LIQUID METAL/CERAMIC INTERFACES IN DENTAL PRACTICE AND JEWELLERY MANUFACTURING

STALJENE VMESNE POVRŠINE MED KOVINO IN KERAMIKO V ZOBOZDRAVSTVU IN PRI IZDELAVI NAKITA

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Metal-ceramic fusing has been the essential step in obtaining materials that benefit from both ceramic and metal constituents, i.e. where the combined properties of metal and ceramic layers are desirable. When considering fusing methods, soldering and active metal brazing are the most effective. These processes involve braze melting and flowing between the two pieces of material.

In the first part the phenomena occurring on the boundary between the ceramics and the active filler metal during the metal-ceramics joining are discussed. Three interconnected sub-processes are considered: (1) wetting of the ceramic surface, (2) chemical reactions at the interface and (3) diffusion with a moving interface. Then, the appearances at the grain boundary grooves of the ceramic surface are presented as phenomena on the catalytic surface.

In the second part, examples from dental practice and jewellery manufacturing are used for comparative analysis. Finally, we discuss the composition and properties of the soldering and brazing alloys used for dental practice and jewellery manufacturing.

Key words: metal-ceramic bonding, brazing, soldering, dentistry, jewellery

Zlitje kovine in keramike je temeljna stopnja za nastanek materiala, ki pridobi lastnosti obeh sestavnih delov, kjer je želena kombinacija lastnosti plasti kovine in keramike. Od metod zlitja sta lotanje in aktivno spajkanje najbolj učinkoviti. Procese sestavljata taljenje in pretok taline med obema materialoma.

V prvem delu razpravljamo o procesih na meji med keramiko in aktivnim polnilnim materialom med spajanjem kovine in keramike. Obravnavamo tri povezane procese: (1) omočljivost keramične površine, (2) kemične reakcije na vmesni površini in (3) difuzijo s premikajočo se mejno površino. Nato obravnavamo nastanek žlebov na mejah zrn na katalitični površini. V drugem delu uporabljamo primere iz dentalne prakse in izdelave nakita za primerjalno analizo. Na koncu je razprava o sestavi in lastnostih spajk in lotov, ki se uporabljajo v dentalni praksi in pri izdelavi nakita.

Ključne besede: vezava keramika-kovina, lotanje, spajkanje, zobozdravstvo, nakit

1 INTRODUCTION

The joining of metals to ceramics has been widely practiced in fabricating structural components to utilise the favourable characteristics of the engineering ceramics. Ceramics offer a huge array of mechanical, thermal and electrical properties.[1–5] These range from low thermal conduction in ceramics such as alumina, to high thermal conduction, e. g. diamond, and from low density electrical insulators to superconducting ceramics. Piezo-ceramics offer the almost unique ability to convert electrical energy into mechanical movement, and vice versa. Materials such as beta-alumina and zirconia, which exhibit ionic conduction, are used as sensors. These materials have found application in a wide range of industries, as well as in medicine. A common thread of the applications is that, at some point, the ceramic component interfaces with something else – another part of the component made from another material, usually metal. At this point, some kind of attachment or joint is required.

Soldering and active metal brazing are the most effective when considering fusing methods. This process basically involves braze melting and flowing between the two pieces of material. This is commonly referred to as 'wetting' and is absolutely critical – particularly when brazing ceramics. There are many materials that can be fused together to produce joints between materials – those that melt above ≈ 450 °C are classed as brazes, and materials melting below ≈ 450 °C are called solders.

There are two basic methods to encourage wetting: to apply something to the surface of the ceramics so that the braze will wet, or, to put something in the braze that will induce wetting. Surface treatments include metallisation, metal coating and metal hydride treatment, while braze modification involves a process known as active metal brazing. In either case the actual brazing operation takes place either in a controlled atmosphere, such as nitrogen or argon, or a vacuum better than 10^{-4} N m^{-2}.

During active brazing or soldering, samples are heated in a furnace to melt braze or solder which is placed between them. The active element in braze or solder, such as Ti, reacts chemically with the components to enable wetting and the formation of a strong bond. While active brazing can produce strong bonds,

the high reactivity of the active metal requires the use of a vacuum furnace in an inert atmosphere to prevent oxidation. In addition, the high melting temperature of active brazes can lead to large thermal stresses on cooling, and fracture or de-bonding of the ceramic. Reactive solders reduce mismatch in thermal strains on cooling by lowering the process temperatures, but significant thermal stresses can still be present. Ideally, a strong metallic bond could be formed at/near room temperature, to avoid large thermal stresses between the components.

