

Metal ceramic joining with active filler metal in dental practice

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ARTICLE INFORMATION :

<https://doi.org/10.56801/MMD33>

Received: 04 June 2024

Accepted: 07 July 2024

Type of paper: Review paper



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ABSTRACT

This paper examines the phenomena that arise at the interface between ceramics and active filler metal during the metal-ceramics bonding process in dental practice. It focuses on three interrelated sub-processes: the wetting of the ceramic surface, the chemical interactions at the interface, and the diffusion across the moving interface. Additionally, the study explores the grain boundary grooves on the ceramic surface, highlighting their role as catalytic surface phenomena.

Following a brief overview of dental metals and bioceramics, the composition and properties of the brazing alloys used in dental practice are presented and explained in detail.

Keywords: metal-ceramic joining, active filler metal, brazing, dentistry.

1. Introduction

Metals and ceramics differ significantly in their thermal and electrical conductivity, hardness, ductility, wear resistance, and corrosion resistance. However, when combined in metal-ceramic joints, they leverage their distinct properties to enhance many modern applications (Mishra et al., 2020). One of the joining procedures, namely joining using active filler metal, is particularly interesting in terms of success and economy. This approach uses the alloying of the filler metal with reactive elements like Ti and Zr to induce wetting of the ceramic surface, which is required for successful joining (Uday et al., 2016). Joining ceramics to metallic materials is a difficult task that requires collaboration from various fields of materials research.

When it comes to fusing techniques, soldering and active metal brazing are the most efficient. In essence, braze melts and flows between the two pieces of material during this process. This process, known as “wetting,” is very important, especially when brazing ceramics. Many different materials can be fused together to create joints between materials; materials that melt at temperatures above ~450 °C are referred to as brazes, and materials that melt at temperatures below ~450 °C are referred to as solders (Raic, 2010).

There are two main ways to promote wetting: either put something in the braze to cause wetting, or apply something on the ceramics' surface to cause the braze to wet. While braze modification entails the use of an

active metal brazing process, surface treatments include metallization, metal coating, and metal hydride treatment. In either scenario, the actual brazing process occurs in a vacuum greater than 10^{-4} Nm⁻² or in a regulated environment like nitrogen or argon (Rudolf et al., 2024, Stamenković et al. 2009).

2. Metal ceramic joining with active filler metal

The most significant phenomena for metal-ceramic joining procedures occur at the liquid active filler metal/ceramic interfaces. Figure 1 illustrates an interdisciplinary effort where many materials science domains must collaborate with transport phenomena. This work presents several methodologies required to address phenomena on ceramic surfaces in detail. Three stages are considered: the wetting of an authentic ceramic surface, the chemical reactions at the contact, and the diffusion with a moving interface. The appearances at the grain boundary grooves of the ceramic surface are then depicted as catalytic surface phenomena.

2.1. Wettability of an authentic ceramic surface

Young was the first to define the contact angle empirically, and this definition forms the basis of most wetting investigations. The horizontal pressures caused by surface tensions acting on a liquid drop in contact with a solid are balanced by this equation. According to Young, when a

