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Type of the Paper (Editorial)

Recent Advances Glass-Ionomer Dental Cements

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Abstract: There is a continuous demand of progression in techniques and materials used in endodontics. Glass ionomer cements (GICs) improvements includes; compomers, condensable/self-hardening GIC, low viscosity/ flowable GIC, fiber-reinforced GIC, chlorhexidine-impregnated GIC, proline-containing GIC, nano-bioceramic-modified GIC, and calcium aluminate GIC, Nano-resin-modified GICs (nano-RMGICs).

Keywords: Ceramics; glass-ionomer; endodontics.

Glass ionomers is as material of choice for a diverse yet distinctly typical procedures ranging from restoration to tooth repair. Glass ionomers are appropriate to many restorative conditions, both as standalone restoratives and in conjunction with resin composite. While glass ionomer cement use as a restorative material, it has some disadvantages. This article highlights about the recent advances and indication of recently introduced modified glass ionomer cements.

Various alterations in GICs could be summarized are as follows:
1. Compomer; It is a combination of composite and ionomer.
2. Self-hardening GIC; which are mainly activated resin-modified glass ionomer cements with no light curing at all. It is used mainly in pedodontics for cementation of temporary metallic crowns, metallic bands, orthodontic brackets and space maintainers.
3. Flowable GIC; It is basically utilized as limner, pit and fissure sealer, endodontic sealers, due to their increased flow.

4. Bioactive glass; formed by acidic dissolution of glass, there is creation of a layer rich in calcium and phosphate around the glass, such a glass can form chemical bioactive bonds between cement and investing bone leads to integrated with the bone. It could be used in retrograde filling, perforation treatment, bone augmentation and cementation of implant.
5. Fiber-reinforced GIC; mainly introduced to improve the depth of cure, reduced polymerization shrinkage, improved wear resistance, and increase in flexural strength of GIC, alumina fibers are mixed with glass powder. This technology is called the polymeric rigid inorganic matrix material, which involves incorporation of a continuous network/scaffold of alumina and silicon di oxide ceramic fibers.
6. Proline-containing GIC; It composed of an amino acid to improve surface microhardness properties. This formulation of lead to a fast-set glass ionomer, with high water sorption without reduction in amount of fluoride release. The material showed a promise biocompatibility, it could be used as a bone cement.
7. Calcium aluminate GIC; It considered as a hybrid composition composed of calcium aluminate and glass-ionomer, it used mainly for cementation of fixed prosthesis. The

calcium aluminate lead to decrease in microleakage, stability, high strength and excellent biocompatibility.

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Type of the Paper (Mini-Review)

Organic Analysis Tools in Dentistry

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Abstract: Organic analytic tools let us to recognize the structural composition and features of unknown constituents. It is particularly valuable in drug production, and therapeutics. Here you will describe how to analyze a completely unknown substance.

Keywords: Ceramics; glass-ionomer; endodontics.

Organic analytic tools let us to recognize the structural composition and features of unknown constituents. It is particularly valuable in drug production, and therapeutics. Here you will describe how to analyze a completely unknown substance.

Organic Analysis Tools:

A majority of methods has been developed for organic analysis; chromatography is very important in trace organic analysis.

1. Chromatography:

Chromatography is a separation method used for chemical analysis. It was initially introduced as an analytical technique in the early twentieth century and was first used as a method of separating colored compounds. Chromatography (chroma) i.e. color where (graphy) means writing. Samples can be gases, liquids or solids, in simple mixtures or in complex blends of widely differing chemicals. The solvent can also be a gas or liquid, depending on the type of chromatography (2).

1.1. Gas Chromatography - Mass Spectroscopy (GC-MS):

Gas chromatography-mass spectroscopy (GC-MS) is one of the combined analytical techniques. Actually, it is a combination of two techniques to form a single method of analyzing mixtures of chemicals. Gas chromatography separates the components of a mixture and mass spectroscopy characterizes each of the components individually. They are considered as the gold standard for analyzing lipids, drug metabolites and environmental analysis.

Gas chromatography is used to separate mixtures of compounds that can be vaporized without decomposition into individual components. Once isolated, the components can be evaluated individually. Separation occurs when the sample mixture is injected into a **mobile phase**. The mobile phase is an inert gas such as helium. The mobile phase carries the sample mixture through what is referred to as a **stationary phase**. The stationary phase is a usually chemical (liquid or solid) that can selectively attract components in a sample mixture. The stationary phase is usually contained in a capillary tube which is referred as a **column**. The mixture of compounds in the mobile phase interacts with the stationary phase. Each compound in the mixture interacts at a different rate. Those interact fastest will exit first, while those interact slowest will exit the last. By changing characteristics of the mobile phase and the stationary phase, different mixtures of chemicals can be separated. As the compounds are separated, they enter a **detector**. The detector is capable of creating an electronic signal whenever the presence of a compound is detected.

The signal is then processed by a **computer**. A schematic representation of the device basic component is provided in figure (1).

As the individual compounds enter the mass spectroscopy, they are bombarded with a stream of electrons causing them to break apart into fragments. They determine the mass of a molecule by measuring the mass-to-charge ratio (*m*/*z*) of its ion. The computer records a graph for each scan where the x-axis represents the M/Z ratios while, the y-axis represents the signal intensity (abundance) for each of the fragments detected during the scan. The mass spectrum produced by a given chemical compound is essentially a fingerprint for the molecule. This fingerprint can be used to identify the compound.

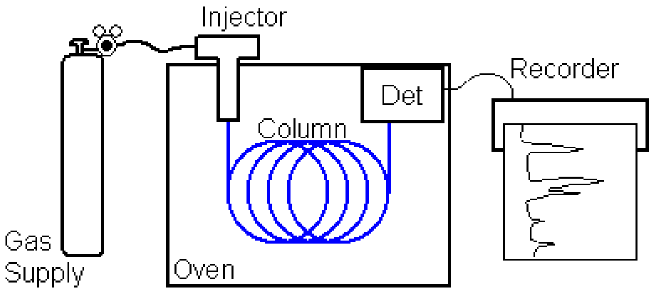

Figure (1): Schematic representation of GC (3).

When GC is combined with MS, a powerful analytical tool is created. A researcher can take an organic solution, inject it into the instrument, separate the individual components, and identify each of them. Furthermore, the researcher can determine the quantities (concentrations) of each of the components (4).

The main ***limitation*** is that the sample must be easily converted into a gaseous form and withstand heat at high temperatures without breaking down or degrading into another molecule (4).

The main ***benefit*** is that it is a powerful instrument capable of analyzing, separating and matching all the ingredients of an unknown mixture (4).

1.2. High-Performance Liquid Chromatography (HPLC):

High performance liquid chromatography (HPLC) is now one of the most powerful tools in analytical chemistry. It has the ability to separate a mixture into its individual components. They are coupled with a detection system that can characterize each type of analyte properly. It is used for separation of organic, inorganic, biological compounds, polymers, and thermally labile compounds. They are commonly used as quantitative and qualitative analyses of amino acids, nucleic acids, proteins in physiological samples. Also, for measuring levels of active drugs, synthetic byproducts, degradation products in pharmaceuticals. In addition to, purifying compounds from mixtures.

The fundamental basis for HPLC consists of passing a sample (analyte mixture) in a high-pressure solvent (called the mobile phase) through a steel tube (called a column) packed with sorbents (called the stationary phase). As the analytes pass through the column, it is separated by the attraction of the compound against the material of the column. This polar and non-polar attraction to the column material is the active force that causes the compounds to separate over time. A schematic representation of the device basic component is provided in figure (2).

HPLC has the following advantages over GC that it is quick, accurate, need a smaller sample for analysis, give a higher resolution record that is easily to read and can analyze less stable compounds as the sample is not subjected to heat as compared to GC (5).

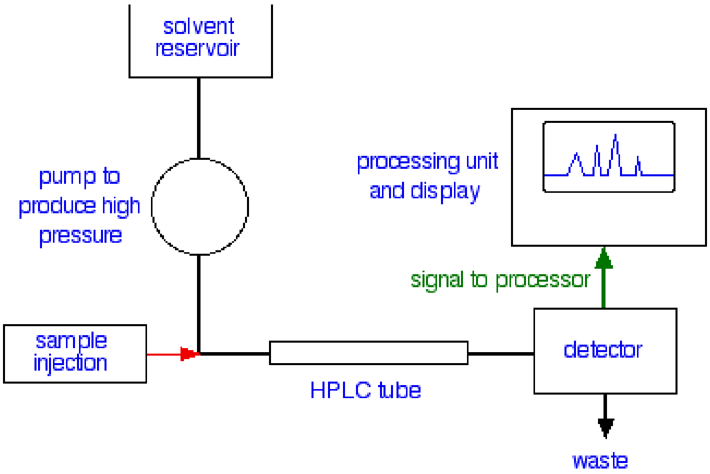

Figure (2): Schematic representation of HPLC (6)**.**

1.3. Size Exclusion Chromatography (SEC):

Size exclusion chromatography (SEC) is also called molecular sieve. This analytical method separates molecules based on their molecular sizes and shapes by using the molecular sieve properties of a variety of porous materials. The SEC column is packed with a resin consisting of beads with pores of defined size. This resin is the SEC stationary phase. The mobile phase is a buffer that usually contains a salt, which is necessary to reduce the interaction between the proteins and the beads. The size of the pores or "holes" in these beads is controlled during the manufacturing process. The separation of chemicals by SEC is based on the amount of time molecules spend included in the pores of these beads. SEC is used to separate and analyze a variety of chemicals, including both synthetic polymers and biopolymers. It is a powerful and popular method to purify and determine the molecular weight of proteins. It is very effective method for the separation of the large molecules from the small (7).

1.4. Gel permeation Chromatography (GPC):

Gel Permeation Chromatography (GPC), also known as gel filtration Chromatography (GFC), is a chromatographic technique that separates dissolved molecules on the basis of their size by pumping them through specialized columns containing a porous packing material. It is used mainly for analysis of synthetic and biologic polymers, purification of polymers, polymer characterization and for study properties like molecular weight, size and viscosity.

In GPC, a solution of the dissolved sample is passed through a column packed with a controlled-porosity packing, typically a polymeric porous gel typically referred to as a stationary phase. The size and shape of the molecule dictate its ability to interact with the pores on the stationary phase. Small molecules typically enter the pores therefore take the longest to elute from the column. Molecules with a very large molecule weight cannot move into the pore spaces available in the stationary phase and elute relatively quickly. In this manner, a whole range of molecular weights can be characterized when compared to the retention time of standard molecular weights (8).

I. Particle Size / Sorting:

Measurement of particle size distributions is carried out across a wide range of analytic tools such as:

1. Flow Cytometer (FC):

Cell sorting is the separation and isolation of various cell populations. Flow cytometers (FC) are automated instruments they can measure cell size, cell granularity, the amounts of cell components such as total DNA, newly synthesized DNA, gene expression as the amount messenger RNA for a particular gene, amounts of specific surface receptors, amounts of intracellular proteins.

Flow cytometer use fluorescent probes to identify and characterize cells or particles. Cells or particles tagged with fluorescent molecules enter the cytometer via a fluid stream. The cells then pass through a **laser**, which emits a specific wavelength of light. The fluorescent probes are excited by the laser and then emit light. The fluorescent signal is detected and amplified, then translated into an electronic signal, which is sent to the computer. Information about the size and granularity of a cell is recorded. The result is a visual presentation describing an individual or group of cellular events. This technique is costly and complicated (9).

2. Air Separation:

Particle separation is an important process in the fields of industrial production, environmental assessment and chemical or biological research. It is a novel approach for particle separation by sizes, using air–liquid interface in a microfluidic channel. The particles with different sizes can be separated by the action of different speed of the air–liquid interface. This separation technique has several advantages: It is totally independent on the properties of the particle and working fluid (such as the optical, magnetic and surface charge). It does not require any pre-treatment of particles such as optical or magnetic labelling. The process is fast and easy to handle (10).

3. Dynamic Light Scattering (DLS):

Dynamic light scattering (DLS), also known as photon correlation spectroscopy is a non-invasive, well-established technique used for measuring the size of molecules and particles which have been dispersed or dissolved in a liquid, typically in the submicron and less than 1nm. The Brownian motion of particles or molecules in suspension causes laser light to be scattered at different intensities. The particle size can be determined by analysis of fluctuation intensity versus time using the Stokes-Einstein relationship. Figure (3) represent DLS diagram. Dynamic light scattering technology offers the following advantages: Accurate, reliable, fast, simple, no need for sample preparation and directly measure high concentration and turbid samples, in addition to their ability to measure sizes less than 1nm (11).