2 LIQUID METAL/CERAMIC INTERFACES

The phenomena occurring on liquid metal/ceramic interfaces are of the greatest importance for metal-ceramics joining techniques. An interdisciplinary task in which different fields of materials science must participate together with transport phenomena is shown in **Table 1**.[4–9] Therefore, in this paper, various approaches are explained which are necessary to treat transport phenomena on ceramic surfaces. In that sense, three steps are considered: (1) wetting of real ceramic surface, (2) chemical reactions at the interface and (3) diffusion with a moving interface.

Table 1: Aspects of investigation
Tabela 1: Teme raziskave

GENERAL VIEW
– physical interface processes (reversible physical forces)
– chemical interface processes (irreversible reactions)
– phase diagrams
– thermodynamic design
transport phenomena (macro scale)
(i) momentum ⇒ slow motion of liquid metal
(ii) heat ⇒ inner/outer (unsteady and/or steady state transport)
(iii) mass ⇒ diffusion with homo/heterogeneous chemical reaction (unsteady state phenomena)

MICROSRUCTURAL VIEW	
ceramic	*liquid metal*
– surface structure, pores, cracks	– structure
– grain size	– composition
– non-bonded areas	
transport phenomena (micro scale)	
diffusivity: at the interface and into the bulk	
mass transfer during homo/heterogeneous appearances	

ATOMISTIC VIEW	
ceramic	*liquid metal*
(covalent or ionic binding)	(metallic bonding)
– phase boundary structure	
– bonding forces	
– interfacial energy	
– epitaxy	
basic equations of transport phenomena ⇔ electronic structure of metal/ceramics interface	

2.1 Wettability of real ceramic surface

In real systems, wettability is quite complex.[3–5,7–13] Even sometimes, something as simple as surface roughness can have complex and contradictory effects on wettability. Furthermore, chemical segregation in both the solid and liquid phases can have a huge effect on surface and interfacial energies and, hence, wettability. Also, it is difficult to estimate the extent of wetting because interfacial reactions change the wetting characteristics as time elapses. The relationship between wetting and interfacial reactions is not well understood, i.e. molten copper shows a high contact angle and low wettability against ceramics such as Si_3N_4, SiC and ZrO_2, although molten aluminium exhibits a low contact angle and high wettability against ceramics. On the other hand, the wetting of an MgO/Al system progresses through three phases: (I) vibratory phase or a chemically quasi-equilibrium phase; (II) constant phase and (III) decreasing phase or a chemically reactive phase. The rate in the decreasing of the contact angle in phase III depends on temperature and the bulk and/or surface properties of the ceramics, since the decrease is caused by the interfacial reactions.

Most wetting studies are based on the contact angle, which was first defined empirically by Young. This equation is a balance of the horizontal forces due to surface tensions acting upon a liquid drop in contact with a solid. Young observed that in most cases when a liquid is placed on a solid, the liquid remains as a drop with a definite contact angle between the liquid and solid phases (**Figure 1**).

The physico-chemical principles underlying wetting action are to be found in standard texts. If the liquid metal is (or is not) under pressure, it will come to rest on a real (porous and/or rough) ceramic surface in some position, determined by the advancing smooth surface-liquid metal contact angle and the shape of the pores in the surface. The surface of practical importance is usually grids formed of roughly spherical atom positions and/or grain boundaries.

One can start from the well known Young-Dupré Eq. (1) and the relationship given by Cassie and Baxter,[13] modified with two coefficients (h^{LS} and h^{SA}),[7–9] Eq. (2):

$$W_{ad} = \gamma_M \, (1 + \cos \varphi) \tag{1}$$
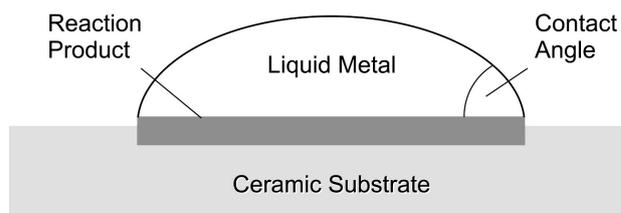
Figure 1: Sessile drop configurations assumed for the most reactive wetting models showing a complete reaction product layer
Slika 1: Konfiguracija premične kapljice, privzeta pri največ modelih reaktivnega omočenja, ki prikazuje plast reakcijskega produkta

