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Production, Characterization, and Mechanical Evaluation of Dissimilar Metal/Ceramic Joints

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1. Introduction

Ceramics and metals are two of the oldest established classes of technologically useful materials. While metals dominate engineering applications, ceramics are used extensively to provide thermal and electrical insulation and are emerging as important structural materials. Properties of individual ceramics and metals can vary widely, but the characteristics of most materials in the two classes diffier significantly (Richerson, 1992). The properties reflect the different lattice binding characteristics of metals and ceramics. Ceramics are neither purely ionic nor purely covalent, and the relative degree of ionicity or covalency of ceramics can be related to the electronegativity of its components. Modern ceramics are gradually becoming important in structural applications because of their high strength to weight ratio, high modulus, high corrosion resistance, excellent high temperature properties, and abundance. The manufacture of component shapes from monolithic engineering ceramics such as Si_3N_4 is difficult, and this has generated a continued interest in the use of joining technologies to produce complex configurations from assembles of simples shapes.

The use of ceramics and ceramics based composites in industrial applications mainly for high temperature has received extensive attention recently. However, the utilization of the full capabilities of ceramics demands an ability to join ceramics to themselves or metals. Significant differences in the mechanical properties of ceramics and metals make it extremely difficult to obtain ceramic/metal joints with adequate mechanical integrity. Silicon nitride (Si_3N_4) and tungsten carbide (WC) are two of the most attractive advanced ceramics materials for specific applications since the resulting microstructure of these ceramics after sintering is similar to that of whisker or particulate-reinforced composites, respectively. Joining ceramics to metals is a key of technology in the use of advanced ceramics in complex structures. Moreover, the use of advanced ceramics depends on the reliability of ceramic/metal joining processes and the properties of the resulting interfaces. Several methods for joining ceramics to metals have been developed, some need an intermediate liquid phase, brazing, thermal spraying, and others are produced by solid state bonding and co-sintering (Tinsley et al., 1998; Tomsia, 1993). In all cases some problems

have to be overcome: (i) morphological adaptation of the surfaces in contact; (ii) formation of bonds: van der Waals bonds, chemical bonds by simple recovery of the molecular orbital or by chemical reaction, where new phases are grown at the interface; (iii) strict control over the residual stresses developed in both materials; (iv) changes in mechanical properties of the alloy and ceramic close to the interface. Mechanical aspects are essential for the last two points and for the first one in the case of the solid state bonding (Treheux et al., 1994).

In the absence of a liquid phase, ceramic/metal joining can only be accomplished with temperature, pressure, and time sufficient to promote mobility and interdiffusion of reacting species, producing adequate interfacial contact between the ceramic and the metal. Initially, the two components contact only at their asperities. In the first stage of the bonding process, more intimate contact is achieved by plastic deformation, which results in two partly joined surfaces with residual voids in between. When ceramic/metal bonds are being formed, and deformation of the metal is permissible, plastic flow generally occurs within the metal, and in the second stage of the bonding process, creep and diffusion eliminate the voids. The key step in the formation of a ceramic/metal interface is to achieve adequate contact between the two materials at the interface. The driving force for the formation of a ceramic/metal interface is the reduction in free energy when intimate contact is established between the ceramic and metal surfaces. In order for this to occur, both surfaces have to be brought into intimate contact, which is usually accomplished by controlling the temperature and atmosphere during interface formation. The application of pressure results in displacement of impurities and adjustment of irregularities due to localized deformation.

Metal ceramic interlayers play an important role in the fabrication of both metal-ceramic joints and in the manufacture of metal-ceramic or metal-matrix composites. In the case of joining interlayers are used to alleviate thermal expansion mismatch or create bonding between the ceramic and metal. Similarly, they may be employed as coatings to ceramic particles to activated their normally inert surface or act as protection from reaction with liquid metal. Therefore, in order to understand the mechanical performance of joints it is important to understand the mechanisms of interface formation between the metal and ceramic.

2. Solid-state diffusion bonding

Diffusion bonding is a solid-state process for the fabrication of metal-metal, ceramic-ceramic and ceramic-metal joints that is conceptually simple. The process requires no localized melting of components or introduction of foreign bonding materials, but merely that mating surfaces are brought into intimate, atomic scale contact so that an interface can be formed by interdiffusion to create a structural continuum. Such interfaces, whether between metals, ceramics or between a metal and a ceramic, can have good mechanical integrity even at high temperatures. The simplest form of diffusion bonding involves the application of a low pressure at a high temperature to achieve bonding of the components. It is important they have smooth and well-matched mating surfaces. Understanding the relationship between processing, structure and properties of metal/ceramic interfaces is becoming increasingly important as performance requirements demand a combination of these different materials in applications ranging from electronic packaging to high temperature aircraft structures (Howe, 1993).

There are two possible mechanisms of the solid phase bonding of ceramics to metals without the intermediary of a liquid filler metal: when the solid-phase ceramic and metal are brought into contact, the metal may undergo plastic deformation, enter the surface

irregularities of the ceramic, adhere and bond to the ceramic. In another possible mechanism, the metal may diffuse through the interface, react with the ceramic and form a continuous layer (Okamoto, 1990). Diffusion bonding has attracted interest as a means of bonding Si_3N_4 and successes have been achieved by controlling the microchemistry and microstructure of the interfaces formed. The first requirement for solid-state diffusion bonding is the creation of intimate contact between the surfaces to be bonded in order that the atomic species come into intimate contact. In addition to a good contact, there should be enough diffusion between the materials in a reasonable time. Pressure can be applied uniaxially (hot-press) or isostatically (hot-isostatic press) on a diffusion couple. Bonding of ceramics by uniaxial pressing has been achieved, but it is not yet an important and widely used industrial process. Figure 1 shows an illustrations of events during metal/ceramic diffusion bonding in solid-state (Nicholas, 1990).

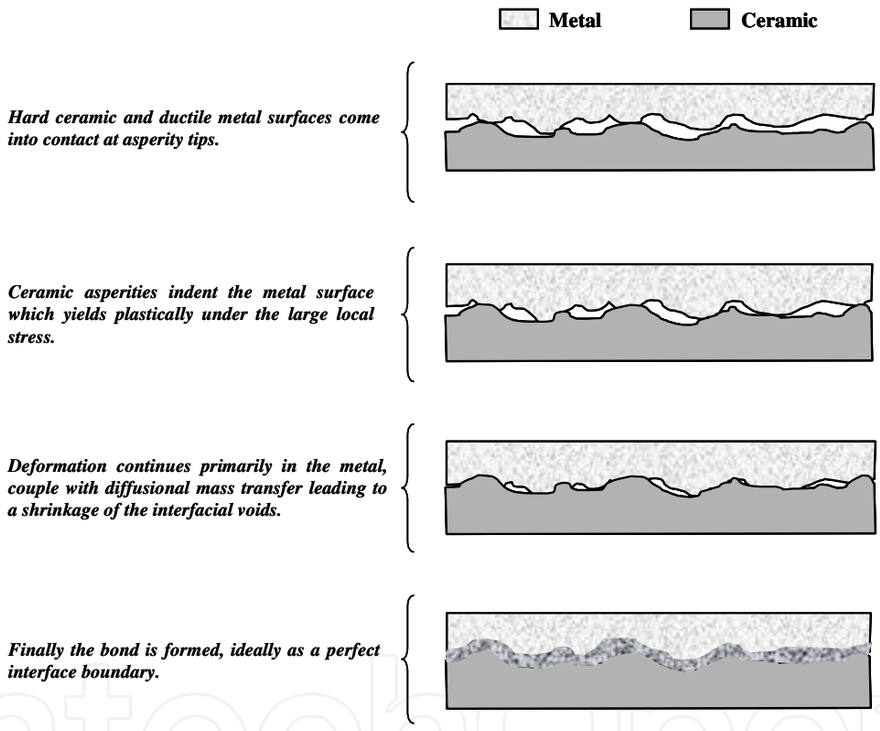


Fig. 1. Sequence of events during metal-ceramic diffusion bonding (Nicholas, 1990)

There are several advantages of solid-state joining. When ceramic have to be bonded to metals, it is a common practice to introduce a metal interlayer between the components. The interlayer should be ductile so that it can deform readily to achieve intimate contact with both mating surfaces at various pressures and temperatures, that it should act as a stress relieving buffer layer if the thermal expansivities of the metal and ceramic components differ significantly, and of course that it should adhere strongly to both the metal and ceramic components. The technique has been applied, so far, mainly for the joining of Al_2O_3 and SiO_2, but its utility has also been demonstrated for joining of Si_3N_4 and other new engineering ceramics like WC. The technological advantages of diffusion bonding are low deformation which enables parts to be joined with little distortion, the ability to join large areas, the applicability of diffusion bonded joints at high service temperatures, and the

possibilities for joining materials in a none conventional way (Dunford & Wisbey, 1993). However, the major disadvantages of diffusion bonding are high capital costs, and the restricted joint geometries that can be produced (Peteves et al., 1996). In addition, specific problems exist when applying diffusion bonding to Si_3N_4. The misfit in the coefficient of thermal expansion *(CTE)* of the joining materials can result in areas of high residual stresses at the interface during the cooling process (Locatelli et al., 1997).