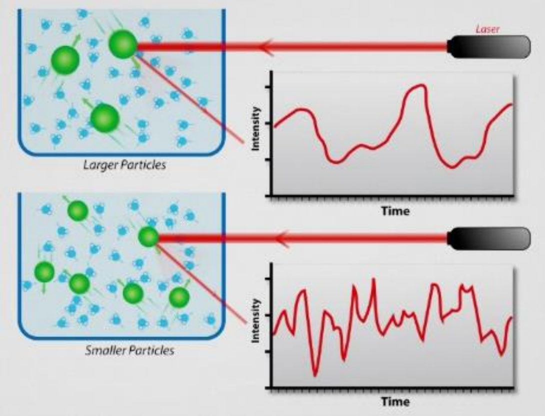

Figure (3): Schematic representation of DLS (12).

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Type of the Paper (Review Article)

Desensitizing Agents

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Abstract: Dentin hypersensitivity (DH) is the short, sharp pain derived from exposed dentin in response to chemical, thermal, tactile, or osmotic stimuli which cannot be explained as arising from any other dental defect or disease[1-3]. The development of DH involves two phases: lesion localization and lesion initiation. Lesion localization is the enamel and/or root surface denudation by attrition, abrasion, erosion, and abfraction resulting in the exposure of the underlying dentin, while lesion initiation follows dentine exposure and the dentinal tubules become patent from the pulp to the oral environment[4, 5]. Treatment of DH has two approaches which are removal of the etiological factor and prevention of DH, and application of desensitizing agents. Desensitizing Agents could be applied at home or in office. Desensitizing Agents treats DH by two mechanisms which are disturbance of the neural response to stimulus, and occlusion of dentinal tubules to block the flow of tubular fluid.

Keywords: *Dentin hypersensitivity;* ***Desensitizing agents; Immediate Dentin Sealing; Fluoride; Oxalates; Iontophoresis.***

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I. Etiology of Dentin Hypersensitivity:

Dentin hypersensitivity is mainly due to the exposure of dentinal tubules by removal of enamel and cementum.

II.1. Removal of Enamel:

The enamel layer can be removed by attrition due to occlusal wear, parafunctional habits (bruxism), improper tooth brushing (toothbrush abrasion), erosion from acids (Gastroesophageal reflux disorder - GERD), fracture of crown, abfraction, defective restoration (improper marginal seal) and bleaching.

II.2. Removal of Cementum:

Poor periodontal health due to incorrect tooth brushing and faulty restorations can lead to gingival recession and periodontal disease. This leads to the exposure of the root surface. Once exposed, the thin cementum layer (20 - 25 μm) can be easily removed by periodontal root scaling, abrasive pastes, acidic foods and toothbrushing, exposing the dentinal tubules.

N.B. In about 10% of the individuals, the enamel and cementum do not meet exposing the dentinal tubules leading to hypersensitivity[1].

III. Mechanisms of dentin hypersensitivity:

III.1. Direct Innervation (DI) Theory:

According to this theory the nerve endings enter dentin through pulp and extend up to the dentin-enamel junction (DEJ) and the mechanical stimuli directly transmit the pain. However, there is not enough evidence that can support the existence of nerves in the superficial dentin where dentin is more sensitive[1, 5].

III.2. Odontoblast Receptor Theory:

According to this theory, odontoblasts act as receptors of pain and transmit signals to the pulpal nerves. But this theory has also been rejected because the cellular matrix of odontoblasts is not capable of exciting and producing neural impulses and there is no synapse between odontoblasts and pulpal nerves[1, 5].

III.3. Fluid Movement / Hydrodynamic Theory:

This theory is the most widely accepted theory for dentin hypersensitivity. The theory based on the movement of the fluid inside the dentinal tubules and claims that tubules are open between the dentin surface which is exposed to the oral environment and pulp. Dentin hypersensitivity is made as the result of fluid movement inside the dentinal tubules, which is due to the thermal, physical changes, and osmotic stimuli. This fluid movement stimulates a baroreceptor and leads to neural stimuli. The number of tubules in sensitive dentin more than the number of tubules in non-sensitive dentin. Also, the tubules of sensitive dentin are wider than those in non-sensitive dentin[1, 6].

IV. Treatment of Dentin Hypersensitivity:

IV.1. Removing the Etiological Factor and Preventing Dentin Hypersensitivity[1, 5]:

Etiological Factor	Solution
Improper Tooth Brushing	The patient should be taught the correct method of tooth brushing and avoid the use of abrasive toothpastes.
Premature Occlusal Contacts	Dentin hypersensitivity can be resolved through correction of occlusion or the use of an occlusal splint
Gingival Recession and Periodontal Diseases	Periodontal treatment and root coverage procedures such as graft or positioning

	flap might be adopted to treat dentin hypersensitivity
Exogenous Acids such as carbonated drinks, citrus fruits, yogurt, and dairy products.	The patient's diet concerning the quality and the frequency of consumption of acidic foods should be monitored.
Endogenous Acids that enter the mouth through reflux or gastro-esophageal regurgitation	The patients are recommended to medical referral.

IV.2. Desensitizing Agents:

IV.2.1. Requirements of the ideal dentin desensitizing agent:

- Should be rapidly acting.
- Should has long-term effect.
- Should be harmless to pulp and painless.
- Should be easy to apply.
- Should not stain the teeth[1].

IV.2.2. Classifications of Desensitizing Agents:

IV.2.2.1. Classification based on the mode of administration:

a) At home: this mode is simple and reasonable.

a.1. Desensitizing Tooth Dentifrice and Toothpastes:

Desensitizing toothpastes containing strontium salts, fluorides, calcium phosphates, 8% arginine/calcium carbonate, carbonated hydroxyapatite, and potassium salts.

a.2. Mouthwashes: Mouthwashes used for dentin hypersensitivity are broadly classified into non fluoride desensitizing mouthwash and fluoride containing desensitizing mouthwash.

a.3. Chewing Gums containing potassium chloride and CPP-ACP[1].

About 2-4 weeks after at- home therapies, the degree of dentin hypersensitivity should be reinvestigated. If the pain still existed, the patient should start the next phase of the therapy; in-office therapy[1].

b) In office: This is a complicated and expensive mode but more effective than at home therapy such as varnishes, laser, bonding agents, gels, etc.[5].

IV.2.2.2. Classification based on the mechanism of action:

IV.2.2.2.1. Disturbance of the neural response to stimulus.

Agents that reduce the excitability of the intra-dental nerves, making them less likely to respond to dentinal fluid shifts such as low output power lasers and potassium salts (potassium nitrate and potassium chloride).

IV.2.2.2.2. Occlusion of dentinal tubules and block the flow of tubular fluid.

Treatments that reduce dentine permeability to the extent that stimuli such as air blasts and probing do not cause dentinal fluid shifts that activate the intra-dental nerves. This can be accomplished by treatments that deliver materials such as particulates that occlude the tubules or agents that interact with the oral environment to encourage the formation of mineral in the dentinal tubules can reduce dentine permeability such as fluoride, oxalates, and bonding agents[1, 7].

IV.2.2.2.1. Disturbance of the neural response to stimulus.

a) Low output power (low-level) lasers [(He-Ne) helium-neon and (GaAlAs) gallium-aluminum arsenide (diode) lasers]:

Laser treatment of exposed dentinal tubules provides a non-invasive, pain free and safe treatment[8]. In low output power lasers, a small fraction of the laser's energy is transmitted through enamel or dentin to reach the pulp tissue. It minimizes pain, reduces inflammatory processes, and discharges the internal tubular nerves[9]. Diode laser leads to increase in mitochondrial ATP through bio-stimulation, therefore formation of secondary dentin by odontoblast is enhanced. Moreover, it increases pain threshold of free nerve ending, provides analgesic effect by increase in endorphins[8].

b) Potassium salts:

Potassium salts such as potassium nitrate and potassium chloride are known as nerve-numbing agents. Potassium salts depolarize nerves resulting in transient excitation. Following this transient activation, the excitability of the nerves becomes depressed, making the nerves unresponsive to stimulus[3,7]. *Potassium nitrate* which is available as aqueous solution, adhesive gel, toothpastes, and mouth rinses is considered one of the most used agents for managing DH [1,10].

Mode of action:

Diffusion of potassium salts along the dentinal tubules, resulting in an increased extracellular potassium ion concentration that is significantly higher than physiological levels. A sustained depolarized state is achieved, during which few or no action potentials can be evoked, decreasing the excitability of the intra-dental nerve fibers. This is referred to as '*axonal accommodation*'. However, once the potassium ions are within the tubules, they must build up and remain at an elevated concentration for axonal accommodation to occur. If treatment with potassium-containing agents is discontinued, the concentration of potassium ions around the nerve fibers will diminish and sensitivity relief will be lost[1, 4, 10, 11].

IV.2.2.2.2. Occlusion of dentinal tubules and block the flow of tubular fluid.

a) Fluorides:

Fluoride is commonly used in *varnishes, mouth rinses, gels, and dentifrices*. Moreover, it can be incorporated into bioactive glasses to form fluoride-containing bioactive glasses (FBaG). FBaG can form fluorapatite (FAp) instead of carbonated hydroxyapatite[12].

Mode of action:

Fluorides form an insoluble compound calcium fluoride (CaF_2) with the tooth substance. This forms a physical barrier and narrows the diameter of dentinal tubules, reducing its permeability. Moreover, fluoride penetrates the pulp and interferes with its function, lowering its vitality. Thus, it is no longer receptive to pain and a reaction between fluoride and the free ions of some electrolytes, such as calcium, makes these ions unavailable for the normal mechanism of pain conduction [8,13].

Fluoride agents:

Sodium fluoride forms a precipitate that can be removed by the saliva or mechanical scrubbing. Therefore, acid has been added to the formula so that the resultant acidulated sodium fluoride can form precipitates deep in the tubules[1].

Stannous fluoride has the same effect as sodium fluoride. If the precipitate of apatite fluoride forms, it can resist salivary action, tooth brushing and dietary substances' action[1]. Moreover, it causes tubule occlusion by the chemical precipitation of a tin-rich surface deposit that provides nearly complete coverage of the dentine surface[4].

b) Oxalates:

The application of oxalate such as potassium oxalate has dual mechanism in treating dentine sensitivity by blocking excitation of the pulp sensory nerve and occluding patent dentinal tubules. However, potassium oxalate can lead to some digestive disorders so it should not be used for a long term[1].

Mode of action:

The decrease in hypersensitivity after application of potassium oxalate is due to nerve depolarization by K^+ ions and tubular occlusion due to the deposition of calcium oxalate crystals within the tubules[14]. Oxalates have the advantage of insolubility in acid, making them resistant to dissolution after treatment[2].

c) Bonding agents:

Bonding agents exhibit a long-term or permanent effect and can effectively seal dentinal tubules through forming a hybrid layer. The old adhesives formed the hybrid layer through removing the smear layer and etching the dentinal surface so that deep resin tags could be formed. The new adhesives modify the smear layer and incorporate it into the hybrid layer[1].

Gluma desensitizing agent contains hydroxyethyl methacrylate (HEMA), benzalkonium chloride, glutaraldehyde, and fluoride. Glutaraldehyde leads to protein coagulation within dentinal tubules. HEMA causes resin tags to be formed and dentinal tubules to be occluded[1].

Immediate Dentin Sealing:

The immediate application of a dentin-bonding agent after tooth preparation and before impression-taking decreases bacterial microleakage, dentin hypersensitivity, gap formation, and bond strength[15].

d) Bioactive glass:

Bioactive glasses (BGs) are highly biocompatible materials; their active ingredient is calcium sodium phospho-silicate. The use of bioactive glass is a promising treatment for DH due to the formation of a bioactive barrier on dentin surface that has the ability to occlude the dentinal tubules and form a mechanically strong layer of hydroxyapatite on the dentin surface, which can resist degradation by acids[16].

