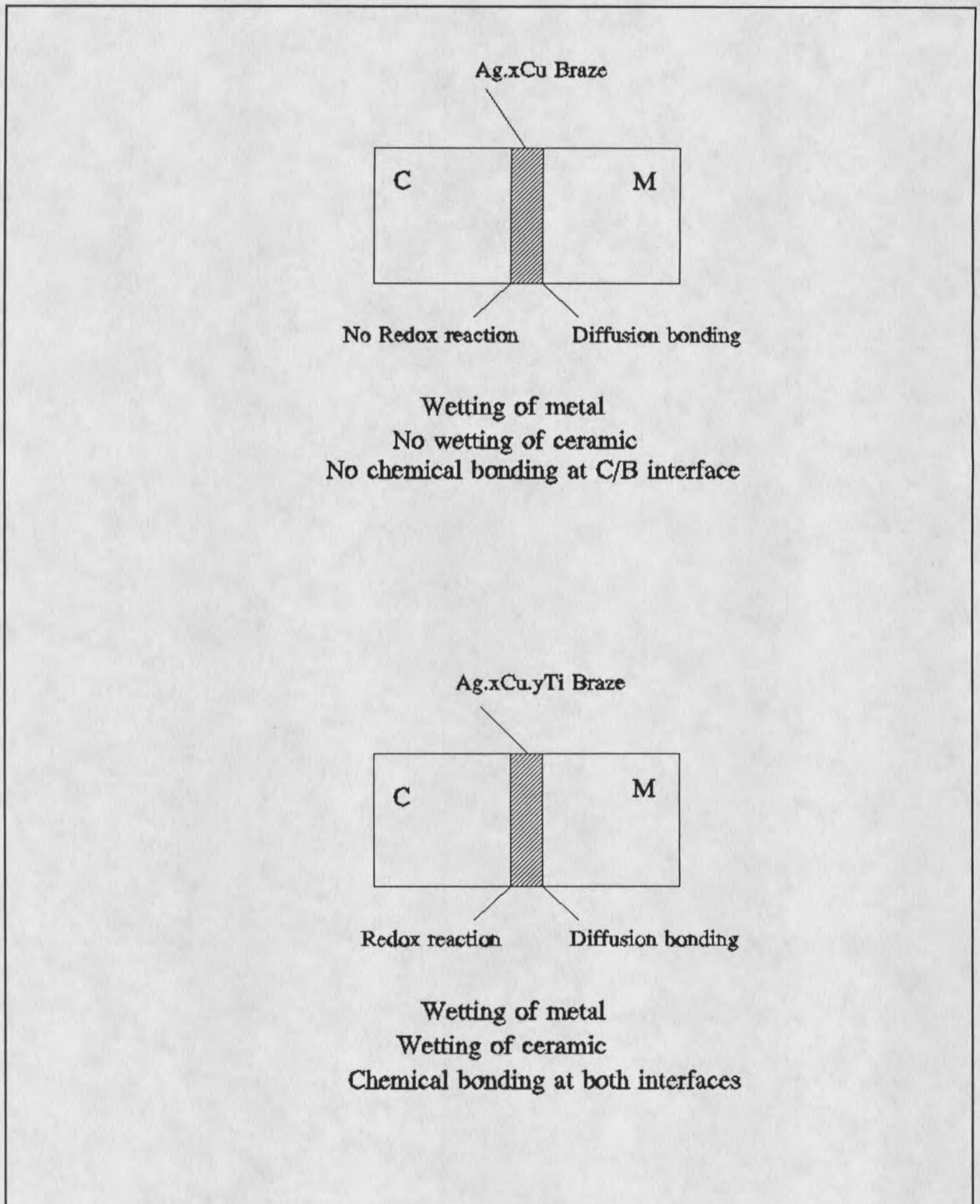

Figure 2. Brazing with and without active metal additions [1].

to metallized ceramic surfaces is easy because the metallized layer ensures wettablity of the ceramic. However, metallizing is a costly and time consuming process and is also an additional step. Some metals and hydrides have the ability to wet ceramic surfaces that have not been metallized. Active Metal and Active Hydride processes are based upon these principles [10]. The use of active metals and hydrides to join ceramic to metal was first applied in the electronic industry.

One of the major factors in choosing a brazing filler metal is its liquidus temperature, which must be sufficiently below the solidus temperature of the base metal. Production methods also impose a major limitation. As regards a certain specific application, the properties that influence the choice of a certain filler metal are electrical conductivity, corrosion resistance, flow characteristics, cost and strength [6].

Brazing Alloys for Ceramics

The inability of conventional brazing alloys to wet ceramics because of low surface energies is a major concern. Hence, brazing alloys for direct brazing of ceramics often contain a reactive element, usually a metal like Ti or Zr, which promotes wetting by reacting with the ceramic and decomposing a thin layer of the ceramic.

Since these brazing filler metals contain reactive metals, they exhibit a high oxygen affinity and also poor corrosion resistance [11]. The oxidation resistance of reactive metal brazing alloys is always very poor, but the addition of aluminum helps form an adherent protective oxide film without sacrificing wettability [12]. It is also known that the affinity of the filler metal, or elements in the filler metal, for oxygen plays a very important role in determining the strength of the brazed interface [13].

Active metal brazing has been used since 1940, but extensive use has not been attained due to inconsistent properties [1]. There are several methods of active metal brazing. One method involves a sheet of titanium cladded by two sheets of braze alloy. Another method uses titanium hydride powders mixed with powders of conventional brazing metals. However, the most economical method uses a filler metal where the active element(s) forms a true alloy with the base filler metal.

According to Mizuhara and Huebel [9], there are currently four recognized active element joining processes. The first process uses titanium hydride powder mixed with a standard brazing filler metal powder. The ceramic surface is coated with the mixture and then the assembly is heated to brazing temperature. In the second process more than one layer is used. Titanium foil is stacked with brazing alloy foils between the ceramic and metal and then the assembly is heated to brazing temperature. The third process involves a commercially available cladded product, which consists of an active element core that is protected from reacting with the