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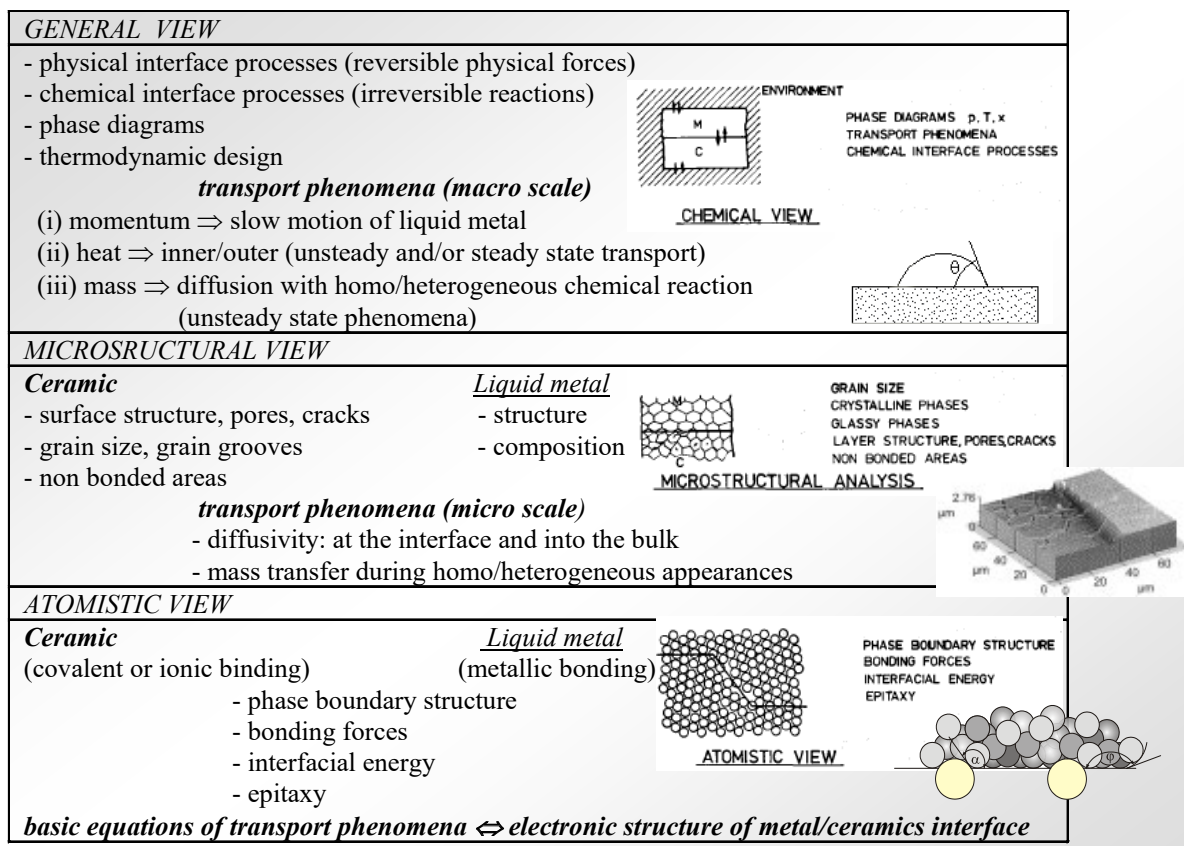


Fig. 1. Interdisciplinary collaboration in addressing phenomena at liquid active filler metal/ceramic interfaces

liquid is deposited on a solid, it usually stays in the form of a drop with a distinct contact angle between the liquid and solid phases. Anyhow, traditional literature contains the physics-chemical principles that underlie wetting action.

Wettability is highly difficult in real systems. Simple surface roughness can occasionally have complicated and contradicting impacts on wettability. Furthermore, surface and interfacial energies, and hence wettability, can be greatly impacted by chemical segregation in both the liquid and solid phases. Additionally, because interfacial processes alter the wetting characteristics over time, estimating the level of wetting is challenging. The connection between interfacial reactions and wetting is poorly understood; for example, molten aluminum exhibits low contact angle and high wettability against ceramics, but molten copper displays a high contact angle and low wettability against ceramics like Si_3N_4 , SiC , and ZrO_2 . In contrast, there are three stages involved in the wetting of a MgO/Al system: (1) the vibratory phase, which is a phase of chemical quasi-equilibrium; (2) the constant phase; and (3) the decreasing phase, which is a phase of chemical reaction. Since the drop is brought on by interfacial processes, the rate at which the contact angle decreases in phase (3) is dependent on temperature as well as the bulk and/or surface characteristics of the ceramics.

The wettability models forecast whether a system will get wet, but they are unable to forecast how quickly a system will get wet. It is difficult to model the spreading kinetics theoretically. Surface abnormalities such as precursor film formation, surface pollution, and irregularities make modeling difficult, even for nonreactive systems. The kinetics of spreading in reactive systems are complicated by interfacial reactions (e.g., oxidation) occurring at the interfaces between liquid and solid. A further obstacle to the verification of a spreading mechanism is the scarcity of experimental data. The gathering of spreading kinetics and reaction-rate data is difficult due to the rapid interfacial reactions and spreading kinetics. Figure 2 displays typical spreading data on alumina for copper-titanium alloys.