2.1 Bonding mechanisms

Diffusion bonding can be defined as the creation of an intimate bond or joint between two materials by thermally assisted processes occurring in the solid state. In order to understand the mechanisms and driving forces of diffusion bonding, the evolution of the bond microstructure must be appreciated. The bonding process can be viewed as two steps operating in parallel. The first is the transition from two surfaces contacting at their asperities to an intimate interfacial conformity. This must involve the elimination of a large volume of interfacial voids accommodated by mass transfer mechanisms, plastic flow and diffusion. In parallel with this, but sequential to each individual contact, there must be an adhesion process giving the interphase boundary strength. A third step, with possible destructive consequences, is a subsequent chemical reaction between the metal and ceramic in contact to form a third phase at the boundary. The driving force for the formation of an interface between materials is the energy decrease of the system resulting from its establishment. The interfacial energy should reach the lowest achievable value as the bond is formed, otherwise further changes that could degrade the stability of the bond may occur under operating conditions.

The mechanisms of diffusion bonding two identical materials and similar surfaces have been studied since the 1960s, and it is now generally accepted that joint formation occurs by collapse of interface voids produced by a number of diffusion and creep mechanisms. The collapse of interfacial voids can be brought about by a number of mechanisms analogous to those occurring in pressure sintering, and these are best grouped in terms of sources and sink for matter and are (Chen & Argon, 1981; Almond et al., 1983).

A. Surface diffusion from a surface source to a neck.
B. Volume diffusion from a surface source to a neck.
B'. Evaporation from a surface source to condensation at a neck.
C. Grain boundary diffusion from an interfacial source to a neck.
D. Volume diffusion from an interfacial source to a neck.
E. Plastic yielding resulting in deformation of original surface asperities
F. Power law creep.

An illustration of the various routes of material transfer is contained in Figure 2. These mechanisms are normally separated in two main stages. ***Stage 1****: Plastic deformation.* The contact area of asperities, though initially small, will rapidly grow until the application load can be supported, which means that the local stress falls below the yield strength of the material. ***Stage 2:*** *Diffusion and power law creep.* The driving force for mechanisms A, B, and B' is the difference in surface curvature. Matter is transferred from the point of least curvature (sharp neck of the void at the bond interface) to the point of greatest curvature. Thus, as the voids change from an elliptical to a circular cross section, the rates of these mechanisms will approach zero because the aspect ratio of the voids tends to unity. In addition to these stages, recrystallization and grain growth may occur during bonding. Interface formation must be accompanied by the collapse and annihilation of voids created

at first contact. The driving force for this collapse is identical to what drives diffusion bonding in metals. Void closure results in a net approach of the two surfaces being joined. This allows mechanical work to be done by the bonding pressure. The reduction in void volume is accompanied by a reduction of void surface energy, which is a further driving force. A number of additional competing mechanisms can occur during the bonding of dissimilar materials such as metals and ceramics.

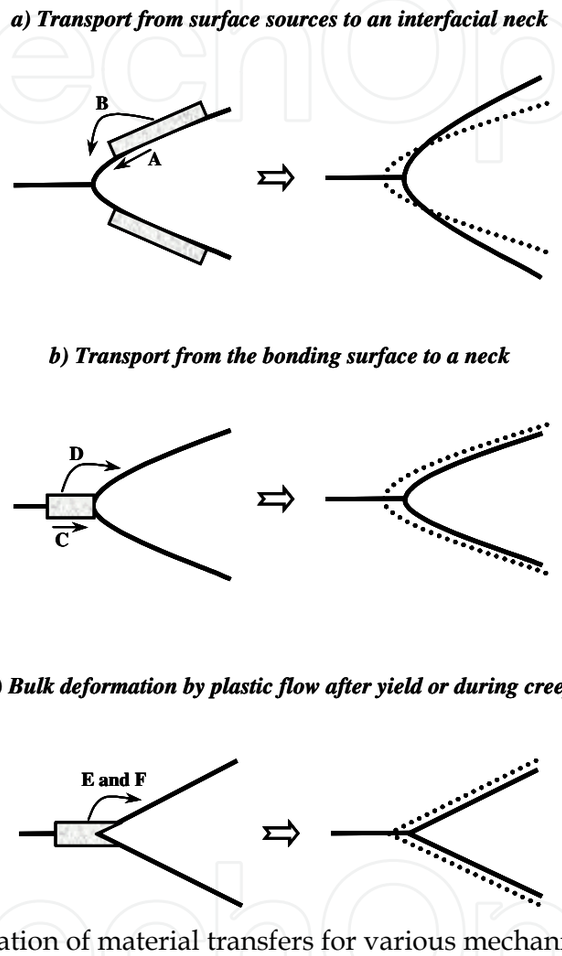


Fig. 2. Schematic illustration of material transfers for various mechanisms involved in diffusion bonding (Chen & Argon, 1981; Almond et al., 1983)

2.2 Metal/ceramic interfaces

Having selected suitable joining materials and decided upon a joint design, consideration can be given to the choosing of equipment and processing parameters that will ensure effective manufacture of the joints. While choices about materials and joint designs usually have to be made based on the nature of the components and the proposed service performance of the bonded assembly, those concerned with process parameters are numerous not only because of their variety but also because of the possibility of making incremental adjustments during trial runs to optimize joint quality by fine tuning. The main variables that affect solid-state bonding are the pressure, temperature, time, surface roughness, and, in some cases environment (Akselsen, 1992).

2.2.1 Effect of bonding temperature

Temperature is the most important parameter in the bonding process due to the fact that: *(i)* in thermally activated processes, a small change in temperature will result in the greatest change in process kinetics, diffusion, creep, compared with other parameters; and *(ii)* virtually all mechanisms in diffusion bonding are sensitive to temperature, plastic deformation, diffusion, creep. Temperature increases interaction across a metal/ceramic interface by increasing the mobility of atoms and also the mobility of dislocations in the metal during bonding. Since the mobility of dislocations increases with temperature and the flow stress correspondingly decreases, the pressure required for bonding decreases with increasing temperature. In general, the temperature required to obtain sufficient joint strength is typically within the range *0.6 and 0.95* T_m, where T_m is the absolute melting point of the base material. The effect of temperature is shown for Si_3N/Nb joints in Figure 3 (Lemus-Ruiz el al., 2006). It is seen that the interface in samples hot-pressed at 1400°C consists of a layer with one phase and thickness average of 2 μm, however the interface in samples hot-pressed at 1600°C consist of one layer with two intermixed phases and thickness average of 18 μm.