$$\cos \varphi = h^{LS} f_1 \cos \alpha - h^{SA} f_2 \qquad (2)$$

where, W_{ad} – work of adhesion, J/m^2; γ_M – surface energy of the metal; φ: apparent contact angle (measured by sessile drop method); α – advancing (receding) contact angle (a not yet well understood parameter); f_1 – the total area of solid-liquid interface; f_2 – the total area of liquid-air (or furnace atmosphere) interface. Areas f_1 and f_2 can be derived from the value α and the dimensions of the grids formed of roughly spherical atom positions (lattice image) and/or surface grain boundaries. (f_1 and f_2 are the reflections of real or simulated surface image), h^{LS} – coefficient of net liquid-solid heterogeneity influence, h^{SA} – coefficient of net liquid-air (furnace atmosphere) heterogeneity influence.

The microstructural parameters that may have an influence on the properties of the metal/ceramic interface (reflected on h^{LS} and h^{SA}) are: (i) structure of the hetero-phase boundary, (ii) characteristic defects such as steps, faces and dislocations at or to the interfaces, (iii) possible chemical reactions, (iv) reaction products, (v) chemical gradients and segregation of impurities at the interface.[14]

While the wettability models predict whether wetting will occur for a given system, they do not predict the rate of wetting. Theoreticall modelling the spreading kinetics is complex. Even for nonreactive systems, modelling is complicated by surface irregularities, surface contamination, the formation of precursor films, and other surface anomalies. The spreading kinetics of reactive systems is further complicated by interfacial reactions at the solid-liquid and liquid-vapour interfaces (e.g., oxidation). The verification of a spreading mechanism is further hindered by a lack of experimental data. The interfacial reactions and the spreading kinetics are very rapid, making the collection of spreading kinetics and reaction-rate data challenging. Typical spreading kinetics
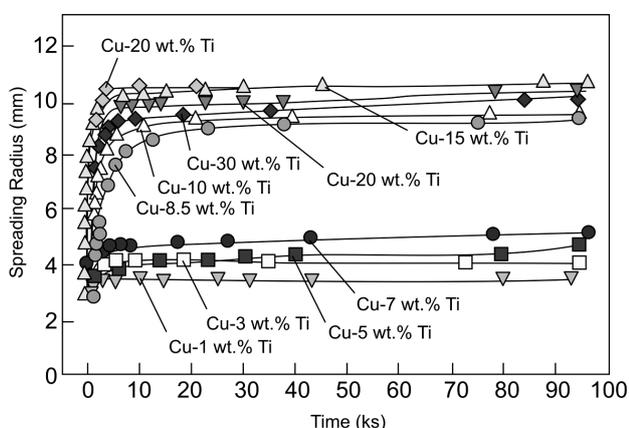
for copper-titanium alloys on alumina is shown in **Figure 2**.[15]

2.2 Chemical reactions at liquid metal/ceramic interface

To explain the action of a polycrystalline surface it is assumed that reactant molecules of liquid metal are somehow changed, energized, or affected, to form intermediates in the regions close to the surface. In one theory the intermediate is viewed as an association of a reactant molecule with a region of the surface, in other words the molecules are somehow attached to the surface. In another theory molecules are thought to move down into the liquid metal close to the surface and be under the influence of surface forces. In this view the molecules are still, but are nevertheless modified. In still a third theory it is thought that an active complex, a free radical, is formed at the solid surface. This free radical then moves back into the main liquid stream, triggering a chain of reactions with fresh molecules before finally being destroyed. In the contrast with the two theories which consider the reaction to occur in the vicinity of the surface, this theory views the surface simply as a generator of free radicals, with the reaction occurring in the main body of liquid metal.[7–9]

On the other hand, in order to obtain knowledge of the reactivity, it is very important to respect the changes of the standard free energy for the formation of nitrides, carbides and oxides against temperature. From these thermodynamic data, when metal was placed in contact with nitride, carbide, or oxide ceramics, we are able to predict whether the metal could decompose the ceramic to form a nitride, carbide, or oxide phase.