Mode of action:

Dissolution of BG in physiological liquid environments induces the formation of calcium phosphate precipitates which are effective in hard tissue regeneration and remineralization. This effect of Bio active glass may be referred as it forms a hydroxycarbonate apatite (HCA) layer on the surfaces of the particles, and to its ability to occlude dentinal tubules mechanically. The presence of HCA layers over BG particles surfaces allows them to bind to each other and to the walls of dentinal tubule (collagen type I), which enhance their effect on the occlusion of dentinal tubules[1, 6, 12, 17].

e.g., NovaMin® toothpaste.

e) Casein-Phosphopeptide-Amorphous Calcium Phosphate (CPP)-(ACP):

Casein-Phosphopeptide is a remineralizing agent containing amorphous calcium phosphate (ACP) and casein phosphopeptide (CPP) proteins that contains phosphoseryl sequences which is helpful in attaching and stabilizing ACP. CPP-ACP remineralizes the early lesions of enamel subsurface, therefore, it is effective in prevention and treatment of dentin hypersensitivity. CPP-ACP is incorporated into various oral health care products such as *mouth rinses, toothpastes, tooth mousse and sugar-free chewing gums* [1].

Mode of action:

ACP-CCP complex creates a firm binding with the biofilm on teeth and form calcium and phosphate reservoir as it delivers bio-available calcium and phosphate for remineralization, resulting in occlusion of dentin tubules[18].

RecaldentTM is a special milk-derived protein containing amorphous calcium phosphate (ACP) and casein phosphopeptide (CPP). ACP-CCP complex creates a firm binding with the biofilm on teeth and form calcium and phosphate reservoir, which is combined into both enamel and dentin surfaces. Due to its ability to block opened tubules it is recommended in dentin hypersensitivity e.g., Recaldent™ and GC Tooth Mousse.

f) Middle output power (Carbon Dioxide Laser (CO$_2$), Nd:YAG, and Er:YAG):

The high-power lasers increase the surface temperature which can result in the complete closure of dentinal tubules after recrystallization of the dentinal surface. Occlusion occurs through coagulation of the proteins of the fluid inside the dentinal tubules. Moreover, absorption of the laser energy by carbonate and phosphate minerals in dentine can lead to the melting of the tubular structure without cracking and results in reducing the permeability and hydraulic conductance[1, 8, 9].

g) Nano hydroxyapatite:

The major advantage of nanohydroxyapatite is its resemblance to the mineral structure of teeth, bioactivity, and biocompatibility. Nanohydroxyapatite has been integrated into products for oral care such as dentifrices, mouthwash, and pastes (such as Desensibilize Nano P) to reduce dental sensitivity by obstructing open dentinal tubules on the surface of the dentin, or for the purpose of promoting the remineralization of enamel by replacing calcium and phosphate ions in the areas from which minerals dissolved, restoring its integrity[19].

Mode of action:

Nano hydroxyapatite promotes tubule occlusion by the deposition and/or penetration of nano-sized particles into the dentin tubules. The particulate nano calcium phosphate exhibits mechanical obliteration properties twice as good as the traditional calcium phosphate compositions. However, the deposits formed by a hydroxyapatite paste is not resistant to acidic and mechanical challenges[13, 17, 20].

h) Resin modified glass ionomer:

Resin modified glass ionomer provides a physical barrier at the dentin surface which can release fluoride, calcium, and phosphate to the aqueous medium. The two latter are a result of the presence of calcium glycerophosphate in the composition of resin modified glass ionomer based desensitizing gent. The released calcium, phosphate, and fluoride during the erosive challenge, increasing their saturation regarding tooth minerals, thereby reducing the demineralization rate[13].

e.g., Clinpro XT Varnish.

i) Arginine/calcium carbonate (Pro-Argin) system:

The proargin system is composed of a positively charged amino acid at physiological pH (arginine), a source of calcium (calcium carbonate) and bicarbonate as pH buffer[4]. Arginine has the capacity to interact directly and rapidly with the dentine surface. Arginine contains several nitrogen atoms that can carry positive charges making this amino acid cationic over the range of physiological pH values. Cationic molecules have a high affinity for dentine since dentine has a negative surface charge. Cationic agents can also facilitate the attachment of other materials to the dentine surface by charge interactions and hydrogen bonding[7].

Mode of action:

Interaction between calcium carbonate and arginine leads to the formation of positively charged agglomerate by the adsorption of the arginine onto the calcium carbonate forming a surface layer rich in calcium (dentin like material) which binds to the negatively charged dentin surface leading to occlusion of dentinal tubules. Moreover, the arginine–calcium carbonate agglomerate has an alkaline pH which enables the precipitation of calcium and phosphate from dentin fluid and saliva[6,17].

j) Strontium salts:

Strontium is an alkaline metal and shares similar biological and chemical properties with calcium. It has a similar charge-to-size ratio and readily substitutes the calcium in hydroxyapatite within dentine. Strontium salts such as strontium chloride and strontium acetate have been widely used in toothpastes to relief DH pain[4].

Mode of action:

Dentin has a high affinity for strontium ions as the application of strontium onto a dentine surface results in the formation of a very compact continuous layer, composed of a high-density calcium–strontium hydroxyapatite (CaSr HA), which can penetrate and fill the dentinal tubules. The formation of CaSr HA results from an ion exchange between strontium and calcium in the dental tissues. CaSr HA has enhanced acid resistance. Moreover, strontium ions can alter neural transmission, calm the dentin nerve, slowing the conduction of the odontoblastic process, and relieve pain. Finally, strontium stimulates the formation of tertiary dentin[4,21].

V. Iontophoresis:

Iontophoresis is based on the principle like charges repel and opposite charges attract. By applying charged direct electrical current, concentrated ionized drugs can be driven rapidly into the tissue and effectively reaches to the therapeutic levels by iontophoresis[8].

Mode of action:

Desensitization by iontophoresis has been explained by several mechanisms. The first mechanism proposed is that electrical current produces paresthesia by altering the sensory mechanism of pain conduction. The second mechanism describes that it causes microprecipitation of the precipitates produced by desensitizing agents such as calcium fluoride around the tubules, thus blocking the hydrodynamically mediated stimuli that induce pain[22]. Another mechanism states that iontophoresis acts by influencing ionic motion by electric currents, thus enhancing ion uptake by the dentinal tubules and achieving desensitization[8].

VI. Natural desensitizing agents:

VI.1. Propolis:

Propolis is a natural, nontoxic, resinous substance, which is yellow brown. This is collected by honeybees from accessible parts of the plants. Chemically is made up of phenolic acids in addition to microelements such as aluminum and calcium. Propolis exhibits properties such as anti-inflammatory, antioxidant, antimicrobial, antiviral, antiparasitic, anesthetic, and that of a free-radical scavenger. The flavonoids present as a component of propolis are the main active and reactive agents capable of stimulating reparative dentin formation. This is one of the main factors that enable propolis to reduce dentin permeability efficiently[18,23,24]. Propolis has sustained effect due to stable nature of the propolis deposits[25].

VI.2. Moringa oleifera:

Moringa oleifera could have a promising effect in treatment of DH. This effect could be attributed to the presence of various nutrients in it such as calcium, phosphorus and others that are associated with dentinal tubule occlusion[6].

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Types of dental alloys and the effect of its microstructure and constituents on its properties and applications in dentistry

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Abstract: Alloying is the process by which two or more metals or even metals with non-metals are combined. It may consist of a single-phase or mixture of phases, depending on the composition of the alloy and temperature provided. Alloying is done to produce material with improved properties that cannot be gained by a single metal. As improving density of the alloy, electrical properties, color, thermal properties, strength, fatigue resistance, creep resistance and tarnish & corrosion resistance. In this review different classifications of alloys are discussed.

Keywords: *alloys; solid solution; eutectic alloy; intermetallic; stainless steel.*

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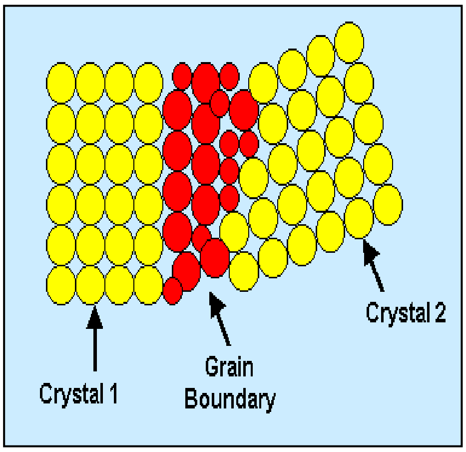
I. Introduction

Alloying is the process by which two or more metals or even metals with non-metals are combined. It may consist of a single-phase or mixture of phases, depending on the composition of the alloy and temperature provided. Alloying is done to produce material with improved properties that cannot be gained by a single metal. As improving density of the alloy, electrical properties, color, thermal properties, strength, fatigue resistance, creep resistance and tarnish & corrosion resistance.(1)

One of the most important reasons of alloying is to improve the yield strength of metal. In metals, plastic deformation occurs through slipping along the crystallographic planes within the grain. By alloying, strength can be improved by increasing the resistance to this slip movement.

Microstructure of metals:

Metal structures are formed of grains which have different crystallographic orientation. The atoms located between the grains or in other words at the boundaries of each grain are not aligned regularly, highly stressed (distorted position), have open structures.

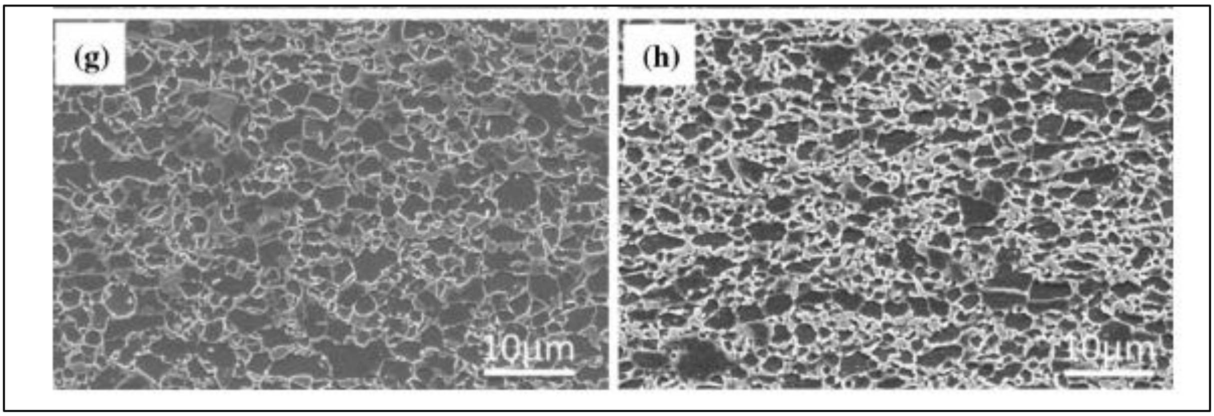


Different factors in microstructure can influence the physical properties of the final alloy as; grain size, grain boundaries and its distribution, dispersed particles and dislocations. All these can affect strength, toughness, ductility, hardness, corrosion resistance, or wear resistance of the alloy.

Different ways of increasing strength are achieved by increasing the resistance to slip movement, which includes; grain refining, solid solution hardening, dispersion hardening, phase transformation and cold working. (1)

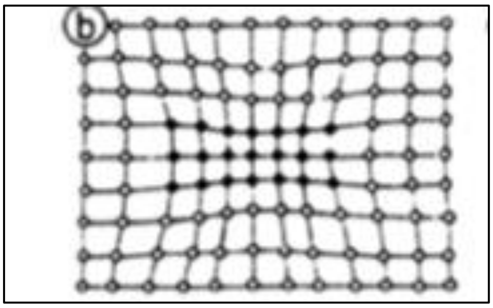
Vanadium, aluminum, tungsten, and nitrogen are examples of **grain refiners** for steel.

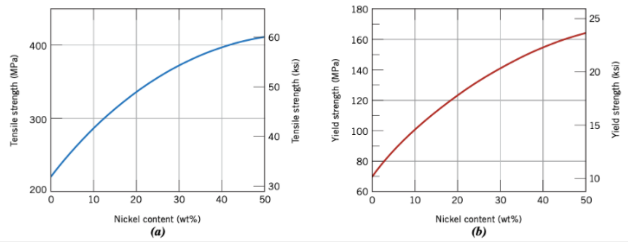
Scanning electron microstructure of (g) vanadium free steel and (h) vanadium containing steel (0.06 wt%)



(2)

In **solid solution hardening**, impurity atoms are added to a metal up to the limit of solubility in this metal. These new atoms form different effective diameter (distance between atoms in the crystal) than the base metal. This difference creates distortion in the crystal lattice that interferes with the slip movement by imposing stains on the host atoms. These strains counteract the dislocation tendency of pure metals. Thus, decreasing the plastic deformation and increasing the strength of the alloy.(1, 3)





Variation with nickel content of (a) tensile strength, (b) yield strength for copper–nickel alloys showing strengthening.