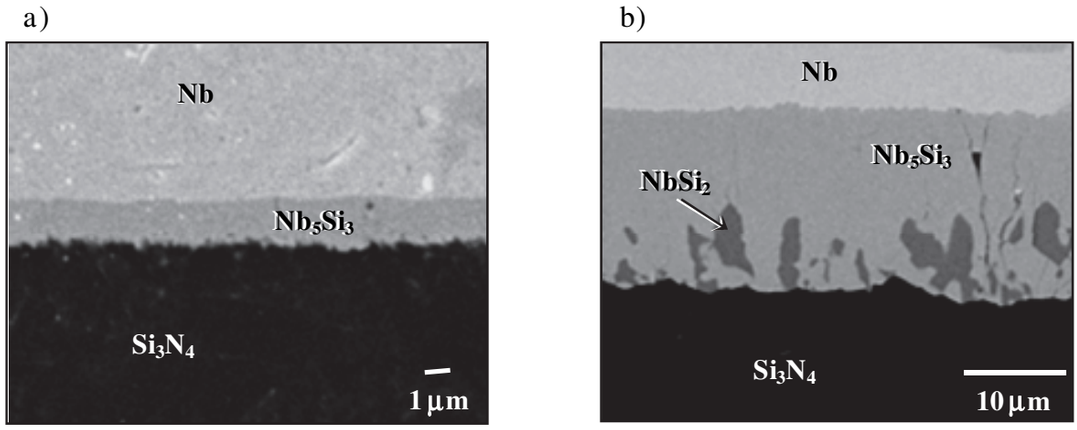


Fig. 3. Cross-section of the Si_3N_4/Nb interface for a sample hot-pressed at a) 1400°C for 120 minutes and b) 1600°C for 60 minutes in vacuum

On joining of metals to silicon nitride (Si_3N_4), an additional difficulty is introduced by the presence of nitrogen gas at the interface. Nitrogen gas is formed upon the dissociation of Si_3N_4, and it may or may not diffuse into the metal, depending on its solubility at the bonding temperature. In general the chemical reactions occurring when silicon nitride is in contact with a metal (Me) follows one of the following three routes (Richerson, 1992; Baker, 1992):

$$Me + Si_3N_4 = Me\ silicide + Me\ nitride \quad (1)$$

$$Me + Si_3N_4 = Me\ silicide + N_{2(g)} \quad (2)$$

$$Me + Si_3N_4 = Me\ silicide + Si \quad (3)$$

Comparing the thermodynamic stability of Si_3N_4 with those of metal silicides and nitrides, it is possible to predict the likely products of diffusion bonding. When the bonding temperature is above the minimum temperature required for reaction (2), it proceeds and

forms intermetallic compounds at the interface. The free nitrogen produced by this reaction diffuses into the metal when it has a high solubility for nitrogen. However, strong nitride formers, such titanium (Ti) and niobium (Nb), promote reaction (1) above the minimum temperature of reaction (2) and below the minimum temperature in the case of reaction (3). This effect can be observed for Si_3N_4/Ti and Si_3N_4/Nb joints in Figure 4 (Lemus & Drew, 2003; Lemus-Ruiz et al., 2006).

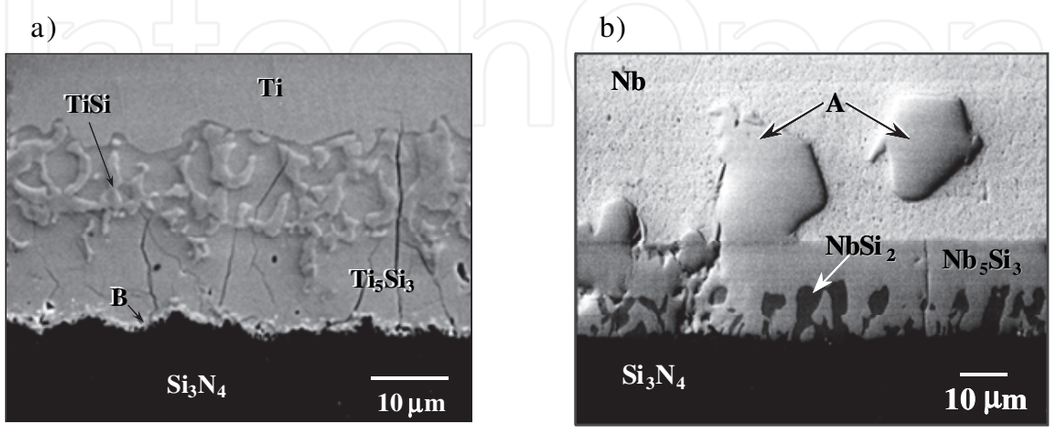


Fig. 4. Cross-section of samples hot-pressed for a) Si_3N_4/Ti at 1400°C for 180 minutes and b) Si_3N_4/Nb at 1600°C for 90 minutes in vacuum

In bonding of Si_3N_4/Ti at 1400°C for 180 minutes (Figure 4a) the interface consists of one layer with three intermixed phases. EPMA performed on this sample indicated that these phases were Ti_5Si_3, TiSi and the zone (B), which is a mixture of TiN containing Y, Al, O and Si. This is associated with segregation of the sintering aids, Y_2O_3 and Al_2O_3, during the decomposition of the ceramic to form an amorphous alumino-silicate. On the other hand, when Si_3N_4 is joined to Nb at 1600°C for 90 minutes (Figure 4b), the interface consists of one layer with Nb_5Si_3 and $NbSi_2$ intermixed phases and a zone (A) inside the metal, which are a mixture of niobium nitride and a trace of silicon. This is associated with the saturation of nitrogen in solution in the interface to form a niobium nitride phase. Because diffusion is the dominating reaction mechanism in solid state joining, silicide transformations may or may not be observed depending on the joining parameters, especially bonding temperature and time. These parameters affect the concentration of diffusing Si at the interface, and therefore, the nature of the resulting silicide. The optimum bonding temperature occurs at a point where the strength reduction due to residual stresses starts to balance the strength enhancement as a result of void elimination.

2.2.2 Effect of bonding time

The pressure applied in diffusion bonding is typically some small fraction of the room temperature yield stress of the base metal to avoid macroscopic deformation of the materials. In addition to establishing contact between the metal and ceramic, an important role of the pressure is to destroy the stable oxide film, through plastic deformation at the bonding temperature, present on the surface of most metals and this has a large effect on the integrity of the metal/ceramic bond. Process parameters as bonding temperature, time and pressure are strongly inter-related. Bonding times may vary from one second to several

hours depending on the metal/ceramic combination and the joining temperature (Schwartz, 1990). A relatively short bonding time is usually required to form a strong bond between a metal and ceramic under temperature and pressure conditions which are sufficiently high to cause rapid deformation of the metal. When prolonged times or higher temperatures are used, chemical reactions can progress at the interfaces of some systems and significantly influence bond quality. These reactions can initially enhance bonding, forming "chemical bridges", but often ultimately cause degradation because their growth progressively generates volume mismatch strains and stresses within the reaction product or at the product/workpiece interfaces.

Figure 5 shows results of bonding cermet of WC-Co to Ni samples produced at 980°C for 25 minutes (Lemus-Ruiz et al., 2009). It can be seen a continuous and homogeneous bonding line interface can be seen. The bonding process is governed by diffusion of Ni through the Co of the WC and diffusion of Co through Ni, forming a thin inter-diffusion zone. Line analysis using electron probe micro-analysis shows an overview of the Co, W, and Ni components through the interface. It can be clearly observed from the micro-analysis profiles of Ni and Co that the accumulation of these components in the bonding line with inter-diffusion of Ni to Co and Co to Ni.

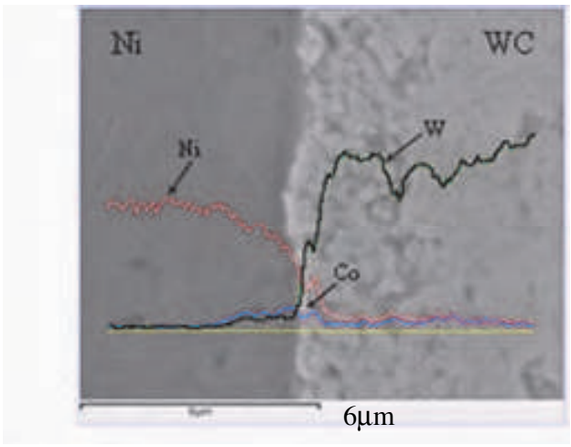


Fig. 5. Cross-section of the interface obtained in a WC/Ni sample bonded at 980°C for 25 minutes

2.2.3 Effect of surface roughness

Surface preparation before bonding is usually necessary for joint components and inserts. There are three main objectives: the first is the production of surfaces that are free of mobile contaminants such as oil films and surface layers of fragile or thick corrosion products, and any other protective layer that might inhibit bonding. Having produced clean surfaces, it is then necessary to ensure that there is macroscopic conformity between the mating surfaces of the components to be bonded. Without this, a lack of surface conformity of components to be diffusion bonded may limit good intimate contact when joining either directly or via thin interlayers. Finally, it is important to create microscopic topographic features on each material surface in order to encourage bonding. The presence of asperities on the bonding surfaces prevents large-scale plastic deformation at the surface because the metal is affixed between the asperities and limits the total area of contact between the metal and oxide-free ceramic, and, in addition, large voids are rarely closed (Treheux et al., 1994). Therefore, it is

necessary to polish the bonding surfaces prior to joining, improving the initial area of contact between the metal and ceramic and prevent the formation of large voids. The removal of rust and other thick corrosion products and the creation of desired macroscopic and microscopic topographies can often be achieved by mechanical treatment of the surfaces. Grinding can be used to prepare both metal and ceramic surfaces. In practice it can be useful also to avoid producing very smooth surface finishes because microscopic asperities can assist the disruption of surface oxides.