2.3 Diffusion with a moving interface

The observed process, in conjunction with chemical reactions at a solid/liquid boundary, involves diffusion steps. One result of these transient processes is the motion of the boundary between the phases.[8] In the general situation, two phases are in contact as in **Figure 3**. The moving phase boundary is at $x = X$, and at this boundary C_o and $C^* = C(X, t)$ represents the equilibrium

Figure 2: An example of rapid spreading kinetics in the spreading data for 1.2 g samples of copper-titanium alloys on alumina at 1120 °C[15]

Slika 2: Primer hitre kinetike o širjenju 1,2 g zlitine baker-titan na korundu pri 1120 °C[15]
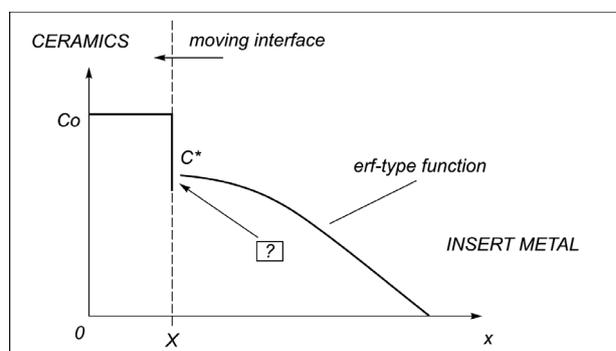
Figure 3: The concentration profile during transient diffusion[8]
Slika 3: Profil koncentracije med tranzientno difuzijo[8]

concentration of, e.g. Al_2O_3, that coexist in ceramics and melted metal respectively at the temperature under consideration.

In the insert metal phase, Fick's second law applies:

$$dC/dt = D \, d^2C/dx^2, \quad x > X \qquad (3)$$

where C is the Al_2O_3 concentration during transient diffusion, D the diffusion coefficient of the Al_2O_3 in melted 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:

$Co = KC^*$, where K is the partition ratio between the phases.

The material balance at the interface takes the form:

$$-D \, (dC/dx)_{x=X} = (C^* - Co) \, dX/dt \qquad (4)$$

Equ. 4 describes the locus of X with time. Relationship between Co and C^*:

$$\pi^{-0.5} \, [C^*/(C^* - Co)] = \beta \exp \beta^2 \operatorname{erf} \beta \qquad (5)$$

when

$$X = 2\beta \, (2D)^{0.5} \qquad (6)$$

is well known. The function of β, $\beta \exp \beta^2 \operatorname{erf} \beta$ may be evaluated from standard handbooks. So the D can be calculated if Co, C^*, X and t are measured. The illustrative calculated surface diffusivities for selected metal/alumina systems with groove widths (w) from 1 μm to 10 μm, are given in **Table 2**.

Table 2: Surface diffusivities for selected metal/alumina systems[10]
Tabela 2: Površinska difuzivnost za izbrane sisteme kovina/korund[10]

System	Temperature (K)	Surface Diffusion, wD (m^3 s^{-1})
Ni/Al$_2$O$_3$	1773	$4.4 \cdot 10^{-19}$
Au/Al$_2$O$_3$	1373	$1.8 \cdot 10^{-24}$
Cu/Al$_2$O$_3$	1423	$2.8 \cdot 10^{-22}$
Al/Al$_2$O$_3$	1373	$1.1 \cdot 10^{-19}$

Groove widths (w)

3 PHENOMENA AT GRAIN BOUNDARY GROOVES

Various processes may cause resistance to the overall reaction which occurs at the liquid-solid interface.[6,9] For an element of single groove between two grains (**Figure 4**) one can visualize: (i) *Liquid metal film resistance*. Reactants diffuse from the main body of the liquid metal to the exterior surface of the solid ceramic specimen. (ii) *Groove diffusion resistance*. Reactants move through the groove into the ceramic. Most of the reaction takes place within the groove. (iii) *Surface phenomena resistance*. At some point in their wandering reactant molecules become associated with the surface of the ceramic. They react to give products which are then released to the liquid phase within the groove. (iv) *Groove diffusion resistance for products*. Products then diffuse out of the
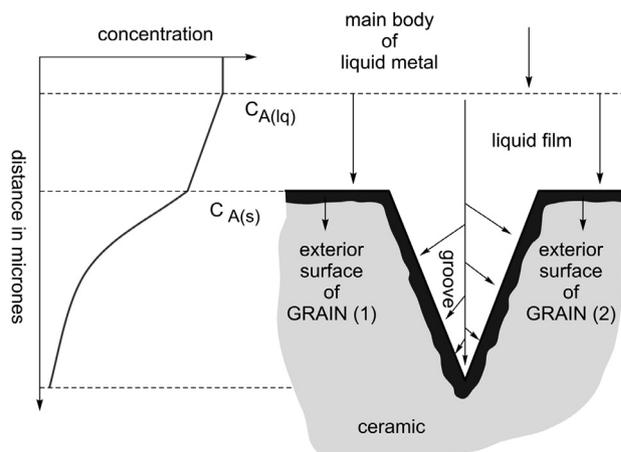
Figure 4: Phenomena around an element of single groove between two grains[9]
Slika 4: Pojavi okoli elementa enostavnega žleba med dvema zrnoma[9]

groove. (v) *Liquid metal film resistance for products*. Products then move from the mouth of the groove into the main liquid stream. (vi) *Resistance to heat flow*. For reactions accompanied by heat release or absorption the flow of heat into or out of the reaction zone may not be fast enough to keep the liquid metal/solid ceramic specimen isothermal. If this happens, the specimen will cool or heat, strongly affecting the rate. Thus the heat transfer resistance across the liquid film or within the ceramic could influence the rate of reaction.