If the amount of the impurities added to the metal is greater than the solubility limit of the base metal. Upon solidification the extra alloying element becomes trapped within the boundaries. As the temperature decreases, alloying atoms in the boundaries try to unite with the base metal to form small regions of intermetallic compound. Although these regions have different crystal structure than the base metal, the two crystals remain coherent, and the mismatch causes strained hardening termed as **age hardening**. (1)

II. Classification of alloys:

II.1. According to number of metallic elements

a. Binary
b. Ternary.
c. Quaternary.
d. Quinary
e. Senary
f. Septenary
g. Octonary

In dentistry, alloys are used in almost every aspect. Dental alloys usually contain at least four metals, and often six or eight different metals. Thus, dental alloys are metallurgically complex.(4)

II.2. According to miscibility

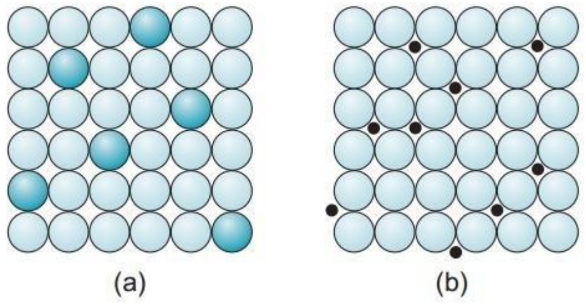
Alloys are classified according to the number of distinct solid phases. A phase is defined as a structurally homogeneous part of the system that is separated from other parts by a definite physical boundary. Each phase will have its own distinct structure and will affect the final properties of the alloy.

A phase may be formed of more than one component as does saline, which is an aqueous solution of sodium chloride. Similarly, phases in metals can consist of a mixture of metals. Copper can contain up to 40% zinc without destroying its FCC structure. Such alloy is called solid solution. (5)

Solid solution An alloy in which the main elements are soluble in any amounts in both solid (isomorphous system) and liquid phases forming an ideal solution. There are two types of solid solutions: **substitutional** and **interstitial.** For the substitutional type, solute or impurity atoms replace or substitute for the host atoms. While, in interstitial solid solution the solute atoms occupy the interstitial positions in the crystal lattice of the solute (host).

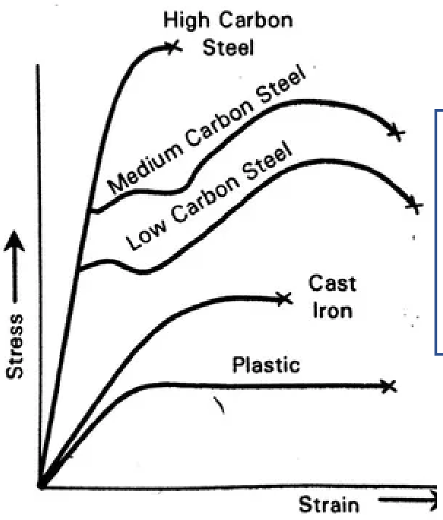
Several features of the solute and solvent atoms determine the degree of dissolution and which type of solid solution will occur. **These are expressed as four *Hume–Rothery rules*** (3)**:**

- Atomic size factor. For substitutional solid solution the difference between the atomic radii of both constituents must be less than or equal 15%. While for interstitial solid solution the difference should be more than or equal 60%.
- Crystal structure. For appreciable solid solubility, the crystal structures for metals of both atom types must be the same.
- Electronegativity factor. The more the difference in the electronegativities of both elements forming the alloy, the greater the possibility to form an intermetallic compound instead of a substitutional solid solution.
- Valency factor. The two elements should have the same valence.

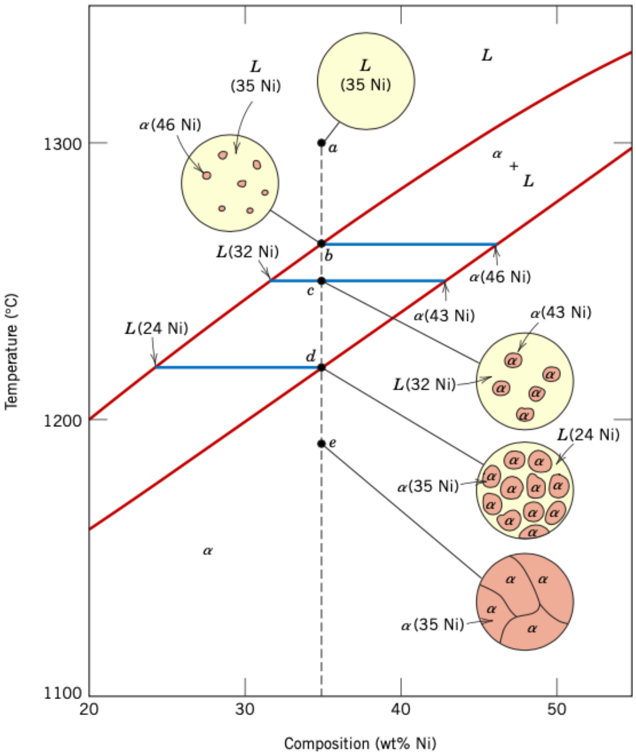


a) Substitutional solid solution

b) Interstitial solid solution



Steel is an example of interstitial solid solution according to the carbon wt % the mechanical properties vary



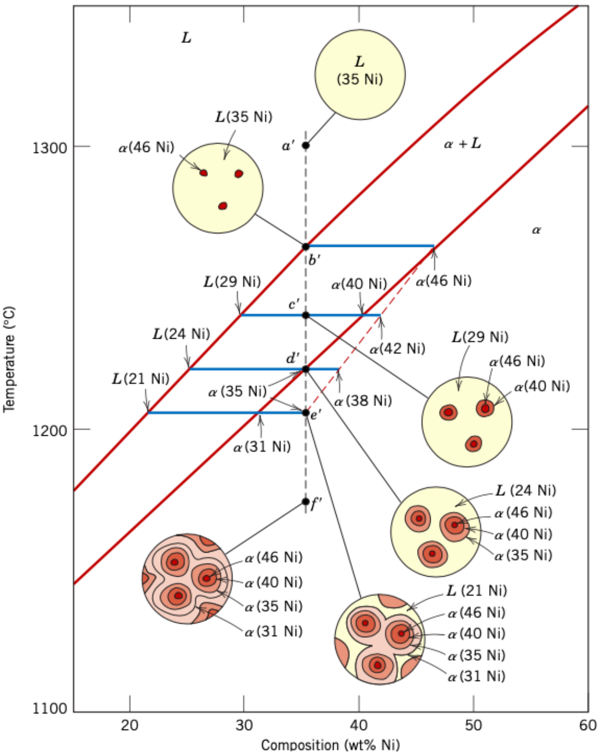
The development of microstructure during the equilibrium solidification of a 35 wt% Ni–65 wt% Cu al-

Development of microstructure in solid solution alloys in equilibrium cooling (3)

- The cooling occurs very slowly, thus phase equilibrium is continuously maintained.
- Solidification occurs gradually upon cooling.
- The composition changes gradually during cooling as presented by the phase diagram .
- As cooling begins, **(a)** no microstructural or compositional changes will be realized until we reach the liquidus line.
- At this point **(b)**, the first solid begins to form, which has a composition obtained by the tie line drawn at this temperature.
- As temperature decreases between liquidus and solidus line compositional changes occur that can be determined by the tie line.
- Subsequent cooling below the solidus line produces no microstructural or compositional alterations.

Diffusion is a time-dependent phenomenon. To maintain equilibrium during cooling, sufficient time must be allowed at each temperature for the appropriate compositional readjustments. Generally, in all practical solidification situations, cooling rates are much too rapid to allow these compositional readjustments to occur and maintain equilibrium. Consequently, other microstructures develop.

Development of microstructure in solid solution alloys in non equilibrium cooling (3)



- In rapid cooling, new layers are formed on top of the pre-existing grains. No diffusion occurs between different layers. As diffusion in the solid-state is very slow. Thus, having different composition at this temperature when compared with the equilibrium cooling.
- As a result, the formation of layered grains and the invalidity of the tie-line method to determine the composition of the solid phase.
- Solidus line is shifted to the right when compared to equilibrium solidification due to higher Ni contents depositions at first.While, the outer part of the grains will be richer in the low-melting component forming cored structure and solidification will be completed at lower temperature.
- Cored structure affects the mechanical properties negatively by decreasing tanish and corrosion resistance and increasing the brittleness that leads to premature failure. This can be eliminated by homogenization.
- **Homogenization heat treatment** is done at temperature below the solidus point for the particular alloy composition. During this process, atomic diffusion occurs, producing compositionally homogeneous grains.

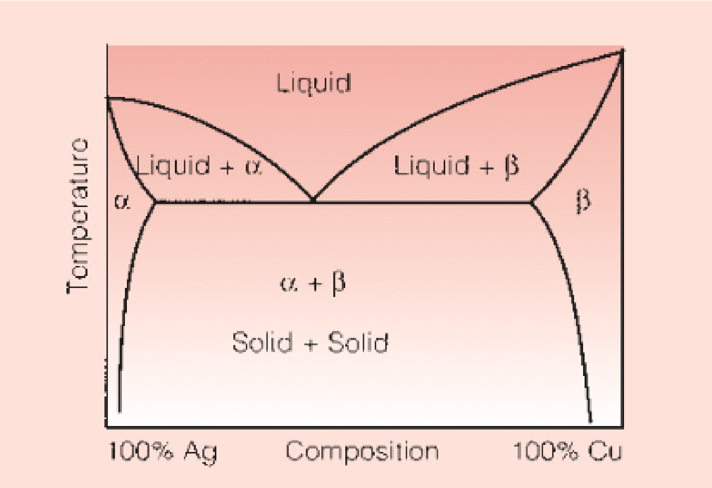
Eutectic alloy (3,5)

In this alloy the components of materials are not sufficiently soluble to form solid solution alloy. Examples of this alloy **silver copper alloy**, which are sufficiently different in atomic size that their atoms are partially soluble in one another.

For a wide range of compositions, the material will consist of two solid phases, one being silver-rich and other being copper-rich, called the α- and the β-phase, respectively. The α-phase consists of predominantly silver, with a small amount of copper dissolved in it, whereas the β-phase consists of copper, with a small amount of silver dissolved in it.

At low concentrations of copper in silver, all of the copper is able to dissolve in the silver, and only a single phase exists. The maximum solubility of copper in silver is **8.8 wt%,** and this occurs at a temperature of approximately **780°C.** At lower temperatures, the solubility of copper in silver decreases, and the excess copper separates out as the second, β-phase. Similar behaviour occurs at the other end of the compositional range.

An important feature of the phase diagram of the Ag–Cu system is the depression of the temperature of the liquidus at a composition of **72Ag : 28Cu** wt%. At a temperature of 780°C, this composition called the **eutectic composition**, and the temperature at the intersection of the three phases is the **eutectic temperature**. If a eutectic liquid is cooled, it changes directly into two solid phases, without an intermediate state as a liquid–solid mixture.



Equilibrium phase diagram for the Ag–Cu system

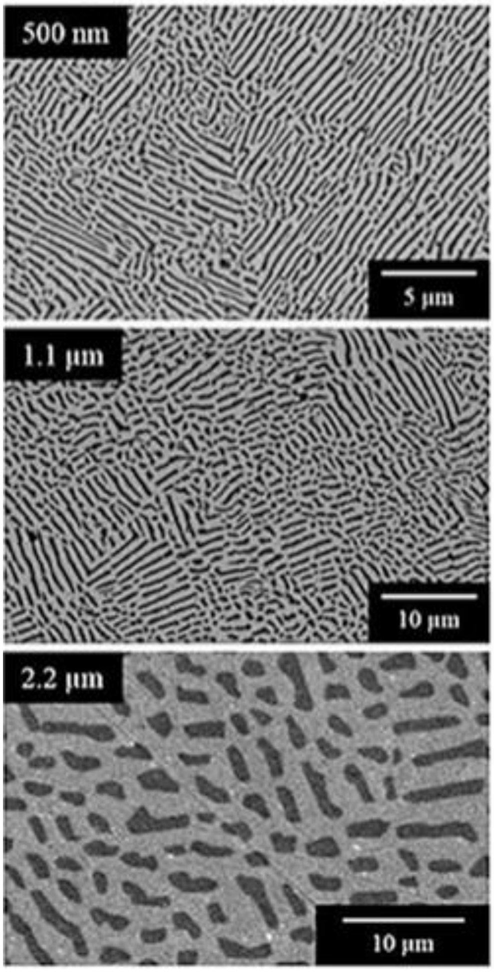
Development of microstructure in eutectic alloys at equilibrium cooling.