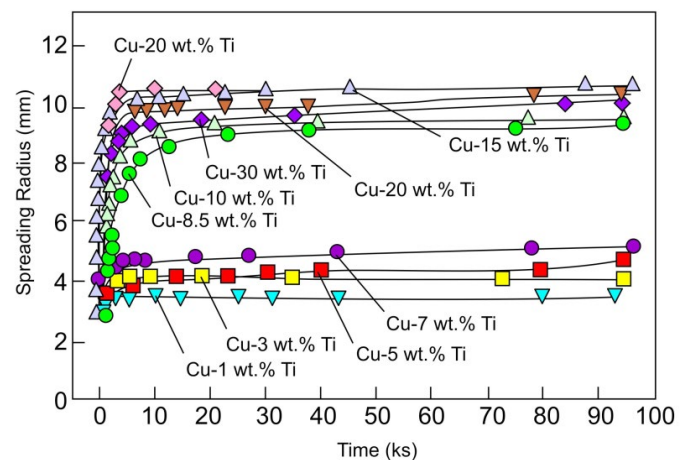


Fig. 2. The spreading data for 1.2 g samples of copper-titanium alloys over alumina at 1120°C provide an example of rapid spreading kinetics. adapted from (Meier et al. 1995)

2.2. Chemical reactions between liquid metal and ceramic surface

It is believed that reactant molecules of liquid metal are altered, energized, or otherwise impacted to produce intermediates in the regions near the surface, explaining the activity of a polycrystalline surface. One theory suggests that the intermediate is formed by the affiliation of a reactant molecule with a specific area of the surface; in other words, the molecules are connected to the surface in some manner. According to a different idea, molecules are believed to descend into the liquid metal near the surface and experience surface forces. The molecules are still in this perspective, but they have undergone modification. According to a third idea, at the solid surface, a free radical, or active complex, is created. After that, the free radical returns to the main liquid stream and starts interacting with new molecules in a series of reactions that end with its destruction. This hypothesis sees the surface only as a source of

free radicals, with the reaction taking place in the liquid metal's main body, in contrast to the other two hypotheses that believe the reaction to occur close to the surface (Raic, 2010, Mihailovic et al., 2015).

On the other hand, it is crucial to consider the variations in the standard free energy for the formation of nitrides, carbides, and oxides with respect to temperature to understand reactivity. By analyzing these thermodynamic parameters, we were able to predict whether a metal could break down ceramics into their respective nitride, carbide, or oxide states when the metal came into contact with the ceramics.

2.3. Diffusion with a moving interface

Diffusion steps are included in the observed process along with chemical interactions at a solid/liquid border (Raic, 2000, 2003). The motion of the phase boundary is one outcome of these transitory processes. Two phases are in touch in the overall scenario, as shown in Figure 3. The moving phase boundary is located at $x = X$. At this boundary, the equilibrium concentrations of, for example, Al_2O_3 , which coexist in ceramics and melted metal at the temperature under discussion, are represented by the symbols C_0 and $C^* = C(X, t)$.

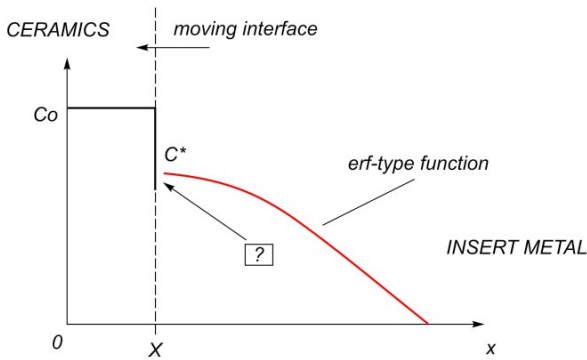


Fig. 3. The profile of concentrations during transient diffusion

At the interface, the material balance looks like this:

$$-D \left(\frac{dC}{dx} \right)_{x=X} = (C^* - C_0) \frac{dX}{dt} \tag{1}$$

where C is the Al_2O_3 concentration during transient diffusion, and D is the diffusion coefficient of Al_2O_3 in the molten metal, assumed to be independent of composition. The next condition is that the concentrations on either side of the interface are related by the equilibrium expression of the form: $C_0 = KC^*$, where K is the partition ratio between the phases.

Eq. 1 describes the locus of X with time. Relationship between C_0 and C^* :

$$\pi^{-0.5} [C^* / (C^* - C_0)] = \beta \exp \beta^2 \operatorname{erf} \beta \tag{2}$$

when

$$X = 2\beta(2D)^{0.5} \tag{3}$$

is recognized. One can assess the function of β , $(\beta \exp \beta^2 \operatorname{erf} \beta)$ from standard manuals. Thus, if C_0 , C^* , X , and t are measured, the D can be computed. Table 1 provides the illustrative computed surface diffusivities for a few metal/alumina systems with groove widths (w) ranging from 1 to 10 μm .