Usually, the reaction layer grew rapidly in the first minute. After approximately a few minutes, further increase in the reaction layer thickness becomes gradual and parabolic in time. In this way, the growth of product layer can be observed as a two-step process: an initial rapid thickening rate and a second parabolic rate, assumed to be diffusion controlled.[11]

Rapid initial layer growth can be related to the substrate/ceramics surface roughness. On the other hand, slower growth is assisted by capillarity. It is well known that capillary mass transport manifests itself with developing a grain boundary groove on the surface of a polycrystalline material wherever a boundary intersects an interface between a solid and another phase. Mass transport can involve several mechanisms: interfacial diffusion, volume diffusion on either side of the interface, and interfacial reaction (solution-precipitation). Depending on the physical characteristics of the system and groove size, one of these mechanisms will be rate controlling, resulting in characteristic groove shapes and growth kinetics.

The rate of reaction for the solid ceramic substrate/liquid metal sample may depend on:
1. Surface kinetics, which may change with development of the grain boundary grooves.
2. Grain boundary groove (GBG) resistance which sets up internal concentration gradients. The effects of

"volume diffusion" and "surface diffusion" on groove development are given in ref.[10]

3. Interface ΔT or temperature gradient at the liquid metal/solid ceramics interface. This is caused by heat release or absorption during reaction.

4. Film diffusion resistance or concentration gradients across the liquid metal film.

The surface kinetics and grain boundary groove (GBG) diffusion cannot be treated as steps in series as they enter the rate equation together. So for a 1st order reaction on a flat plate specimen, analysis gives the rate of reaction:

$$-r_A''' = k''' C_{As} \varepsilon \qquad (7)$$

with

$$\varepsilon = (\tanh M_T)/M_T \qquad (8)$$

Where, ε: effectiveness factor = (actual reaction rate within GBG)/(rate if not slower by GBG diffusion), M_T: Thiele modulus, $M_T = L(k'''/D_{eff})^{1/2}$; D_{eff}: effective diffusion coefficient in porous solids [$m^3_{liquid(metal)}/m_{solid(ceramic)}$ s], L: characteristic size of ceramic sample/specimen, usually flat plate [L = (volume of sample)/(exterior surface) = thickness/2].

The "effective diffusivity" must be measured experimentally; it depends generally on the concentration of active species, temperature and on the groove structure. The actual mechanism for diffusion in grooves is complex, since the groove dimensions may be smaller than the mean path of the diffusing molecules.

We have no GBG resistance when: $M_T < 0.4$ here $\varepsilon = 1$ and $-r_A''' = k''' C_{As}$; and strong GBG diffusion effects when: $M_T > 4$ here $\varepsilon = 1/ M_T$ and $-r_A''' = [(k''' D_{eff})^{1/2} C_{As}]/L$ (see **Figure 5**). The presented description is similar to the phenomena on a catalytic particle[6].