In order to establish the effect of the surface roughness of the materials to be joined on the interface growth, a series of unpolished $Si_3N_4/Ti/Si_3N_4$ samples were hot-pressed. These samples were as-ground, without final polishing. The average surface roughness of polished Si_3N_4 and Ti surfaces was *63.4 nm* and *53.4 nm*, respectively. By contrast the values for unpolished samples were *584 nm* and *1140 nm* for Si_3N_4 and Ti, respectively. Figure 6 shows a plot of the thickness of the interfaces as a) function of the square root of holding time for the samples hot-pressed at joining temperatures of 1400°C and 1500°C and b) as a function of temperature. The error bars correspond to the standard deviation for the average thickness of at least twenty measurements for each sample. Figure 6 shows an excellent parabolic fit of the growth of the reaction zone, which is characteristic of processes of reactive diffusion through an interface that is growing. It can be observed in Figure 6b that the interface obtained in samples hot-pressed with unpolished materials is significantly lower than that obtained with polished samples, however only a slight change is observed when the temperature is increased.

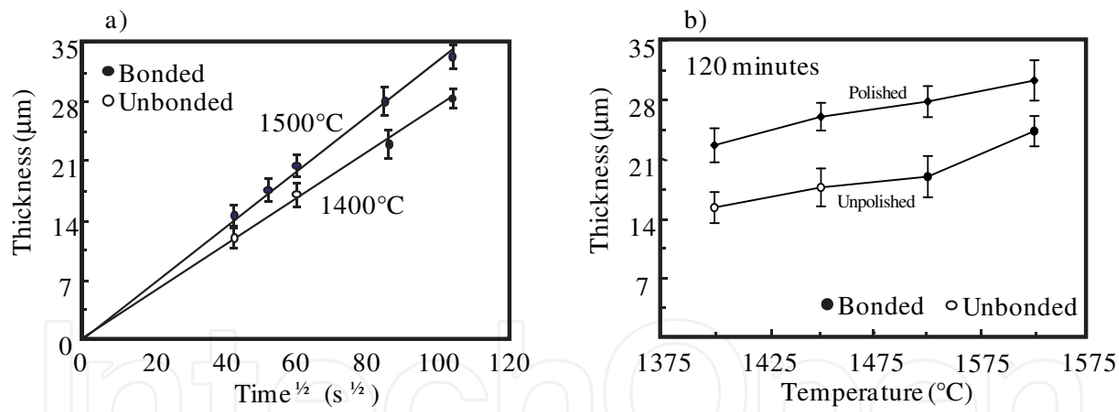


Fig. 6. Thickness of the reaction zone as a function of a) time and b) temperature in $Si_3N_4/Ti/Si_3N_4$ joining samples

3. Liquid-state diffusion bonding

The use of a liquid or a solid foil that flows readily under low applied stress to join materials can have advantages. Flow of a wetting liquid or of the ductile solid can fill irregularities in the surface and therefore imposes less stringent demands on surface preparation and the degree or extent of surface mating required. Indirect joining is the most common method of achieving high integrity joints using a wide range of intermediate bonding materials. The major categories of joining using an intermediate layer include joining with adhesives, cements, glasses or glass-ceramics, and brazes. The indirect bonding of ceramics includes

those techniques in which a liquid medium is responsible for bonding. Liquid phase bonding using molten metals has been widely used to create ceramic/ceramic and ceramic/metal joints. In cases where ceramics are being introduced into predominantly metal structures, brazes provide a more familiar joining material. Brazing is commonly used in the manufacture of high-integrity joints with good mechanical properties. However, brazing requires wetting of the ceramic into contact angles less than 90°C, which is often difficult to achieve because of the high stability of ceramic compounds. One way to promote wetting is to metallize the ceramic surface. Another alternative is to add small percentages of a reactive metal, e.g. Ti, which reacts with the ceramic and generally facilitates wetting via the formation of a more metallically bonded reaction product at the interface (Loehman et al., 1990), in order to promote wetting of the surface by the braze. A solid/liquid interface can be formed if the liquid wets or spreads thereby penetrating between irregularities at the solid surface. It has been widely considered that wetting is an essential prerequisite for the creation of a good bond. It is understood, however, that wetting alone is not sufficient to guarantee good adhesion since wetting can occur with either van der Waals or stronger 'chemical' bonding across the interface (Savov et al., 1997; Mortensen & Jin, 1992).

3.1 Wettability and contact angle

The wettability is the capability of solids to build interfaces with liquids, in other words, it is the ability of a liquid to spread over a solid surface. It describes the extent of intimate contact between a liquid and a solid; but it does not represent an index of the strength of the interface. The wettability of a given solid/liquid couple can be measured by considering the equilibrium forces in a system consisting of a drop resting on a flat solid surface in a given atmosphere, this method for evaluating wettability is called the sessile drop method. This technique enables measurement of both, θ and γ_{SG}, however, this method is an oversimplification of true and complex phenomena. The contact angle, θ, of a liquid on the solid surface is the parameter used to measured the degree of wetting; $\theta > 90°$ means non-wetting, $\theta = 0°$ means perfect wetting and $\theta < 90°$ indicates partial wetting. It is, however, ordinary practice to say that a liquid wets a solid when $\theta < 90°$. The shape of the drop results from the balance between the surface force and the interfacial forces that are trying to minimise the surface free energy of the system. Under thermodynamic equilibrium and steady state conditions, the contact angle is related to the three tensions γ_{SG}, γ_{SL} and γ_{LG} of the interfaces solid/gas, solid/liquid and liquid/gas, respectively, by the well-known Young equation;

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL} \quad (4)$$

High temperatures and extended contact times, usually promote chemical reactions enhancing or inducing wetting (Landry et al., 1996; Asthana, 1998). The Figure 7 shows the effect of time at temperature of 900°C on the contact angles of several Al-alloys with TiC ceramic in argon (Contreras et al., 2001). The criteria for selection of brazing alloys are that they must wet or coat the ceramic, form a chemical bond at the interfaces resulting in a strong joint, and they should cause minimal degradation of the base material or materials. Successful brazing alloys produce bonds that are, strong, reliable, and relatively inexpensive to manufacture. As is the case for any joining process, there are also some important constraints and concerns, many of which are the direct consequence of the presence and action of the reactive metal.

A popular technique adopted to enhance wetting is to add suitable alloying elements to the melt. Alloying additions can promote wetting with a solid surface by three mechanisms; 1) by decreasing the surface tension of the liquid due to adsorption onto` the surface of the liquid, 2) by decreasing the solid/liquid interfacial tension due to segregation of solute to the interface, and 3) by inducing a chemical reaction at the solid/liquid interface which in turn decreases the solid/liquid interfacial tension by forming a stable compound at the interface. Another method for improving wettability is the application of a metal coating to the surface of the ceramic which, in principle, increases the surface energy of the solid and acts as a diffusion barrier delaying the onset of reaction. Nickel and copper coatings are commonly used (Yokokawa et al., 1991).