Table 1: Several metal/alumina systems' surface diffusivities (Saiz et al., 1999)

System	Temperature (K)	Surface Diffusion, wD (m^3s^{-1})
Ni/ Al_2O_3	1773	4.4×10^{-19}
Au/ Al_2O_3	1373	1.8×10^{-24}
Cu/ Al_2O_3	1423	2.8×10^{-22}
Al/ Al_2O_3	1373	1.1×10^{-19}

Groove widths (w)

2.4. Appearances at the grain boundary grooves

Several processes can generate resistance to the overall reaction that occurs at the liquid-solid interface (Raic, 2003; Mihailovic et al., 2006). Figure 4 depicts a single groove between two grains. (i) Liquid metal film resistance: Reactants diffuse from the main body of the liquid metal to the outer surface of the solid ceramic. (ii) Diffusion resistance at the groove: Reactants pass through the groove into the ceramic. The majority of the reaction occurs within the groove. (iii) Surface phenomenon resistance: At some point during their migration, reactant molecules become attached to the ceramic's surface. They react and form compounds, which are then released into the liquid phase within the groove. (iv) Product diffusion resistance through grooves: The reaction products then disperse from the groove. (v) Liquid metal film resistance to products: The products encounter resistance as they move through the liquid metal films. The products are subsequently transferred from the mouth of the groove to the main liquid stream. (vi) Resistance to heat flow: For reactions involving heat release or absorption, the heat flow into or out of the reaction zone may be insufficient to maintain the isothermal condition of the liquid metal/solid ceramic specimen. If this occurs, the specimen will cool or heat, significantly affecting the reaction rate. Therefore, the reaction rate may be influenced by the heat transfer resistance across the liquid film or within the ceramic (Levenspiel, 1998).

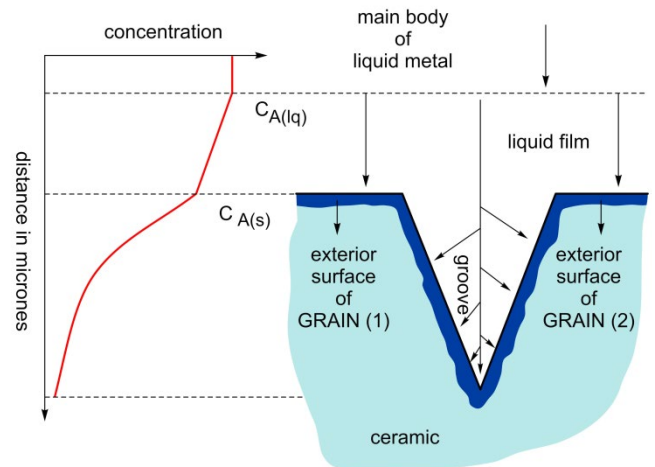


Fig. 4. Appearances around an element of single groove between two grains (Raic et al., 2010)

Typically, the reaction layer expands significantly within the first minute. After a few minutes, the thickness of the reaction layer gradually increases, following a parabolic pattern over time. Therefore, the growth of the product layer can be observed as a two-step process: an initial rapid thickening phase followed by a second phase with a parabolic rate, which is considered to be diffusion-controlled (Baldwin et al. 1994).

The roughness of the substrate/ceramics surface may contribute to the rapid initial development of the layer. However, capillarity supports slower growth. Capillary mass transfer is known to cause a grain boundary groove to form on the surface of a polycrystalline material when a boundary contacts an interface between a solid and

another phase. Mass transport can occur through various mechanisms, including interfacial diffusion, volume diffusion on either side of the contact, and interfacial reaction (solution-precipitation). Depending on the system's physical characteristics and groove size, one of these mechanisms will regulate the rate, resulting in distinct groove shapes and growth dynamics.

The rate of reaction for the solid ceramic substrate/liquid metal sample could depend on several factors:

1. Surface dynamics, which can vary when grain boundary grooves form.
2. Resistance at the grain boundary groove (GBG), creating internal concentration gradients. The effects of "volume diffusion" and "surface diffusion" on groove growth are discussed in Saiz et al. (1999).
3. Temperature gradients at the contact between the liquid metal and solid ceramics, induced by heat loss or absorption during the process.
4. Diffusion resistance or concentration gradients in the liquid metal film.