At pure α- and β- phases, solidification proceeds in the same manner as for isomorphous solid solution alloys.

Compositions to the left of the eutectic composition are called **hypoeutectic compositions** while the compositions to the right are called **hypereutectic compositions**.

- Hypoeutectic composition (α+L) α is the primary solid phase to precipitate.
- Hypereutectic composition (β +L) β is the primary solid phase precipitate.

At the eutectic composition, below 780°C simultaneous formation of α and β phases will induce a layered lamellar microstructure that is called eutectic structure.



Lamellar structure of the eutectic alloy

Intermetallic compounds

Intermetallic compounds exist when there is a **chemical affinity** between metals. On cooling of some metals, an intermetallic compound of specific composition is formed. The compound is represented on the phase diagram as a vertical line since the composition has a fixed value. There are two types of intermetallic compounds either stoichiometric or non-stoichiometric compounds.

a. **Stoichiometric compounds**: Compounds which have a single well-defined composition.

b. **Non-Stoichiometric compounds**: Compounds with a composition that can vary over a finite range.

Intermetallic compounds formation depends on **electrical affinity** that is formed between electropositive and electronegative elements, **composition** and **crystal structure** that allow the component atoms to be packed together well.

Stainless steel(5)

Iron is an **allotropic** material. It changes between two solid-states with temperature. At room temperature, pure iron has a body- centred cubic (BCC) structure, known as the α-phase. This structure is stable up to a temperature of 912°C, where it transforms to a face- centred cubic (FCC) structure, the γ-phase. At 1390°C the FCC iron reverts to BCC, and retains this structure until it melts at 1538°C.

Steel is an interstitial solid solution formed of iron and carbon (less than 2wt%). Steels are available in a wide variety of compositions, each has very specific properties that are carefully tailored to suit their particular application. One feature of steels that makes them such popular materials is the enormous range of mechanical properties that can be obtained with only small changes in composition.

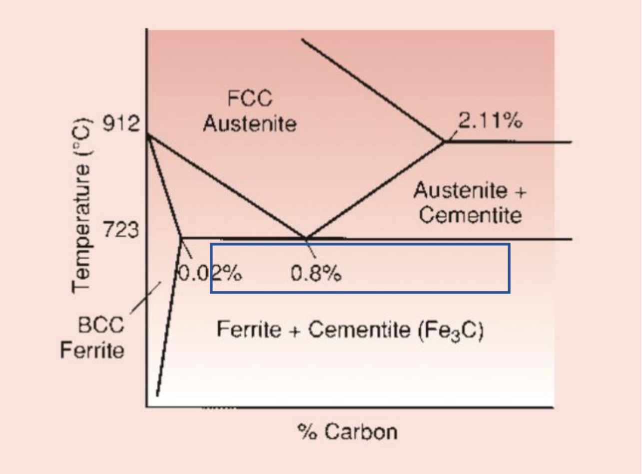
Carbon steels

Carbon steel is an alloy of only iron and carbon. In its BCC form, when small amounts of carbon are dissolved in the iron, the material is known as α-iron or ferrite. While if the iron is in the FCC form of the steel is known as austenite. Both **Ferrite** and **austenite** steel are **relatively soft and ductile.**When the limit of solubility for the carbon is exceeded for either of these forms of steel, the excess carbon precipitates as Fe_3C known as **cementite** which is a **hard** and **brittle** phase.

Hypereutectoid and hypoeutectoid steels

At a carbon concentration of 0.8% and at 723°C the alloy shows transformation from single-phase austenite to a two-phase structure consisting of ferrite and cementite (pearlite).

This solid transformation is defined as a eutectoid, derived from eutectic, which is the transformation of a single liquid phase directly into two solid phases.



Steels with a carbon content of exactly the eutectoid composition are called **eutectoid steels**. Those with a carbon content of greater than 0.8% are **hyper-eutectoid steels**, while those with a carbon content of less than 0.8% are **hypo-eutectoid steels.**

The eutectoid transformation is very important in the production of steels. When carbon steel is cooled from its austenitic high-temperature condition to room temperature according to the rate of cooling different phases can be precipitated.

Slow cooling

On slow cooling, the austenite is converted into a mixture of ferrite and cementite, which is described as **pearlite**.

Rapid cooling (Quenching)

When austenite is quenched in water, the ferrite and cementite cannot form because there is no enough time for diffusion and rearrangement of the atoms. Instead, a rapid transformation occurs into a body-centred tetragonal structure (distorted BCC). This form of steel is described as **martensite.** Martensite is extremely hard and brittle. (Too hard and brittle for any practical purposes)

By reheating of martensite to a temperature in the range of **200–450°C** and then cooling rapidly, transformation of the martensite into pearlite (ferrite + cementite) occurs. The degree of conversion can be carefully controlled by the temperature and duration of the heat treatment, a process known as **tempering**.

Hyper-eutectoid steel (carbon content >0.8%):

It combines the hard martensite with a large presence of the hard cementite. Therefore, it is used for cutting instruments and burs. By this microstructure, cutting edge can be produced which does not blunt easily.

Hypo-eutectoid steels (carbon content <0.8%):

It is formed of predominantly ductile ferrite, while the hardness is controlled by the presence of martensite and much lower amounts of cementite.

It is used for instruments such as forceps. where the brittle nature of hyper-eutectoid steel would be unacceptable.

Clinical significance:

Excessive heating up of cutting instruments (e.g. cutting blades in a bunsen flame) will result in loss of hardness due to changes in the microstructure.

Stainless steel

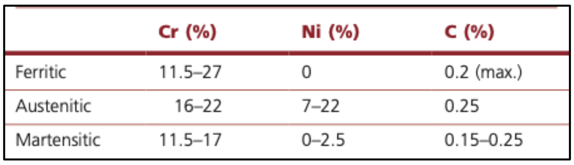
Although many other elements can be added to the basic carbon steels to improve the properties (e.g. molybdenum, silicon, cobalt, manganese), the two of greatest importance for dentistry are **chromium** and **nickel** for the production of stainless steel.

Stainless steel is an alloy of iron that is resistant to corrosion. The addition of chromium to the carbon steel improves the corrosion resistance of the metal by forming a protective surface coating of chromium oxide. For this to be effective, the chromium content of the alloy has to exceed 11%.

Austenitic stainless steel

The addition of 8% **nickel** prevents the transformation of austenite to martensite on cooling, such that the austenite becomes stable at room temperature when cooled rapidly. Slow cooling would allow the formation of ferrite and cementite.

There are three main forms of stainless steel used for dental applications.

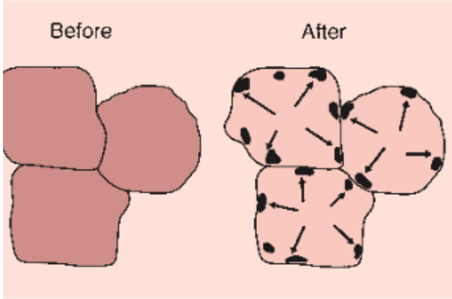


	Cr (%)	Ni (%)	C (%)
Ferritic	11.5–27	0	0.2 (max.)
Austenitic	16–22	7–22	0.25
Martensitic	11.5–17	0–2.5	0.15–0.25

Austenitic stainless steels have a very wide application and are used in orthodontic wires, auxiliaries, ligatures, files, reamers and stainless steel crowns. The martensitic steels are mainly used for cutting instruments. The attraction of the austenitic stainless steel is that it is highly malleable and so can be readily shaped for a wide variety of purposes. The alloy cannot be heat-treated, but it can be cold-worked to improve the yield stress (although this will be at the expense of the ductility) while maintaining its high corrosion resistance.

Stabilized austenitic stainless steel

Although most wrought alloys are subjected to stress-relief annealling, this is not possible with the austenitic stainless steels due to microstructural changes that occur at the annealing temperature.



Weld decay due to overheating of the alloy

At temperatures exceeding 500°C, chromium and carbon react to form chromium carbides that precipitate at the grain boundaries, increasing brittleness. Moreover, the corrosion resistance is decreased due to depletion of chromium from the central regions of the crystals, which has migrated to the boundaries to form the carbides. This process is known as **weld decay.** This problem can be overcome by adding titanium to the alloy, which has the effect that carbon preferentially reacts with the dispersed titanium leaving the chromium where it is most effective. Addition of titanium produces **stabilized austenitic stainless steel.**

Austenitic stainless steels are favored for orthodontic applications as it has excellent corrosion resistance in the biological environment. Wide range of mechanical properties available (a range of mechanical properties are produced depending on the degree of cold working carried out by the manufacturer in forming the orthodontic wire).(5)

Different additives were added to the stainless-steel alloy to improve its properties as Molybdenum (Mo) which improved the corrosion resistance.it was found that small amount of Mo (2–4 wt %, up to 6 wt %) is frequently used with conventional austenitic stainless steels because of its distinct advantages in increasing localized corrosion resistance. Molybdenum is known to promote the strength of the passive film by formation of the Molybdenum and Chromium-enriched film and byincreasing thickeness of the passive film. Molybdenum was also reported to be beneficial in enhancing repassivation characteristics.(32) Mo was added to an alloy containing approximately 18% weight of Cr and 8% weight of Ni and with reduced carbon (C) content from 0.08 to 0.03%. The alloy was named as SS 316L. (6)

II.3. According to principal element

Alloys may also be classified based on the principal element (e.g., a palladium-based alloy), or they may be named based on the two or three most important elements (e.g., Ni-Cr or Ni-Cr-Be alloys). Casting alloys can be based on Au, Pd, Ag, Ni, Co, Cu, or Ti as the principal element. When an alloy is identified according to the elements it contains, the components are listed in decreasing order of concentration. An exception to this rule is the identification of certain alloys by elements that significantly affect physical properties or that represent potential biocompatibility concerns. For example, nickel-chromium-molybdenum-beryllium alloys are often designated as nickel-chromium-beryllium alloys because of the contributions of beryllium to the control of castability and surface oxidation at high temperatures and because of the relative toxicity potential of beryllium compared with other metals even its presence in low concentration.1)

II.4. According to ADA Classification:

The classification system most used by dental practitioners is the American Dental Association (ADA) compositional classification system. The ADA system divides casting alloys into three groups based on wt% composition. The **high-noble alloys** are those with a noble metal content (sum of gold, palladium, and platinum) of at least 60 wt % and a gold content of at least 40 wt %. **The noble alloys** must contain at least 25 wt % noble metal but have no specific requirement for gold content. Finally, the predominantly **base-metal alloys** contain less than 25 wt% noble metal, with no other specification on composition. [2]

The ADA also classifies alloys on physical properties of yield strength and elongation (Table 1). Four categories of alloys are defined in this scheme.

Soft alloys are defined for use in low-stress conditions under which the restoration bears no significant occlusion. **Medium** alloys are recommended for conditions of moderate stress and light occlusal stress. **Hard** alloys are recommended for full occlusal loads with single units or short-span fixed partial dentures, and **very hard** alloys are recommended for removable partial dentures and longer-span fixed partial dentures. Each casting alloy is defined by two ADA classification systems; one for composition and one for physical strength. [2]

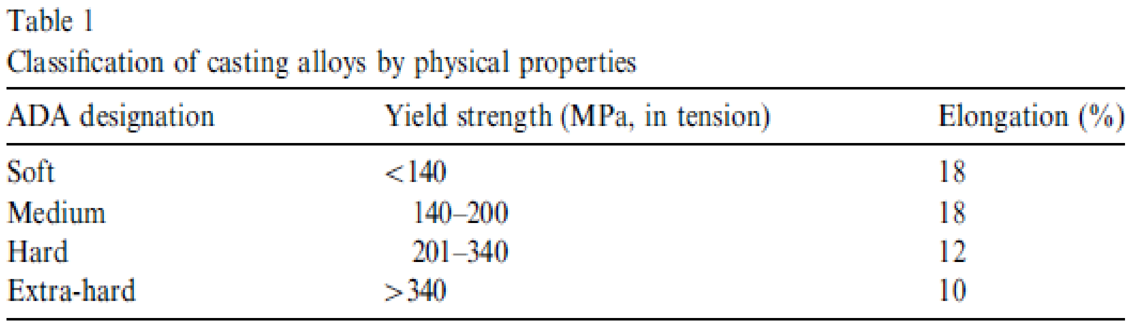


Table 1
Classification of casting alloys by physical properties

ADA designation	Yield strength (MPa, in tension)	Elongation (%)
Soft	<140	18
Medium	140–200	18
Hard	201–340	12
Extra-hard	>340	10

Four types of dental casting gold alloy (types 1 to 4) are given in ISO 1562:1995 as follows: **Type 1** low strength – for castings subject to very slight stress, e.g. inlays. **Type 2** medium strength – for castings subject to moderate stress, e.g., inlays and onlays. **Type 3** high strength – for castings subject to high stress, e.g. onlays, thin cast backings, pontics, full crowns and saddles. **Type 4** extra high strength – for castings subject to very high stress and thin in cross section, e.g. saddles, bars, clasps, crowns, bridges and partial denture frameworks.