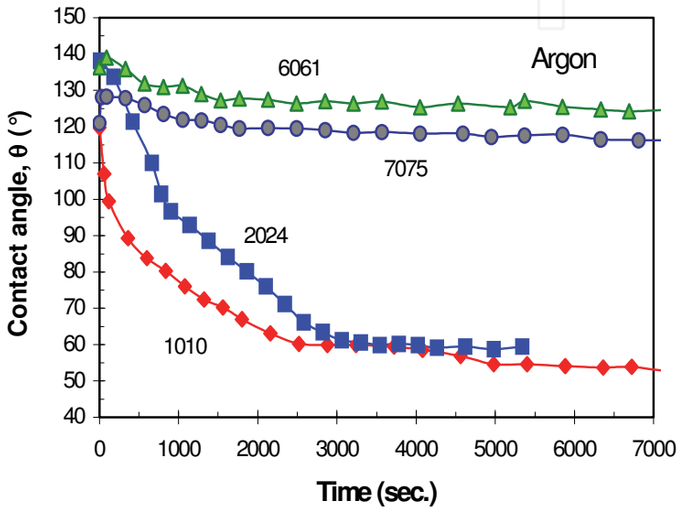


Fig. 7. Wetting behaviour of Al-alloys with TiC in Ar at 900°C (Contreras et al., 2001)

3.2 Brazing of silicon nitride

Joining ceramic/ceramic and ceramic/metal structures by brazing is attractive because of the flexibility of design that can be accommodated, the wide availability of the processing equipment, and the established use of brazing technique for high-integrity metal/metal structures such as aero-engine components. However, new and specially developed braze alloys are generally required to join ceramics because they are not wetted by conventional brazes based on Ag, Au, or Cu. These alloys, called "active brazes", contain components that react with the ceramics to change the chemistry of their surfaces to promote wetting and bonding. Many commercially available brazing alloys meet the main mechanical requirement of metal/ceramic joints, in which the more frequently used braze includes a Cu-Zn based alloy. Addition of small quantities of Ti increases the ceramic wettability and reactivity by diffusion of Ti across the interface (Zhang & He, 2010; Zou et al., 2009).

The Figure 8 shows a cross-section interface of diffusion bonding Si_3N_4/Cu/Ti combinations joined at temperature of 980°C. Liquid formation can occur by the interaction of Si with the Cu promoting bonding. Joining formed through the formation of a reactive interface on the metal side of the sample as a result of diffusion of N and Si and interaction of these species with Cu and Ti. Liquid formation can occur on the first step of the bonding, as a consequence of the interaction of Cu with Si and Ti.

The interface consisted of a continuous and homogeneous reaction layer free of porosity and containing several intermixed phases produced by chemical interaction, as well as the high affinity of Ti, Cu, Si and N. It can be observed that phase A correspond to reaction zone rich in Ti and Cu, however, in phase B increase the amount of Cu and Si, on the other hand, the phase C correspond to Cu interlayer remaining, and Ti and Si increase in phase D, which represent the diffusion-reaction produced during joining process.Liquid formation plays an important role in the joining process, because it increases the rate of the interface formation, improving the contact area between the bonding materials, and consequently the interaction is higher, promoting rapid diffusion of the material, since liquid diffusion is much faster than the diffusion in solid-state.

	Concentration (%at.)		
Phase	Ti	Cu	Si
A	52.34	33.54	14.12
B	41.30	40.62	18.07
C	11.20	80.95	7.85
D	57.51	14.97	27.53

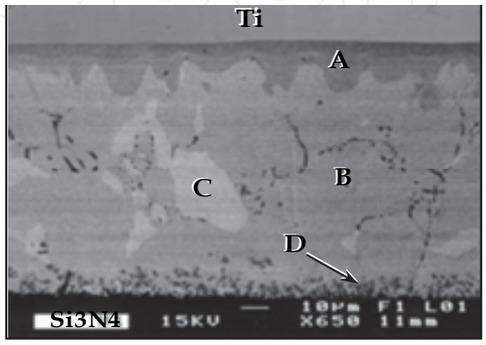


Fig. 8. Cross-section interface of a Si_3N_4/Cu/Ti sample bonded at 980°C for 5 minutes in Ar

3.3 Brazing of WC-Co cermets

On the other hand, during joining at 980°C of WC-Co cermets to Ni using Cu-Zn alloy as joining element, liquid formation occurs (melting point of 70Cu-30Zn (wt%)≅ 950°C) and joining takes place by liquid state diffusion of Co and Ni and interaction of these species with Cu and Zn of the liquid Cu-Zn alloy. Figure 9 shows a cross-section of the interface observed in brazing samples of WC/Cu-Zn/Ni produced at 980°C for 15 minutes (Lemus-Ruiz et al., 2008). It could be observed that increasing the bonding time, the diffusion increase forming a continuous bonding layer free of porosity. Electron probe micro-analysis performed on these samples indicated that Ni, Co, Cu, and Zn are in the diffusion interface, however no phases were detected and the components are in solution in the bonding interface. According to the thermodynamic, WC is stable at the bonding temperature; therefore W and C interactions with Ni or Cu-Zn are not expected in the joining zone. Diffusion is the dominating reaction mechanism; consequently the high affinity of Co and Ni for Cu and Zn resulted in immediate diffusion. Joining parameters, such as bonding temperature and time, affect the concentration of diffusion of the components at the interface, and therefore, the nature of the resulting interface.

An overview of the different components in the interface was obtained in a WC/Zn-Cu/Ni sample joined at 980°C for 15 minutes by line analysis using electron probe micro-analysis. The results are illustrated in Figure 10 where the Ni and WC are on the left and right, respectively. The scan line was chosen to start on the Ni side of the sample through the interface, Cu-Zn, finishing on the WC side.

Inter-diffusion of Cu-Ni and Cu-Co could be observed. The micro-analysis profile indicates the presence and even distribution of Zn concentration. In the region corresponding to diffusion zone high levels of Cu and Zn were observed, however evaporations of Zn during bonding could be occurred.

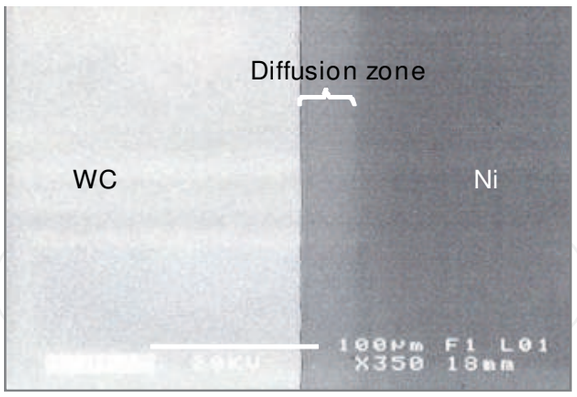


Fig. 9. Cross-section of the interface obtained in a WC/Cu-Zn/Ni sample bonded at 980°C for 15 minutes in Ar

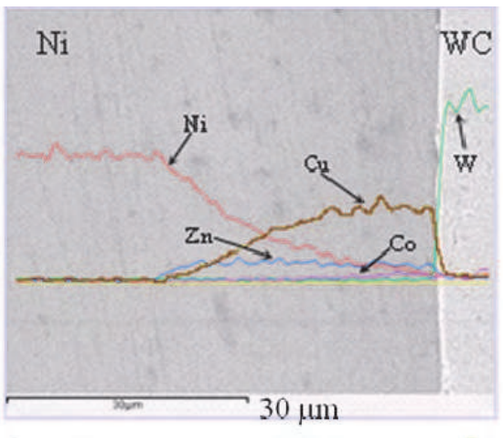


Fig. 10. Line analysis through the interface obtained in a WC/Cu-Zn/Ni sample joined at 980°C for 15 minutes in Ar

4. Mechanical evaluation

Several problems have been associated with the joint strength influencing the reliability of a joint. Figure 11 shows the schematic illustration of several important defect categories, which may cause scatter in strength directly (Suganuma, 1993). From the microscopic view, the reaction structure caused by wetting or by chemical and physical bond-ability between two faces may be of concern. These factors will reflect the distribution of un-joined or weakly bonded island-like defects on interfaces resulting in substantial reduction in joint strength. Un-joined areas reduce joint strength especially in solid-state joining. From the more macroscopic view, when a reaction layer grows, cracking occurs in the layer, which frequently influences joint strength. Thermal or residual stress in a joint becomes another important factor.

The development of residual stresses at the interface when the material is cooled down from the bonding temperature to room temperature is one of the major problems in ceramic/metal joining. These residual stresses reduce the strength of the bonded material

and in some cases lead to joint failure during or after the joining process. The mechanical characterization of a metal/ceramic joint is a complex problem. There are a variety of different properties to be considered in ceramic/metal joints. Depending on the application of the joint, some properties are more important than others. However, the mechanical performance is one of the most important properties for any joint (Anderson, 1989). The strength of metal/ceramic joints materials is generally characterized by bend testing where the test specimen can have a circular, square, or rectangular cross section and is uniform along the complete length.