3. Dental practice

Dental materials can be divided into three categories: auxiliary, restorative, and preventive (Craig and Powers, 2002).

Pit and fissure sealants, leak-proof sealing agents, materials principally utilized for their antibacterial properties, liners, bases, cements, and other similar materials are examples of *preventive materials*. Sometimes a material intended for prevention can also be utilized temporarily as a restorative substance.

All synthetic components that can be utilized to replace or repair tooth structure are referred to as *restorative materials*. These components include ceramics, denture polymers, amalgams, primers, bonding agents, liners, cement bases, resin-based composites, hybrid ionomers, cast metals, metal-ceramics, and denture polymers (Gross et al., 1988). Additionally, these materials can be created as controlled-delivery tools for the release of medication or diagnostic materials. Restorative materials can be applied longer-term (dentin bonding, agents, inlays, onlays, crown, removable dentures, fixed dentures, and orthodontic equipment) or short-term (temporary cements, temporary crown and bridge resins). Depending on whether they are used extraorally, where materials are formed indirectly on casts or other replicas of the teeth and other tissues, or intraorally, where materials are used directly on the teeth or tissues to fabricate restorations or prosthetic devices, these materials can also be categorized as direct or indirect restorative materials. A perfect restorative material would have qualities akin to those of dental enamel, dentin, and other tissues, link with other visible tissues, and be biocompatible.

Materials used in the creation of dental appliances and prostheses that do not become part of the final product are known as *auxiliary dental materials*. These include dental waxes, acrylic resin for impression and bleaching trays, acrylic resins for mouth guards and occlusion aids, impression materials, casting investments, gypsum cast and model materials, and finishing and polishing abrasives.

Metals. As far as materials go, metals are arguably the most popular and oldest kind utilized in dental implants. Their superior resilience to fatigue and fracture made them the preferred material for usage in conventional load-bearing applications. Endosseous implants have been utilized in orthopedics, cranio-maxillofacial surgery, and dentistry over a wide range of metals and alloys (Table 2). Because they were readily available in dentistry and because they encouraged the fibrous contact with a bone, or a distant osteogenesis with a brief lifespan, gold-based alloys were among the first metals to be utilized for implants. Additionally, cobalt-chromium alloys were created and employed as endosseous implants. The fibrous reaction that these metals and alloys encouraged in the bone, however, was the underlying issue with

them. None of these materials accomplish osseointegration by today's standards, most likely due to the elements being released into the tissue and the corrosion caused by the live tissue. These days, titanium and titanium alloys have essentially taken the role of these metals (Raic et al., 2024)

Bioceramics. A class of physiologically active ceramics rich in phosphate and calcium are known as bioceramics. Tricalcium phosphate and hydroxyapatite can be used to fill bony deficiencies and accentuate alveolar ridges due to their composition being similar to that of bone and teeth. Bioceramics can be classified into different types, including single crystals (sapphire), polycrystalline (hydroxyapatite), glass (bioactive glass), glass ceramics (ceravital), and composites (bioglass bonded with stainless steel). There are approximately four categories of bioceramics:

- **INERT:** Affixed by compact morphological fixing, such as carbon and alumina.
- **POROUS:** Connected via vascularization via pores; one example of this is porous alumina.
- **SURFACE ACTIVE:** Chemically link directly with bone, such as with hydroxyapatite or bioglass.
- **RESORBABLE:** Intended for gradual replacement by bone, such as tricalcium phosphate (TCP).

Although their clinical predictability is still debated, ceramic coatings on dental implants, such as calcium phosphates (hydroxyapatite or HA), appear to elicit a superior biological response compared to cpTi or Ti alloy alone. Coatings appear to encourage osseointegration (the joining of the bone to dental implants) as well as quicker bone adaption, stronger bone implants, improved osteoblast precursor activity, and bone development surrounding the implants. Because HA coatings promote osseointegration, more mineralized extracellular matrix (ECM) is formed, and bone forms more quickly than with Ti substrates alone, they were thought to be highly advantageous. According to the theory, HA is superior to smooth Ti surfaces because it has (i) a bioactive surface as opposed to an inert Ti surface, (ii) a stronger link between the implant and the bone, and (iii) more bone-to-implant contact. HA coatings have been shown to improve osseointegration despite reports of overstraining, fast bone resorption near HA-coated implants, short-term survival rates (between 6 months and 6 years), and other reasons of failures. Other ceramic coatings for implantology, such titanium carbide (TiC) and titanium nitride (TiN), have been proposed recently (Rudolf et al., 2024, Stamenković et al. 2009).