5 DENTAL PRACTICE

Dental materials may be classified as preventive materials, restorative materials or auxiliary materials.[16–21] Preventive materials include pit and fissure sealants, sealing agents that prevent leakage, materials that are used primarily for their antibacterial effects, and liners, bases, cements, etc. In some cases a preventive material may also serve as a restorative material that may be used for a short-term application.
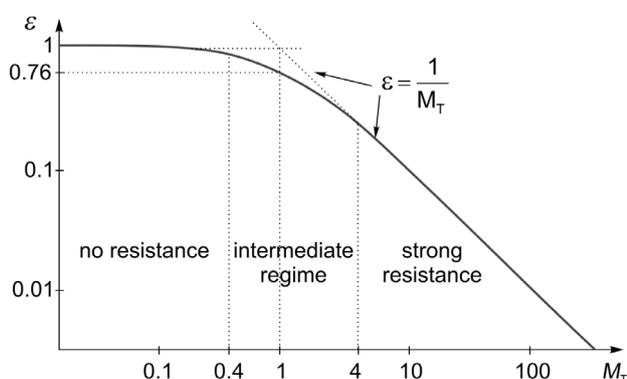
Restorative materials consist of all synthetic components that can be used to repair or replace tooth structure, including primers, bonding agents, liners, cement bases, amalgams, resin-based composites, hybrid ionomers, cast metals, metal-ceramics, ceramics, and denture polymers.[16,21] These materials can also be designed as controlled-delivery devices for the release of therapeutic or diagnostic agents. Restorative materials may be used for temporary, short term purposes (temporary cements, and temporary crown and bridge resins) or for longer-term application (dentin bonding, agents, inlays, onlays, crown, removable dentures, fixed dentures, and orthodontic appliances). These materials may further be classified as direct restorative materials or indirect restorative materials, depending on whether they are used –intraorally to fabricate restorations or prosthetic devices directly on the teeth or tissues or extraorally, in which materials are formed indirectly on casts or other replicas of the teeth and other tissues. An ideal restorative material would be biocompatible, bond with other visible tissues, exhibit properties similar to those of tooth enamel, dentin and other tissues, etc.

Auxiliary dental materials are substances which are used in the process of fabricating dental prostheses and appliances, but which do not become part of these devices. These include acid-etching solutions, impression materials, casting investments, gypsum cast and model materials, dental waxes, acrylic resin for impression and bleaching trays, acrylic resins for mouth guards and occlusion aids, and finishing and polishing abrasives.
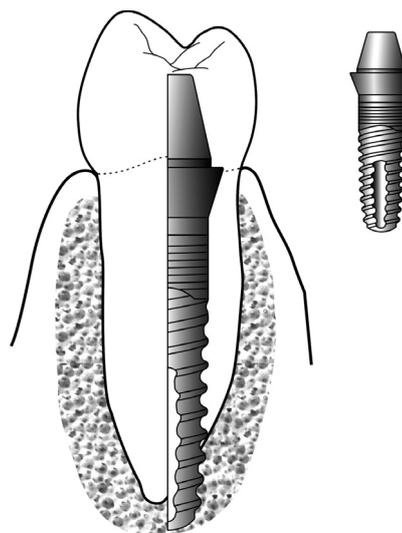
Figure 6: Schematic illustration of a cross-sectional view of a natural anterior tooth and supporting tissues (left) in combination with restorative dental materials (right)
Slika 6: Shematičen prikaz prereza naravnega zoba in nosilnega tkiva (levo) v kombinaciji s restavrativnim dentalnim materialom (desno)

Figure 5: Effectiveness factor (ε) v. Thiele modulus (M_T) [6]
Slika 5: Faktor učinkovitosti (ε) v odvisnosti od modula Thiele (M_T) [6]

Figure 6 is a schematic cross-section of a natural tooth and supporting bone and soft tissue (left) in combination with restorative dental materials (right). Under healthy conditions, the part of the tooth that extends out of adjacent gingival tissue is called a clinical crown, and that below the gingival tissue is called the tooth root. The crown of a tooth is covered with enamel and the root is covered with cementum, and it consists of dentin and tissue within one or more root canals.

The surface of implantable biomaterials is in direct contact with the host bone and soft tissue and it plays a critical role in determining its biocompatibility, functional compatibility, osteoinduction of bone and osseo-integration of implants. The goal of regenerative therapy around orthopaedic and dental implant devices is to create a suitable environment in which the natural biological potential for functional regeneration of the bone and of the periodontal ligament can be stimulated and maximised. In implantology, wide arrays of biomaterials have been used so far with variable success rates.[17–20]

Metals are probably the oldest form of materials used for dental implants and the most common type of materials used so far. Superior fracture and fatigue resistance caused them to become the materials of choice in traditional load-bearing applications. A large spectrum of metals and alloys were used as endosseous implants, in orthopaedics, cranio-maxillofacial surgery and dentistry (**Table 3**). Gold-based alloys were among the first alloys to be used for implants, probably because these alloys were available in dentistry, but also because they promoted the fibrous interface with a bone, i.e. a distant osteogenesis with a short lifespan. Cobalt-chromium alloys were also developed and used as endosseous implants. However, the fundamental problem with these metals and alloys was the fibrous response which they promoted with the bone. By today's standards, none of these materials achieve osseointegration, probably because of their corrosion effected by the living tissue and the release of elements into the tissue. Today, these metals have largely been replaced by titanium and titanium alloys.