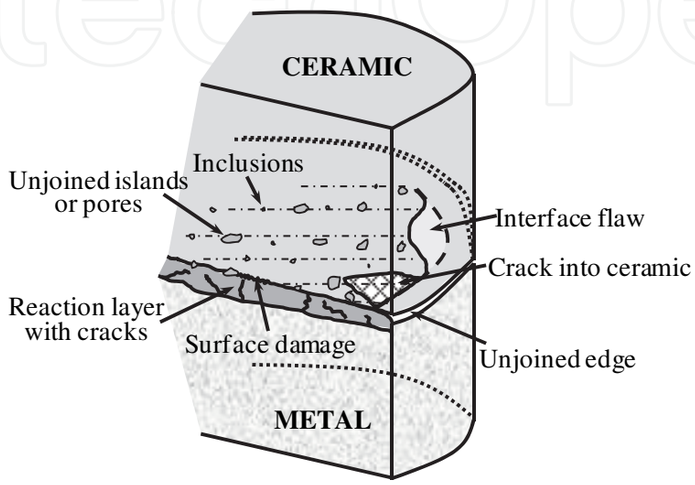


Fig. 11. Schematic illustration of various structural defects in ceramic/metal joint

The final goal for joining research will be in establishing a technique producing a tightly.
The interfacial strength of metal/ceramics joints is determined by four-point bending test using a universal testing system and a bending jig. The specimen is carefully placed in the bottom part of the jig, with the interface plane parallel to the plane of vertical displacement of the plunger. The load is applied at a low vertical speed of 0.5 mm/min until the applied load resulted in fracture of the specimen (Lemus-Ruiz & Aguilar-Reyes, 2004). The bend strength is defined as the maximum tensile stress at failure and is often referred to as the modulus of rupture *(MOR)*. The bend strength for a circular test specimen can be calculated using the general flexure stress formula described in equation (Richerson, 1992):

$$X = \sigma_{4\text{-pt}} = 16.F.d \;/\; \pi.D^3 \tag{5}$$

Where F is the load at fracture, d is the distance between the outer and inner span of the four-point bend jig and D is the diameter of the specimen. For each set of experimental conditions studied, temperature and time, an average of at least five samples must be used to determine the bending strength for each joining condition.

4.1 Bonding strength of Si_3N_4/Ti and WC/Ni

The strength of diffusion-bonded ceramics to metals depends on the nature and microstructure of the interface between the materials. In order to establish a mechanical evaluation of joints in hot-pressed Si_3N_4/Ti/Si_3N_4 samples, and WC/Cu-Zn/Ni and WC/Ni samples, the joint strength was measured using four-point bending (Lemus-Ruiz & Aguilar-Reyes, 2004; Lemus-Ruiz et al., 2009). The samples used for bend testing were of 50 mm in

length and 7 mm in diameter. An example of a test sample is shown in Figure 12. The modulus of rupture (MOR) was calculated for $Si_3N_4/Ti/Si_3N_4$ samples hot-pressed at 1500°C and times varying from 30 to 180 minutes: the results obtained are shown in Figure 13. The error bars correspond to plus or minus the standard deviation for the average joint strength of at least five samples for each set of experimental conditions. It can be observed in Figure 13a that the strength of the joint increased from a value of 18 MPa and reached a maximum value of 147 MPa, when the time was increased from 30 to 120 minutes, respectively, and decreased beyond this time. The detrimental effect of the thickness of the reaction layer can be observed in the case of samples hot-pressed for three hours, where the strength of the joint decreased on compare with those samples hot-pressed for two hours. The effect of the growth of the reaction layer on the modulus of rupture of the $Si_3N_4/Ti/Si_3N_4$ samples can be more clearly observed in Figure 13b, which presents the results of the bending strength as a function of temperature for $Si_3N_4/Ti/Si_3N_4$ samples hot-pressed under vacuum for a constant time of 120 minutes. The effect of the temperature was more pronounced than the effect of the time. It can be observed that the strength of the joint increased from 64 to 147 MPa when the temperature was raised from 1400 to 1500°C. However, the joint strength decreased, above 1500°C.

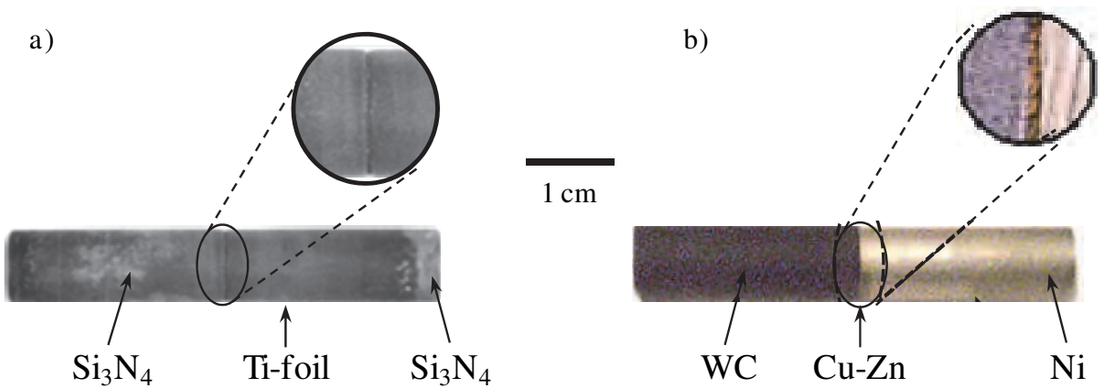


Fig. 12. Schematic representation of a) $Si_3N_4/Ti/Si_3N_4$ and b) WC/Cu-Zn/Ni samples

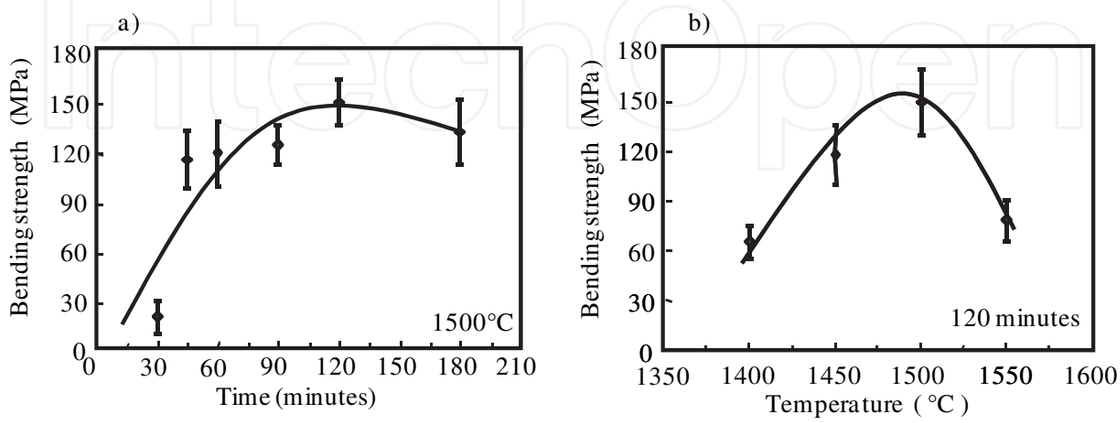


Fig. 13. Modulus of rupture in function of a) time and b) temperature for $Si_3N_4/Ti/Si_3N_4$ samples hot-pressed at 1500 C in vacuum

On the other hand, the results of modulus of rupture calculated for a) WC/Cu-Zn/Ni and b) WC/Ni samples diffusion (liquid and solid state, respectively) joining at 980°C and times varying from 5 to 60 minutes in argon atmosphere, are shown in Figure 14. In Figure 14a, it can be observed that the strength of the joint increased from a value of 233 MPa and reached a maximum value of 255 MPa, when the time was increased from 5 to 15 min, respectively, and decreased beyond this time. This improvement was attributed to the increase of interface reaction and formation of a strong chemical bridge between the two materials. On the other hand, the thickness of the reaction zone increases with time and may dominate in the final strength.