II.4.A. High-noble alloys

High-noble dental casting alloys can be divided into three categories; gold-platinum (Au-Pt), gold-palladium (Au-Pd), or gold copper-silver (Au-Cu-Ag). The first two alloy types are suitable for all-metallic or metal-ceramic restorations. The latter type is suitable only for all-metallic applications because of its higher silver and copper content and its lower melting range. [3]

Gold-platinum (Au-Pt):

The Au-Pt alloys were designed to avoid the use of palladium, which became expensive and biologically controversial between 1995 and 1999. Both of these issues have since resolved, but this class of alloys is still available. [4]

Composition

Platinum (Pt) is used primarily in PFM alloys to increase the melting range, hardness, strength, and elastic modulus. Like palladium (Pd), it also decreases the α of gold alloys. Additions of Pt affect the properties of gold alloys to a lesser extent compared with Pd. [1]

Contain a high percentage of gold, usually in the range of 80% to 85%. The alloy is strengthened with the addition of 7% to 10% platinum, and trace elements such as indium, zinc, and tin are added to provide an oxide layer for adequate porcelain bonding. [5]

These alloys are complex metallurgically because gold and platinum are not completely soluble in one another (**Figure 1)** and are generally strengthened by a dispersed zinc phase. Some formulations contain silver to strengthen the alloy through solid solution hardening with gold.[3]

Zinc is added to crown and bridge alloys as an oxygen scavenger, thereby reducing gas porosity in castings. For PFM alloys, zinc can be added also to strengthen and harden the alloys and/or to increase α. It also decreases the melting range.[6]

Iron is used primarily to strengthen Au-Pt alloys for PFM applications. Like Sn and In, it also forms a bonding oxide.

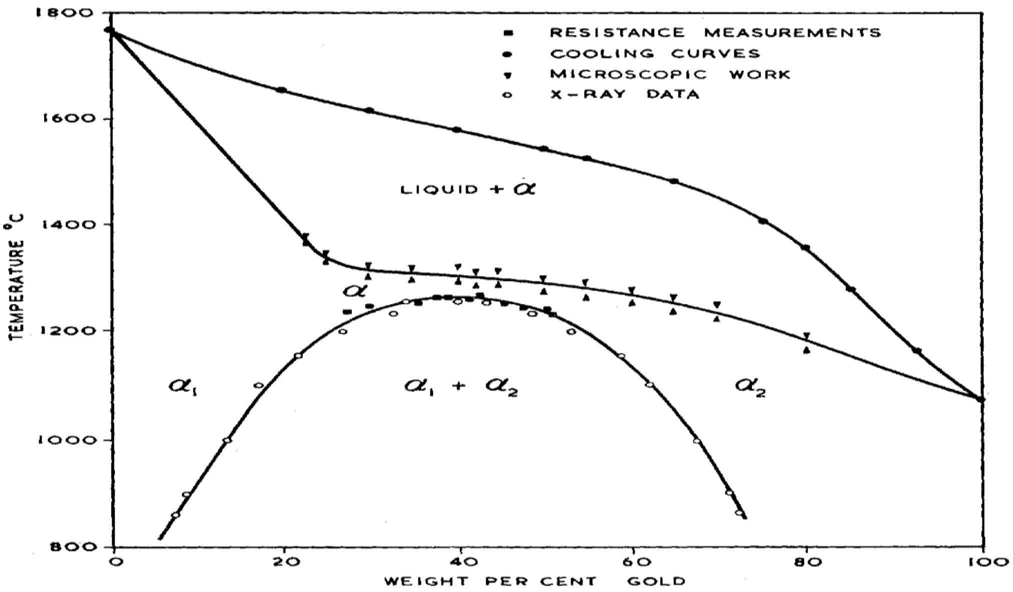


Figure 1: Phase diagram of the gold platinum system

Properties:

These alloys are white (silver) in color and have a moderately high melting range and moderate hardness, modulus, and strength. Because of their high noble metal content (97 wt %), they are expensive. Their corrosion is highly variable depending on the phase structure and appropriate manipulation of the alloy by the laboratory. Au-Pt alloys are especially susceptible to overheating, which can disrupt the dispersed zinc phase and increase its corrosion significantly.[4]

Microstructure:

The alloy composition:(Au-86.9;Pt-10.4;Zn-1.5;Ir-0.2;Rh-0.2;In-0.1). By SEM, the microstructure of Au-Pt alloy was composed of an Au dominant α_1 phase(98.44 wt%) and a minor Pt-dominant α_2 phase (1.56 wt%) with minor phases($AuZn_3$ and Pt_3Zn). [7]

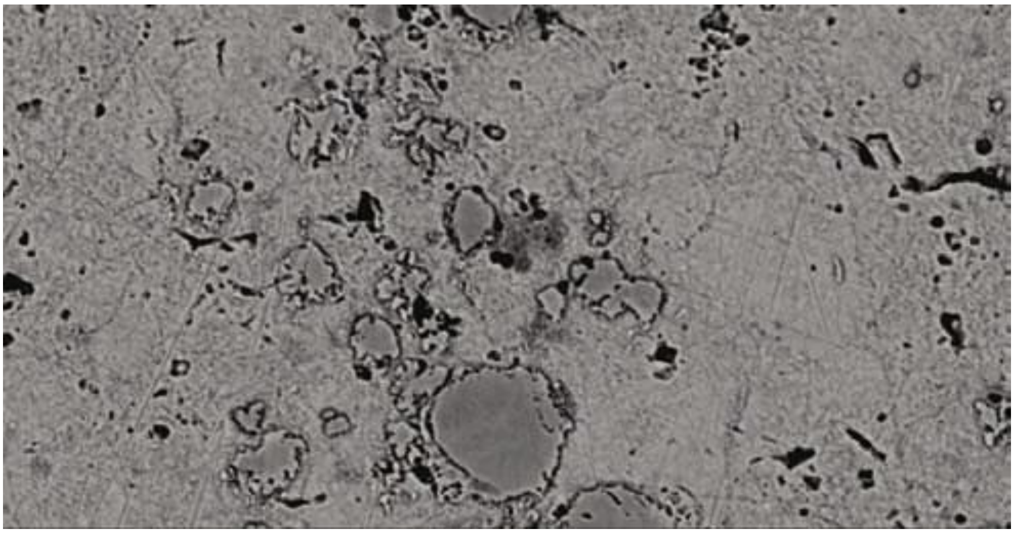


Figure 2: The SEM microstructure of Au-Pt alloy

Gold-palladium (Au-Pd)

Composition:

A high **gold** concentration provides a high tarnish and corrosion resistance, excellent ductility and excellent wear resistance for its alloys, also is useful to raise the thermal expansion coefficient of palladium alloys.[8]

Palladium has a higher melting point than gold and a higher modulus of elasticity. The thermal expansion coefficient of palladium is too low for it to be used with most commercial porcelains, so elements such as silver are needed to raise α of palladium alloys. On the other hand, palladium is used to lower the α of gold-based PFM alloys. Palladium whitens gold alloys markedly. It raises the melting range of gold alloys as well as their elastic modulus, strength, and hardness. Palladium lowers the density of gold alloys. Small amounts of palladium improve the tarnish and corrosion resistance of Au-Ag-Cu crown and bridge alloys, especially of alloys containing less than 68% Au. [9]

The Au–Pd alloys were developed to address the two main problems associated with silver-containing alloys: porcelain discoloration and a high coefficient of thermal expansion. Their only significant disadvantage is having a thermal expansion incompatible with porcelain. In an effort to address this problem, a number of Au–Pd alloys have recently been developed that contain less (<5%) silver. Due to these alloys' low silver content, porcelain does not discolor, castability is improved, and the coefficient of thermal expansion is increased. [6]

Properties:

Au-Pd alloys are common in **metal-ceramic restorations**. These alloys have moderate strength, elastic moduli, and hardness and have a moderately high melting range. The Au-Pd composition is sometimes supplemented with silver to increase the physical properties through solution hardening with gold and palladium. They are always white in color because the Pd concentrations are greater than 10 wt %. The corrosion of these alloys is low in biologic environments, even at low pH or during toothbrushing.[10]

Microstructure:

Au-Pd alloys are nearly always single-phase alloys. Gold and palladium are completely soluble in one another and they are common components in many noble PFM alloys because they offset each other's limitations.[6]

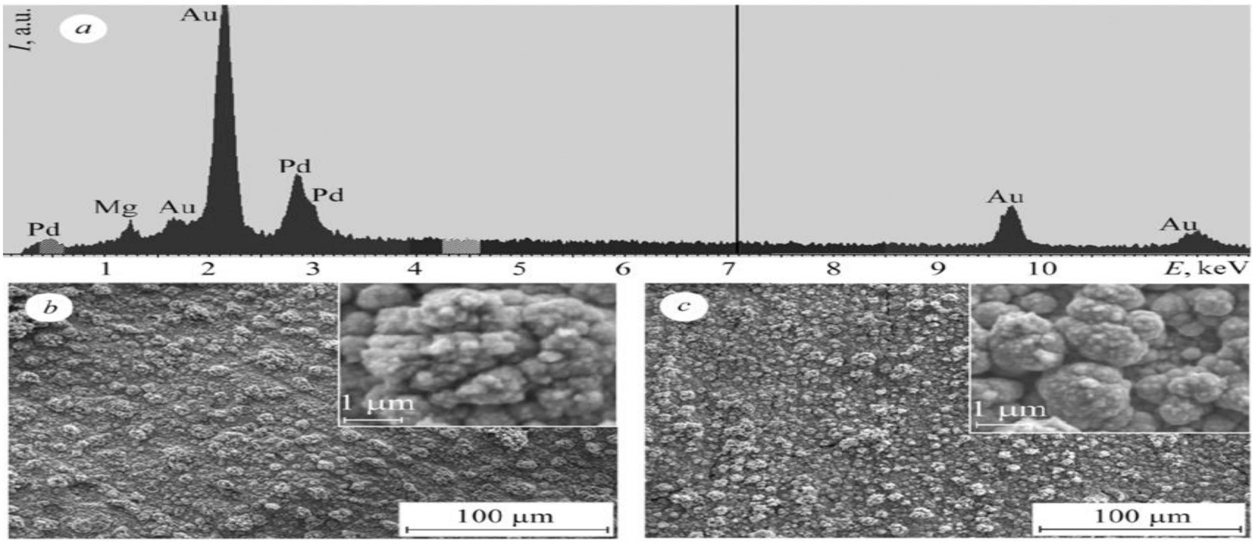


Figure 3: SEM of Au-Pd alloy

Gold-copper-silver (Au-Cu-Ag):

Composition and Properties:

Copper strengthens and reddens Au-Ag-Cu crown and bridge alloys. However, it is not used in alloys with high gold contents because, like Ag, it also tends to discolor porcelain. It is added to Pd-based PFM alloys to increase their α. However, higher Cu contents produce dark-colored oxide layers that may adversely affect the esthetics of metal-ceramic (PFM) restorations. Copper does not seem to cause porcelain discoloration if it is alloyed primarily with Pd. Cobalt has been used as an alternative to Cu in Pd-based PFM alloys. However, like Cu, it also forms dark-colored oxides. [11]

Silver is added to Au-Ag-Cu casting alloys to offset the reddish hue contributed by Cu. However, Ag-rich Au-Ag-Cu alloys tend to have a slightly greenish hue. In Pd-based PFM alloys, Ag is used primarily to raise the thermal expansion coefficient. Silver decreases the melting range of both Pd and Au alloys. It also tends to improve the flow of casting alloys and solders. [11]