Bioceramics are a group of ceramics which are biologically active materials rich in calcium and phosphate. Hydroxyapatite and tricalcium phosphate are similar in composition to bone and teeth and can be used for the augmentation of alveolar ridges and filling bony defects. The various forms of bioceramics are Single crystals (Sapphire), Polycrystalline (Hydroxyapatite) Glass (Bioactive glass) Glass ceramics (Ceravital) Composites (Stainless steel reinforced Bioglass). There are about four types of bioceramics:

INERT: Attached by compact morphological fixation, e.g. Alumina, Carbon

POROUS: Attached by vascularization through pores, e.g. Porous Alumina.

SURFACE ACTIVE: Directly attach by chemical bonding with bone, e.g. Bioglass, Hydroxyapatite

RESORBABLE Designed to be slowly replaced by bone, e.g. Tricalcium Phosphate (TCP).

Ceramic coatings on dental implants, such as Calcium phosphates (hydroxyapatite- HA) appear to have better biological response than cpTi or Ti alloy alone, even if their clinical predictability remains controversial. Coatings seem to promote faster bone adaptation, higher bone implant strength, better osteoblast precursor activity, bone growth around dental implants and thus, bonding of the bone to the implants, i.e. osseointegration. HA coatings were considered highly because they enhance osseointegration, and they lead to the formation of more mineralised extracellular matrix (ECM) and to faster bone formation with respect to Ti substrates alone. The philosophy was that HA has an

Table 3: Example of dental and medical materials and their applications
Tabela 3: Primeri dentalnih in medicinskih materialov in njihove uporabe

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	Bone and joint replacement, dental implants, dental
Ni-Ti	Bone plates, stents, orthodontic wires
Gold Alloys	Dental restoration
Silver products	Antibacterial agents
Platinum and Pt-Ir	Electrodes
Hg-Ag-Sn amalgam	Dental restorations
Ceramics and Glasses	
Alumina	Joint replacement, dental implants, dental
Zirconia	Various parts of dental replacement
Calcium Phosphates	Bone repair and augmentation, surface coatings on metals
Bioactive glasses	Bone replacement
Porcelain	Dental restorations
Carbons	Heart valves, percutaneous devices, dental implants

advantage over smooth Ti surfaces having: (i) a bioactive surface versus an inert Ti surface; (ii) higher bond strength of the bone to the implant; and (iii) increased bone-to-implant contact. In spite of reports about overstressing, rapid bone-resorption adjacent to HA-coated implants, short-term survival rates (from 6 months to 6 years), or other causes of failures, there is still evidence of positive effects of HA coatings on osseointegration. Recently, other ceramic coatings, such as titanium nitride (TiN) and titanium carbide (TiC), have been proposed for implantology.

Most dental solders are either gold-based or silver-based alloys (**Table 4**). These alloys contain special elements such as tin to encourage a lower melting range and better flow. Gold-based solders are used primarily to solder cast alloys, whereas silver solders are used more in orthodontic applications. A variety of gold-based solders are available with various melting ranges to meet specific applications. The manufacturer of the cast alloys generally specifies the compatibility of solders with their alloys, and it is common for a manufacturer to offer both a series of dental casting alloys and compatible solders together. The strength, hardness, and corrosion of dental solders also depend on the composition. In general, solders with a higher melting range are stronger and harder than lower fusing solders.

5 JEWELLERY MANUFACTURING

The joining of many different materials is necessary in jewellery manufacture (the metal frames of rings, earrings, necklaces, etc. with different kinds of stone – precious, semi-precious, synthetic stones, coral, and pearls).

One of the phases in jewellery manufacturing is placing the precious stone into the metal frame. The stones are initially cut into the desired sizes and shapes, and then polished. The metal frame cast is ground and polished and the stones are joined to it by adhesives, soldering, or by mechanical clamping.[22] The attachment between stone and metal becomes weaker over time, because of elastic deformation. If the stone is soldered to the metal frame the joint between stone and metal is stronger. Different stones have different mechanical and physical properties and it is necessary to find an appropriate combination of solder components for each stone. For example, sapphire is an AlB_2BOB_3B mineral. Sapphire can be soldered after bonding or brazed without bonding. If the sapphire is brazed to titan without bonding, an alloy with 72 % Ag could be used. Diamond could be brazed to steel with L-Ag40Cd, L-Ag30Cr, or L-Ag20Si.