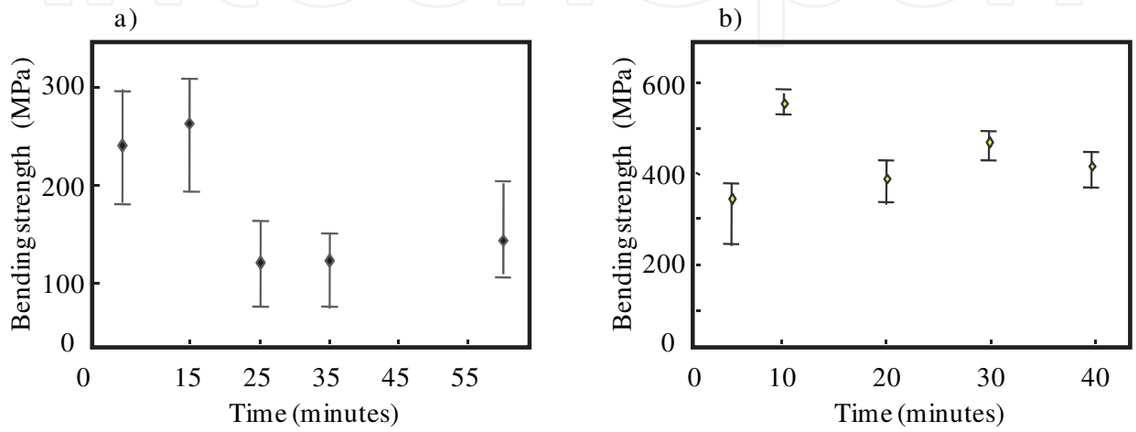


Fig. 14. Modulus of rupture for a) WC/Cu-Zn/Ni and b) WC/Ni samples joined at 980°C

Reaction products are generally brittle, and as the thickness of these phases increases, the joint strength, at first, rises due to the creation of a strong, integral bond and then reaches a maximum at a certain thickness and then decreases as the interface continues to grow. The strongest joint was obtained for joining conditions of 980°C and 15 minutes, with a resulting average bending strength of 255 MPa; however, joint strengths greater than 100 MPa in average were produced at 980°C and times vary from 5 to 60 minutes. In Figure 14b, four-point bending testing gave a maximum average joint strength higher than 300 MPa for WC/Ni samples produced by solid state diffusion bonding at 980°C. It can be observed a maximum average value joint strength of 576 MPa when the time was of 10 minutes, however, it value decreased when the time increase until 307 MPa at 5 minutes. The effect of a reaction layer on the interface strength depends on a number of factors such as the mechanical properties of the reaction layer, its thickness and morphology. The choice of suitable conditions to prepare ceramic/metal joints requires knowledge concerning the mechanism of reaction between the materials and the evolution of the interface. The thickness of the metal layer is very important, due that it affects directly the mechanical properties of a metal/ceramic joint. Therefore, the reaction layer thickness must be controlled in order to ensure good joint strength.

4.1.1 Interpretation of joint strength

The effect of a reaction layer on the interface strength depends on a number of factors such as the mechanical properties of the reaction layer, its thickness and morphology, the strength of the interfacial bond and the mode of loading at the interface. Reactions formed at

metal/ceramic interfaces include solid solutions, amorphous and crystalline phases. Each of these reaction products forms a different type of interface between the metal and ceramic and the relative efficiency of these various types of reaction products on the strength of metal/ceramic interfaces is not fully understood. However, most reaction layers are brittle and therefore potentially detrimental to the interface properties. Although the concentration of residual stresses in joints is a function of the joining temperature, the thickness of the reaction zone may dominate in the final strength. Reaction products are generally brittle and as the thickness of these phases increases, the joint strength, at first rises due to the creation of a strong, integral bond and then reaches a maximum at a certain thickness and then decreases as the interface continues to grow. Therefore, the reaction layer thickness must be controlled ensure good joint strength. It is clear that the amount of interfacial reaction played a major role in determining the final mechanical properties of the joints. Furthermore, the nature of the reaction products may also have influenced the mechanical properties of the joints. The mechanical properties of a metal/ceramic interface depend upon many factors such as the elastic properties of the metal and ceramic, the thickness of the metal layer, the specimen geometry and the mode of loading.

In summary, the choice of suitable conditions to prepare ceramic/metal/ceramic joints requires knowledge about the mechanism of reaction between the materials and the evolution of the interface. The maximum value of 147 MPa was obtained for $Si_3N_4/Ti/Si_3N_4$ samples hot-pressed at 1500°C and 120 minutes. This strength is of the same order as the MOR reported for diffusion bonding of Si_3N_4/Si_3N_4 joints using a ZrO_2 interlayer made at 1550°C and 60 minutes (175 MPa) (Akselsen, 1992), and higher than that reported for brazing of Si_3N_4 to different metals, i.e. Mo/Si_3N_4 joints brazed with Cu-5%Cr alloy reports 120 MPa (Okamoto, 1990).

4.1.2 Fractography

All joints $Si_3N_4/Ti/Si_3N_4$ fracture samples showed the same type of fracture mode shown in Figure 15. The fracture originated and mainly propagated along the Si_3N_4/reaction zone interface and passed through the Ti metal to the other side of reaction zone/Si_3N_4 interface.

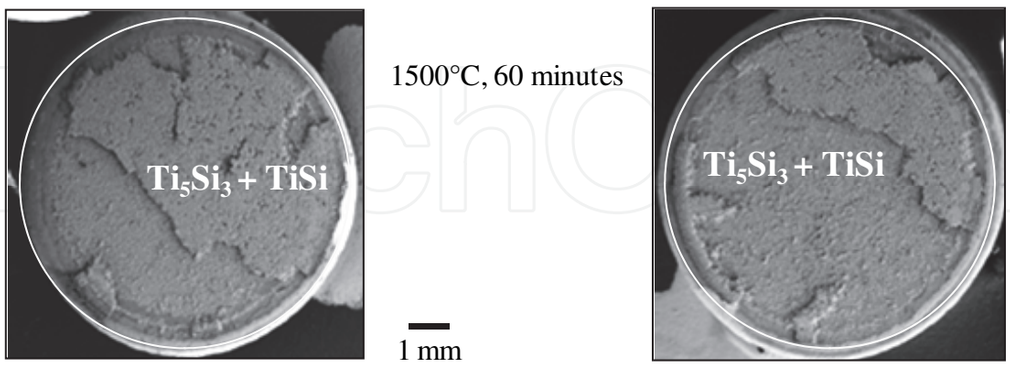


Fig. 15. Fractograph of $Si_3N_4/Ti/Si_3N_4$ samples after four-point bending test

The main part of the fracture surface was on the Ti-silicide of the Si_3N_4/reaction zone interface and probably initiated at the edge of the sample. Edges and corners are a major source of failure for metal/ceramic interfaces when there is a mismatch in either the thermal expansion or elastic modulus of the metal and ceramic. When a metal has either a larger

thermal expansion coefficient or a lower modulus than the ceramic or both (which is often the case), the unconstrained metal develops a smaller lateral expansion at the interface than the ceramic. In order to maintain continuity at the interface, the metal must be uniformly extended by the application of edge forces. Surface forces which are equal in magnitude but opposite in sign must then be applied to the metal in the bonded state to achieve stress-free conditions at the surface and this introduces large normal and shear stresses near the edge of the metal/ceramic joint. A mismatch in modulus generates interfacial tensile stresses at the edge and thus always enhances the propensity to fracture. On the other hand, ceramics are more brittle, stiffer, and have lower thermal expansion coefficients than metals, thus, the interface between the ceramic and the metal will be in a state of stress when cooled from the joining temperature. If the metal, Ti, undergoes plastic deformation during the cooling cycle, some of the interfacial stresses could be relieved, resulting in an increased joint strength (El-Sayed et al. 1997). The amount of the plastic deformation depends on the yield strength of the metal. Generally the lower the yield strength, the more plastic deformation will occur and consequently this could lower the residual stresses. However the interface could have some defect or point of high stress concentration where fracture is initiated.

On the other hand, all WC/Cu-Zn/Ni joints fracture samples showed the same type of fracture mode where the fracture originated and mainly propagated along the WC/reaction zone interface and passed through the other side of reaction zone/Ni interface. However, in the case of WC/Ni samples the fracture did not occur in the interface of the joint, but the failure occurred in the metal Ni.