They are common for **all-metallic** restorations. These alloys generally are yellow in color and have moderately high yield strengths and hardness but only moderate elastic moduli. Their relatively low melting range makes them castable using gypsum-bonded investments and gas-air torches.[4]

Microstructure:

The dental alloys of this type are hardened by ageing at 400 C. Hardening is due to precipitation of copper-rich and silver-rich phases, also to the order-disorder transformation in the gold-copper system. During ageing, holding at low temperatures for a long time results in continuous phase precipitation. The degree of hardening depends on the amount of copper present which is from (1-10%). [12]

II.4.B. Noble alloys

Noble alloys are much more compositionally diverse than high-noble alloys because they include gold-based alloys and those based on other elements such as palladium or silver. They involve four groups: Au-Cu-Ag, Pd-Cu-Ga, Pd-Ag, and Ag-Pd.[13]

Au-Cu-Ag

Composition:

Au-Cu-Ag noble alloys are similar in composition and metallurgy to the high-noble Au-Cu-Ag alloys. These alloys have **decreased gold** content and compensate for the reduced gold by increasing copper, silver, or palladium. [13]

Properties:

They are higher in hardness and yield strength than their high-noble counterparts. Depending on the amount of silver or copper present, Au-Cu-Ag alloys may be used in porcelain–metal applications but are more commonly used for full-cast restorations. The melting range of these alloys is lower than that of their high-noble counterparts if the copper or silver has been supplemented, and the color of these alloys varies from yellow to reddish-yellow to silver depending how the reduced gold is compensated for in the composition. For example, alloys with 10 wt % or more of palladium have a silver color, whereas those with 20 to 30 wt % of copper are more reddish in color. Most often single-phase alloys, the Au-Ag-Cu alloys generally have poorer corrosion properties than their high-noble counterparts if the copper or silver has been increased to more than 15 wt % .[14]

Pd-Cu-Ga

- **Composition and properties:**

Gallium is used primarily in Pd-based PFM alloys. Gallium strengthens these alloys and decreases their melting range.[1]

The Pd-Cu-Ga alloys are the most metallurgically complex of the noble alloys. They nearly always have multiple phases, but their corrosion is highly variable depending on the specific nature of the phases. The phase microstructure of these alloys is complex and dependent on how the alloy is manipulated.[4]

The Pd-Cu-Ga alloys are among the strongest alloys used in dentistry for cast restorations and are 25% stiffer than any of the high-noble alloys or the Au-Cu-Ag noble alloys. These alloys have high melting ranges and must be cast using induction-casting and special high-temperature investments. They are difficult to finish and polish. Depending on the amount of copper and its high-temperature volatility, the Pd-Cu-Ga alloys are useful for porcelain–metal applications. These alloys also are susceptible to sag during porcelain application. [4]

Microstructure:

SEM images shows short lamellae and rod-shaped morphology of this constituent Pd-Cu-Ga.[15]

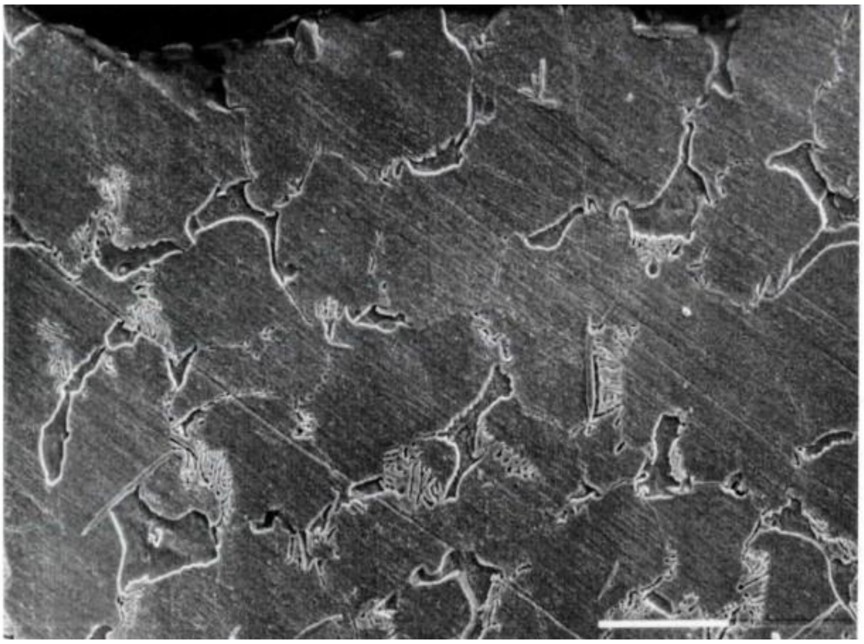


Figure 4: SEM of the microstructure of Pd-Cu-Ga alloys

Pd-Ag and Ag-Pd

Properties:

Pd-Ag alloys are far more common in dentistry and are far superior in strength, corrosion resistance, modulus, and hardness. The Pd-Ag alloys are used for porcelain–metal restorations, but the high silver content of the Ag-Pd systems makes them only for full-cast restorations. Because palladium has a very high melting point (over 1400°C), the Pd-Ag alloys (which typically contain over 60 wt %Pd) have high melting ranges and obtaining good clinical fit of these alloys depends heavily on properly compensating for casting shrinkage.[9]

Furthermore, these alloys require the use of induction-casting and high temperature investments. Of all the noble and high-noble alloys, the Pd-Ag alloys have the **highest moduli**, making them most suitable for long-span fixed partial dentures; however, even these alloys are not as stiff as the nickel- or cobalt-based alloys. The Ag-Pd alloys are usually only in the noble category by the use of a minimal amount of Pd (25 wt %) or a combination of palladium and gold totaling 25 wt % Silver-palladium alloys.

The silver–palladium alloys contain little or no gold. There is generally a minimum of 25% palladium along with small quantities of copper, zinc and indium, in addition to gold which is sometimes present in small quantities. These alloys have significantly lower density than gold alloys, a factor which may affect castability. Alloys containing large quantities of palladium have a probability for dissolving oxygen in the molten state which may lead to a porous casting. The properties of silver–palladium alloys are similar to those of type III gold. [9]

Microstructure:

While the microstructures of as-cast specimens representative of dental restorations were inhomogeneous, after simulated porcelain-firing heat treatment these microstructures were substantially homogenized with the formation of numerous precipitates. [16]

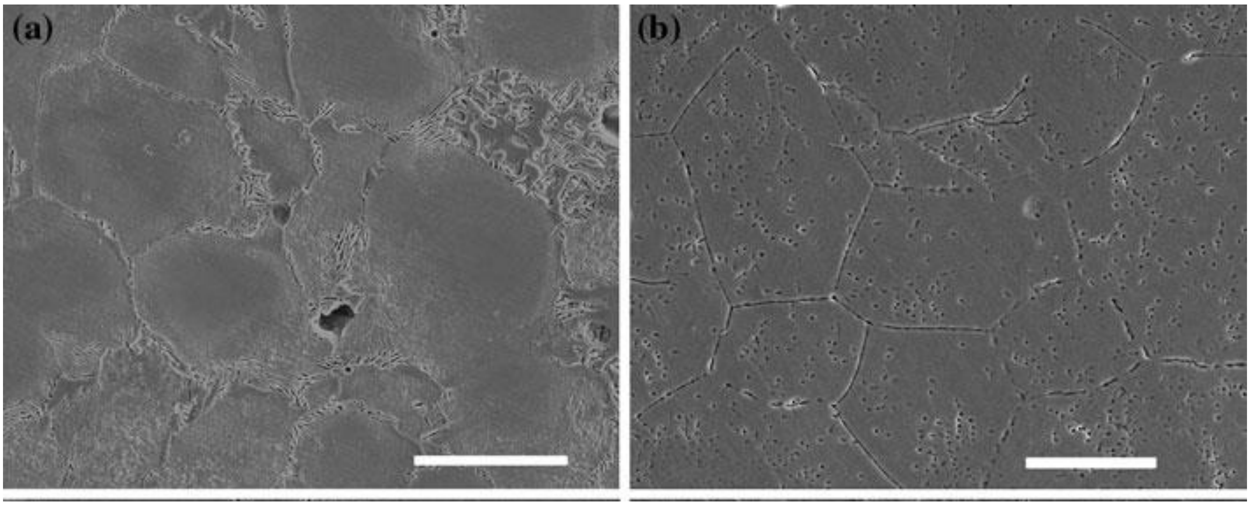


Figure 5: SEM images showing the microstructures of (a) as cast and (b) heat-treated Pd-Ag.

<u>**Effects of Alloy Elements on Properties of High Noble and Noble Metal Alloys**</u>

Indium (In) is used in some Au-Ag-Cu casting alloys to improve their castability. In Au- and Pd-based alloys, it strengthens and hardens the alloys, increases their α, and decreases their melting temperature range. It also contributes to the formation of a bonding oxide in PFM alloys[17]. **Tin** also contributes to the formation of a bonding oxide and it strengthens and hardens Au- and Pd-based PFM alloys. It also decreases the melting range of Au-based and Pd-based alloys and increases the α of these alloys.[2]

Three noble elements that are used to refine the **grain** structure of alloys are iridium (Ir), rhenium (Re), and ruthenium (Ru). Smaller grains block dislocation movement from grain to grain, resulting in increased yield strength. The three elements have a fairly high melting point and tend to be the first to form crystals in the molten matrix. Their low concentration allows their atoms to distribute themselves more or less evenly throughout the melt. The even distribution of grain formation throughout the solution limits the size of the larger grains as well.[1]

II.4.C. Predominantly base-metal alloys

The base-metal alloys can be divided into four groups: Ni-Cr, Co-Cr, stainless steel and titanium alloys. Ni-Cr and Co-Cr, when used for cast restorations, these alloys generally do not contain carbon. However, when used for partial denture frameworks, carbon is generally added and is a potent enhancer of yield strength and hardness. Ni-Cr and Co-Cr **may be used for all-metallic or metal-**

ceramic restorations, and all are silver in color. For metal-ceramic application, these alloys all form heavy, dark oxide layers that are more difficult to esthetically manage than those formed by alloys in the noble and high-noble alloy groups. The base-metal alloys have **the highest moduli** of any alloys used for cast restorations. They are all equally difficult to solder because of their tendency for formation of surface oxides.[18]

Nickel-chromium alloys

Composition and properties:

The chemical composition of these alloys specified in the ISO Standard for Dental Base Metal Casting Alloys (Part 2) is as follows: Nickel main constituent, Chromium no less than 20%, Molybdenum no less than 4%, Beryllium no more than 2%,(Nickel + cobalt + chromium) no less than 85%. Ni-Cr alloys have adequate properties for use with ceramics.[19] The hardness and elastic modulus of the Ni-Cr alloy allows for the use of a thinner cross-section of material; the thinner cross-section provides more space for porcelain veneering while still offering good resistance. Another advantage is their linear thermal expansion coefficient, which is similar to that of veneering porcelain. The similarity in thermal expansion reduces the risk of cracks and fractures during processing. Nickel sensitivity may be a concern with these alloys. [2]

Beryllium is used primarily to lower the melting range of the alloy to a point where gypsum-bonded investments can be used for casting. Although beryllium is advantageous in terms of casting manipulation of this alloy by the laboratory, the Ni-Cr-Be alloys corrode far more than their non-Be counterparts This corrosion is particularly evident in acidic environments. In some studies, the amount of nickel released from these alloys in an acidic environment in 30 minutes is more than that released in 1 year in a neutral environment. [23]

The Ni-high-Cr alloys are the most corrosion resistant of the Ni-based group and have Cr contents of over 20 wt %. The corrosion of these alloys is far better than the Ni-Cr-Be alloys but not as good as many alloys in the noble or high-noble groups. The common hypersensitivity to nickel (10% to 20%) makes use of any of the Ni-based alloys a higher biologic risk than many others.[20]

Microstructure:

The microstructure of the nickel-chromium-molybdenum alloy was dendritic, typical of cast materials. The dendrites are constructed mainly of intermetallic phases γ, enriched with nickel, and the increased content of molybdenum causes its segregation into the interdendritic areas. In the Ni-Cr-Mo alloys, no strong chromium segregation is observed, however, its content in the interdendritic areas is lower in comparison with the material base. The presence of Fe and C in the alloy also has an important effect on the final microstructure of the cast Nr-Cr-Mo alloy. These additions are accumulated in the interdendritic areas in the form of minor precipitations.[21]