There are two groups of precious stones according to their price: first-order stones (diamond, ruby, sapphire and emerald) and second-order stones (aquamarine, topaz, zircon, onyx, quartz topaz, etc.). Many of them have similar chemical compositions, but their colours are different. The chemical composition of diamond is 99.95 % carbon. Emerald is a green mineral made of aluminium, and its colour comes from chrome or vanadium. Sapphire and ruby are minerals of AlB_2BOB_3B. Sapphire could have a blue colour from titan and iron, and violet from vanadium. Ruby could have a red colour from chrome or a chestnut colour from chrome and iron. The chemical compositions of stones could be very important when joining different kinds of stones. Many stones in the second group are very sensitive to heat. The result of heating the stone above its critical temperature could be

Table 4: Examples of solders used in dental practice
Tabela 4: Primeri lotov, ki se uporabljajo v dentalni praksi

Name of the solder, (Chemical composition, %)	Melting interval	Form of solder	Operation temperature	Colour	Application
Auroker L 1040 PF (79.0 % Au, 17.0 % Ag, 3.0 % Pt, 1.0 % Zn)	980 – 1040 °C	Strip (0.25× 1) mm	1040 °C	yellow	soldering metal-ceramics gold alloys
7 Aurodur HL 750 (73.0 % Au, 11.0 % Ag, 2.0 % Pt, 11.0 % Zn, 3.0 % Cu)	710 – 750 °C	Strip (0.25× 1) mm	750 °C	yellow	soldering dental alloys and alloys for metal-ceramics application
Auroker L 1060 (72.0 % Au, 5.0 % Ag, 12.0 % Pd, 2.0 % Zn, 8.0 % Cu, 1.0 % In)	1010 – 1070 °C	Strip (0.25× 1) mm	1060 °C	white	before firing ceramics
Midor L (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× 1) mm	820 °C	Light yellow	joining gold alloys for casting
Silopal L 890 (26.0 % Au, 16.0 % Ag, 30.0 % Cu, 15.0 % Pd, 13.0 % Zn)	850 – 890 °C	Strip (0.25× 1) mm	890 °C	white	soldering alloys based on the silver-palladium, before firing (baking) and the midfielder element for non-precious and precious metals
Witex lot (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

a change in colour. Turquoise has a critical temperature at 250 °C, when its colour then changes from sky blue to green. At the critical temperature interval of tanzanite (from 400 °C to 500 °C), the nuances of yellow gradually disappear and the blue colour is intensified. Other precious stones can also express changes in their colours (quartz, topaz, amethyst, aquamarine, etc.). Therefore, it is very important during the joining of stones to the metal frame, that the stones are not heated above their critical temperatures.

The composition of brazing alloys used for jewellery applications is Au-Ag-Cu, with the addition of metals such as zinc and cadmium. Cadmium is very toxic, especially its vapour, during the melting process, and is replaced with non-toxic elements. Cadmium could be substituted with the following metals: tin (Sn), indium (In), gallium (Ga), and zinc (Zn). Also, some solders without cadmium have very high concentration of Ni (5 % to 9 %). According to EU Directive 76/769 EES (January 2000), the concentration of nickel in jewellery cannot exceed the maximum of 0.05 %. This EU Directive is a prerequisite for the prevention of allergic reactions caused by nickel. Nano-foil, with properly selected solder or braze components (without Ni), placed between metal parts could prevent allergic reactions to nickel and could enable a high quality of metal-metal joints.

6 CONCLUSIONS

Attempts to investigate the phenomena occurring on liquid metal/ceramics interfaces during metal ceramic joining in dental practice and jewellery manufacturing are still in their early stages. In this paper we carefully explain only the basic concepts and approaches necessary to treat wetting with diffusion phenomena accompanied by chemical reactions. The attention is confined to the typical examples taken from the actual practice and literature.

Nowadays, in dentistry, attention is increasingly focusing on the extensive range of alternative materials. These new materials include titanium and cobalt/nickel base alloys and all ceramic crowns. The latter have excellent aesthetic properties, but do not have the long-term clinical approval that gold has. For example, zirconia has only passed clinical tests during the last 8 years. In addition, the CAD/CAM techniques associated with the use of these materials are, in many cases, prohibitively expensive. Moreover, the problems of poor aesthetics often associated with porcelain-fused-to-metal techniques might be addressed through the use of extremely high gold content alloys, which have recently been patented. It is considered that, as CAD/CAM technology progresses, special high gold alloys should be developed which are well suited to milling and grinding operations and sufficiently high strength for long span bridges and small cross sections. Besides long term clinical approval and longevity, the most important advantages of gold alloys are easy workability, biocompatibility, aesthetics and maximum range of indications.

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