Table 2: Example of dental and medical materials and their applications (Raic et al., 2010)

MATERIALS	PRINCIPAL APLICATIONS
Metals and Alloys	
316 Stainless Steel-CP-Ti, Ti-Al-V, Ti-Al-Nb, Ti-13Nb-13Zr, Ti-Mo-Zr-Fe	Fracture fixation, stents, surgical instruments, bone and joint replacement, fracture fixation, dental implants, pacemaker, encapsulation
Co-Cr-Mo, Cr-Ni-Cr-Mo Ni-Ti	Bone and joint replacement, dental implants
Gold Alloys Silver products Platinum and Pt-Ir Hg-Ag-Sn amalgam	Bone plates, stents, orthodontic wires Dental restoration Antibacterial agents Electrodes Dental restorations
Ceramics and Glasses	
Alumina Zirconia Calcium Phosphates	Joint replacement, dental implants, dental Various parts of dental replacement Bone repair and augmentation, surface coatings on metals
Bioactive glasses Porcelain Carbons	Bone replacement Dental restorations Heart valves, percutaneous devices, dental implants

Table 3: Examples of brazes used in dental practice (Raic et al., 2010)

Chemical composition, %	Melting interval	Form of solder	Operation temperature	Colour	Application
79.0% Au, 17.0% Ag, 3.0% Pt, 1.0% Zn	980 – 1040 °C	Strip 0.25 x 1 mm	1040 °C	yellow	brazing metal-ceramics gold alloys
73.0% Au, 11.0% Ag, 2.0% Pt, 11.0% Zn, 3.0% Cu	710 – 750 °C	Strip 0.25 x 1 mm	750 °C	yellow	brazing dental alloys and alloys for metal-ceramics application
72.0% Au, 5.0% Ag, 12.0% Pd, 2.0% Zn, 8.0% Cu, 1.0% In	1010 – 1070 °C	Strip 0.25 x 1 mm	1060 °C	white	before firing ceramics
58.0% Au, 21.0% Ag, 18.0% Cu, 2.0% Zn, 1.0% Sn	790 – 820 °C	Plate 0.33 mm Strip 0.25 x 1 mm	820 °C	Light yellow	joining gold alloys for casting
26.0% Au, 16.0% Ag, 30.0% Cu, 15.0% Pd, 13.0% Zn	850 – 890 °C	Strip 0.25 x 1 mm	890 °C	white	brazing alloys based on the silver-palladium, before firing (baking) and the midfielder element for non-precious and precious metals
39.0% Co, 22.0% Cr, 19.0% Ni, 10.0% Fe, 5.0% Si, 3.0% Mo, 1.0% B, 1.0% V		Wire Ø 1 mm	1180 °C	white	joining of materials for mobile prosthetic, CoCr alloys

Brazes. The majority of dental brazes, are alloys based on either silver or gold (Table 3). Tin is one of the unique constituents added to these alloys to promote improved flow and a reduced melting range. Silver brazes are more frequently utilized in orthodontic applications, while gold-based brazes are mostly employed to solder cast alloys. Different melting ranges of gold-based brazes are offered to suit different application needs. The compatibility of brazes with cast alloys is often specified by the cast alloy manufacturer, and it is typical for them to offer a range of dental casting alloys in addition to compatible brazes. The composition of dental brazes also affects their strength, hardness, and corrosion resistance. Higher melting range brazes are typically harder and stronger than lower fusing brazes.

4. Conclusions

Attempts to examine the phenomena that occur at active liquid metal/ceramics interfaces during metal-ceramic joining in dental treatment are still in their early phases. Therefore, this study carefully discusses only the fundamental concepts and methodologies required to address wetting with diffusion processes accompanied by chemical reactions. The appearances at the grain boundary grooves of the ceramic surface are then described as catalytic surface phenomena.

Finally, the focus is limited to typical instances in dental practice, drawn from actual experience and literature. Brazes utilized in dental treatment are introduced and described, along with a brief overview of dental metals and bioceramics.

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