5. Conclusion

The amount of reaction between the ceramics and metal is an important factor in the mechanical reliability of the joints. Excessive growth of the reaction layer decreased joint strength.

Bending tests performed on $Si_3N_4/Ti/Si_3N_4$ joints hot-pressed at different joining temperatures confirmed the important relationship between the interface thickness and joint strength. Increasing the joining time further reduced the joint strength. Thickness of the reaction interface increases when bonding time increases. On the other hand, eutectic liquid formation during joining process plays an important role in promoting bond and interface formation. The surface roughness of the starting materials is an important factor affecting the extent of the interface growth. For similar joining conditions, hot-pressing of samples using unpolished materials produced thinner interfaces than polished samples.

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7. References

Akselsen, O.M. (1992). Diffusion bonding of ceramics. *Journal of Materials Science,* Vol. 27, No. 3, pp. 569- 579

Almond, E.A., Cottenden, A.M. & Gee, M.G. (1983). Metallurgy of interfaces in hardmetal/metal diffusion bonds. *Metals Science*, Vol. 17, pp. 153-158

Anderson, R.M. (1989). Testing advanced ceramics. *Advanced Materials Procesing,* Vol. 3, pp-31-36

Asthana, R. (1998). Reinforced cast metals-part II evolution of the interface. *Journal of Materials Science,* Vol. 33, no. 8, pp. 1959-1980

Baker, H. (1992). *Alloy Phase Diagrams,* (Vol. 3), ASM handbook International, Materials Park, Ohio, USA

Chen, I.W. & Argon, A.S. (1981). Diffusive growth of grain-boundary cavities. *Acta Metallurgy*, Vol. 29, pp. 1759-1768

Contreras, A., Lopez, V.H., Leon, C.A., Drew, R.A.L & Bedolla, E. (2001). The relation between wetting and infiltration behavior in the Al-1010/TiC and Al-2024/TiC systems. *Advances in Technology of Materials and Materials Processing Journal*, Vol. 3, pp. 27-34

Dunford, D.v. & Wisbey, A. (1993). Diffusion bonding of advanced aerospace metallics. *Materials Research Society Symposium Proceeding,* Vol. 314, pp. 39-50

El-Sayed, M.H., Naka, M. & Schuster, J.C. (1997). Interfacial structure and reaction mechanism of AlN/Ti joints. *Journal of materials science,* Vol. 32, pp. 2715-2731

Howe, J.M. (1993). Bonding, structure and properties of metal/ceramic interfaces. *Materials Research Symposium Proceeding,* Vol. 314, pp. 27-37

Landry, K., Kalogeropuolou, S., Eustathopoulos, N., Haidich, Y. & Krasovsky, V. (1996). Characteristic contact angles in the aluminiumn/vitreous carbon system. *Scripta Materialia*, Vol. 34, No. 6, pp. 841-846

Lemus, J. & Drew, R.A.L. (2003). Joining of silicon nitride ceramics using a titanium foil Interlayer. *Materials Science and Engineering A,* Vol. 352, pp. 169-178, ISSN 0921-5093

Lemus-Ruiz, J. & Aguilar-Reyes, E.A. (2004). Mechanical properties of silicon nitride joints using a Ti-foil interlayer. *Materials Letters*, Vol. 58, No. 19, pp. 2340-2344, ISSN 0167-577X

Lemus-Ruiz, J., Ceja-Cárdenas, L., Salas-Villaseñor, A.L. & Bedolla-Becerril, E. (2009). Mechanical evaluation of tungsten carbide/nickel joints produced by direct diffusion bonding and using a Cu-Zn alloy, *Proceeding of the 4th International Brazing and Soldering Conference,* American Welding Society, ISBN 978-0-87171-751-1, Orlando, Florida, USA

Lemus-Ruiz, J., Ceja-Cardenas, L., Verduzco, J.A. & Flores, O. (2008). Joining of tungsten carbide to nickel by direct diffusion bonding and using a Cu-Zn alloy. *Journal of Materials Science*, Vol. 43, pp. 6296-6300, ISSN 0022-2461

Lemus-Ruiz, J., León-Patiño, C.A. & Aguilar-Reyes, E. (2006). Interface behaviour during the self-joining of si_3n_4 using nb-foil interlayer. *Scripta Materialia*, Vol. 54, No. 7, pp. 1339-1343, ISSN 1359-6462

Locatelli, M.R., Dalgleish, B.J., Nakashima, K., Tompia, A.P. & Glaeser, A.M. (1997). New approaches to joining ceramics for high-temperature applications. *Ceramics Internationals,* Vol. 23, pp. 313-322

Loehman, R.E., Tomsia, A.P., Pask, J.A. & Johnson, S.M. (1990). Bonding mechanisms in silicon nitride brazing. *Journal of the American Ceramic Society,* Vol. 73, No. 3, pp. 552-558

Mortensen, A. & Jin, I. (1992). Solidification processing of metal matrix composites. *International Materials Reviews*, Vol. 37, No. 3, pp. 101-128

Nicholas, M.G. (1990). *Joining of Ceramics; Advanced Ceramic Reviews-Institute of Ceramics,* Chapman and hall, New York, USA

Okamoto, T. (1990). Interfacial structure of metal-ceramic joints. *ISIJ International,* Vol. 30, No. 12, pp. 1033- 1034

Peteves, S.D., Ceccone, G., Paulasto, M., Stamos, V. & Yvon, P. (1996). Joining silicon nitride to itself and to metals. *JOM,* (January), pp-48-52

Richerson, D.W. (1992). *Modern Ceramic Engineering,* (2nd Edition), Marcel Dekker, New York, USA

Savov, L., Heller, H.P. & Janke, D. (1997). Wettability of solids by molten metals and alloys. *Metallurgy*, Vol. 51, No. 9, pp. 475-485

Schwartz, M.M. (1990). *Ceramic Joining,* ASM international, Materials Park, USA.

Suganuma, K. (1993). Reliability factors in ceramic/metal joining. *Research Society Symposium Proceeding,* Vol. 314, pp. 51-60

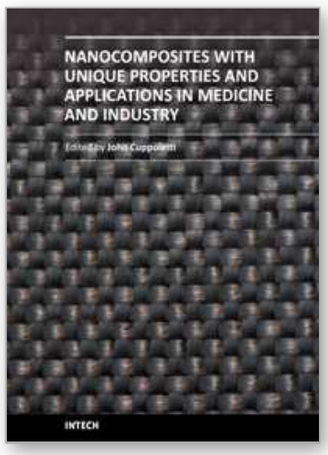
Treheux, D., Lourdin, P., Mbongo, B. & Juve, D. (1994). Metal/ceramic solid state bonding: mechanisms and mechanics. *Scripta Metallurgy et Materials,* Vol. 31, No. 8, pp. 1055-1060

Yokokawa, H., sakai, N., Kawada, T. & DokiYA, M. (1991). Chemical potential diagram of Al-Ti-C system: Al_4C_3 formation on TiC formed in Al-Ti liquids containing carbon. *Metallurgical and Materials Transactions A*, Vol. 22, pp. 3075-3076

Zhang, J. & He, Y. (2010). Effect of Ti contento n microstructute and mechanical properties of Si_3N_4 joints brazed with Ag-Cu-Ti+Mo composite filler. *Materials Science Forum,* Vol. 654-656, pp. 2018-2121 doi:10.4028/www.scientific.net.

Zou, J., Jiang, Z., Zhao, Q. & Chen, Z (2009). Brazing of Si_3N_4 with amorphous $Ti_{40}Zr_{25}Ni_{15}Cu_{20}$ filler. *Materials Science and Engineering A,* Vol. 507, pp. 155-160. www.elsevier.com/locate/msea.

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Nanocomposites with Unique Properties and Applications in Medicine and Industry

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This book contains chapters on nanocomposites for engineering hard materials for high performance aircraft, rocket and automobile use, using laser pulses to form metal coatings on glass and quartz, and also tungsten carbide-cobalt nanoparticles using high voltage discharges. A major section of this book is largely devoted to chapters outlining and applying analytic methods needed for studies of nanocomposites. As such, this book will serve as good resource for such analytic methods.

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