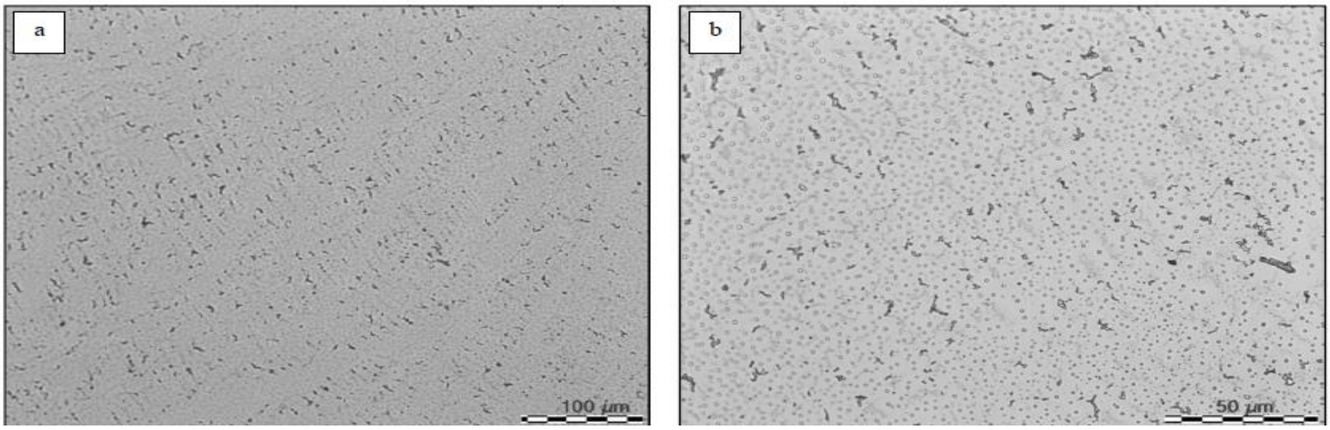


Figure 6: microstructure of Ni-Cr alloy

Co-Cr alloys

Composition:

The chemical composition of these alloys specified in the ISO Standard for Dental Base Metal Casting Alloys (Part 1) is as follows: Cobalt main constituent, Chromium no less than 25%, Molybdenum no less than 4%,(Cobalt + nickel + chromium) no less than 85%. A typical material would contain 35–65% cobalt, 25–35% chromium, 0–30% nickel, a little molybdenum. [19] Cobalt is the main component of Co-Cr alloys, while chromium improves strength and corrosion resistance, maintaining the alloy's brightness. Chromium percentages greater than 30% lead to improper alloy casting and potentially, **a brittle sigma phase**, which will affect the alloy's properties.[22]

The σ phase precipitates in grain boundaries causing brittleness of the alloy. The quantity of released Cr, Mo and Ni ions increases with increasing the σ phase,Figure 8.[22]

Metals such as molybdenum, tungsten, and nickel may be added to Co-Cr alloys. The addition of these metals will change the properties of the Co-Cr alloys. Despite the similarity with Ni-Cr alloys, Co-Cr alloys present lower ductility and their thermal expansion coefficient is not compatible with porcelains.

Properties:

These alloys are the most common base-metal alternative for patients known to be allergic to nickel. With the exception of titanium-based alloys, the Co-Cr alloys have the highest melting ranges of the casting alloys, and laboratory manipulation (casting, finishing, and polishing) of these alloys is difficult. The surface oxide of Co-Cr alloys is particularly difficult to mask, and the compatibility of coefficients of thermal expansion between these alloys and porcelains may be problematic.

Microstructure:

Figures 7 show the optical microscopy images of the Co-Cr alloy specimens prepared using casting (CS) and milling (ML)techniques. In both techniques, the typical dendritic grains predominated and the intermetallic phases were precipitated along the grain boundaries, but the ML group showed a substantially larger grain size than the CS group.

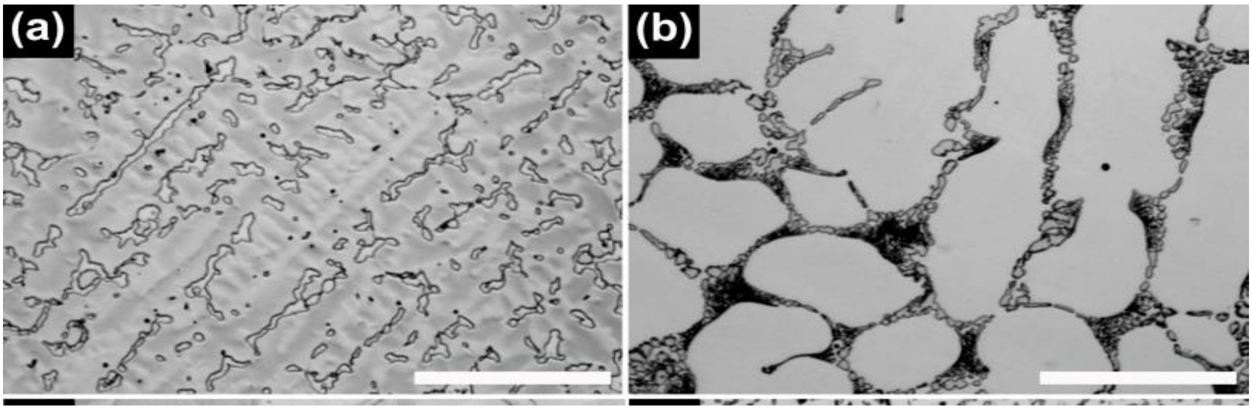


Figure 7: Optical microscopy images of the Co-Cr alloys tested. (**a**) CS; (**b**) ML

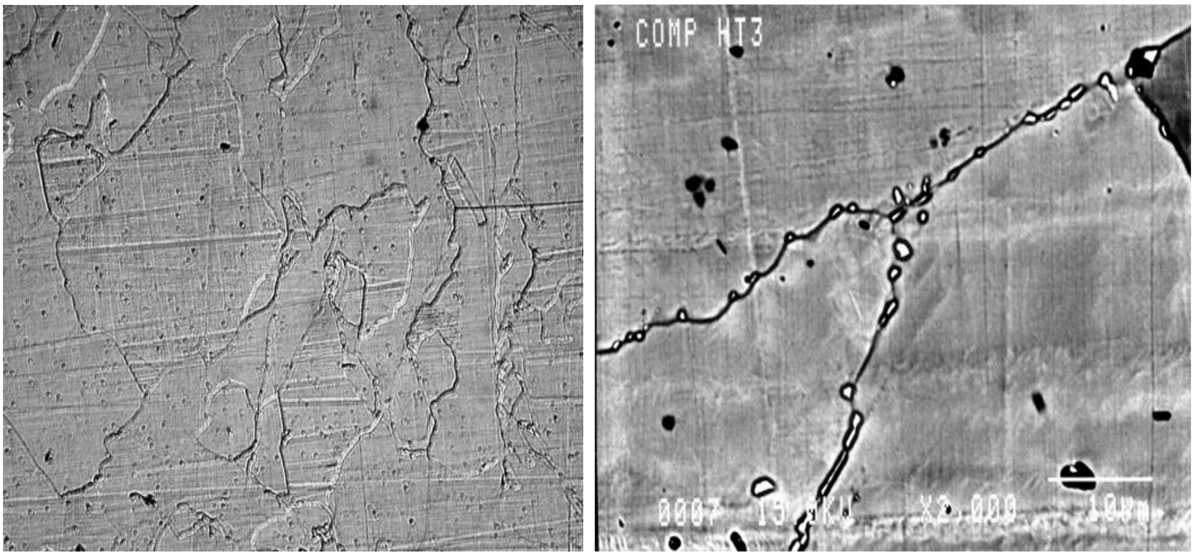


Figure 8: Optical micrograph and backscattered electron image showing sigma phase brittleness of cobalt-chromium alloy.

II.5. According to dental Application

A) Metallic restorations.

i. Gold-based restorations (Type I, II, III)

ii. All metal fixed prosthesis [19]

- **High noble and noble alloys**

Gold-based alloys (Type III and IV) and Ag-Pd**.**

- **Predominantly base metal alloys**

(Ni-Cr, Co- Cr, Ti-6Al-4V and Ti-6Al-7Nb)

iii. Stainless steel (austenitic type) for construction of pediatric crowns

B) Metal ceramic restorations

i. Highly noble and noble metal ceramic alloys

ii. Base metal ceramic alloys

C) Removable partial dentures

i. Type IV gold alloys

ii. Co-Cr alloys and Cp Ti and Ti-6Al-4V alloys. [19]

D) Implants

- Stainless steel Type 316L is used for fabrication of implants.
- CP titanium and titanium alloys are used for fabrication of implants

E) Orthodontic brackets, wires & ligatures.

- Austenitic type of stainless steel as 18/8, is used for the fabrication of brackets, archwires, bands, ligatures.
- Stainless steel Type 316L is used for fabrication of brackets
- Titanium alloys are used for fabrication of orthodontic wires

F) Instruments

- For cutting instruments and burs hyper eutectoid steel is used.
- For non-cutting instruments as forceps hypo eutectoid steel is used.
- For dental posts titanium or Tanium alloys could be used.
- For endodontic files and reamers hyper eutectoid steel is used.

G) Surgical plates and screws

- Stainless steel Type 316L is used for fabrication of surgical plates.
- Titanium screws and plates have been used also.
- Biodegradable alloys such as Mg-based or zinc-based metal alloys.
- Amorphous metals

Biodegradable alloys (28,29)

Biodegradable alloys are alloys that dissolve in the human body. When used as screws or plates for fixation of fractured bone, their elimination after the recovery period of the fractured bone is no longer necessary.

Mg-based metal alloys are biodegradable metal materials with a good osseointegration property. It has low modulus of elasticity (41–45 GPa), near to that of human bone when compared to other metals, which prevents the negative effect of stress-shielding in bone structure. Moreover, Mg biomaterials and their alloys are currently used as temporary implants as it degrades completely in the biological environment. Being replaced by newly formed bone, eliminates the need for surgical reintervention to remove the implant, which is mandatory in case of permanent implants.

In the biological environment Mg alloys degrade rapidly, thus requiring a precise control of the corrosion rate that is adjusted with the repair/healing processes of the affected bone tissue. The rapid corrosion process involves other consequences such as its mechanical properties deteriorate before the newly formed bone can take on the necessary mechanical load, such as body weight, toxic effects due to large amount of hydrogen accumulated as subcutaneous gas bubbles.

Addition of different elements (alloying) was done to adjust the rate of biodegradability as **aluminium and zinc** (AZ). Moreover, several solutions have been proposed, such as improving the quality of the surface by reducing surface roughness, modifying the implant surface with plasma, and using new additives or new compounds, covering the implant surfaces, and using technologies that allow the modification of the microstructure of the material.

Al, Mn, Ca, Zn, and rare earth elements were found to improve the corrosion resistance of Mg alloys, enhance the performance of Mg-based biomaterials for orthopedic applications by generating different microstructures and improve the mechanical properties of the resulting Mg alloy. The characteristic impurities in Mg alloys are copper (Cu), nickel (Ni), iron (Fe) and beryllium (Be). For biomedical applications, these impurities must be strictly controlled so that they are below the limits of toxicity. (29)

Biological nutrients as Ca can be used as grain-refining agent in Mg alloys which does not cause detrimental local tissue responses and can be easily absorbed by surrounding tissues.

Mg alloys have been developed for use in orthopedic applications, including Mg-Ca, Mg-Sr, Mg-Zn, and Mg-RE alloy systems.

It has been reported that Mg-1Ca alloy does not induce cytotoxicity and osteoblasts and osteocytes are highly active around Mg-1Ca alloy pins implanted in rabbit femoral shafts, thus demonstrating good biocompatibility and bioactivity

Zinc (Zn) is one of the most abundant essential nutrients in the human body and is safe for use in biomedical alloys.The rate of Mg corrosion can be reduced by increasing the mass fraction of Zn mixed with Mg, thus strengthening the mechanical properties of Mg through solid solution hardening.

Alloy Microstructures

Alloying elements in Mg alloys may exist in the form of second-phase particles that precipitate in grains or grain boundaries, substantially enhancing mechanical properties through second-phase strengthening. The second phases have higher phase stability than Mg matrix. Thus increases the resistance to corrosion when compared to pure Mg matrix.

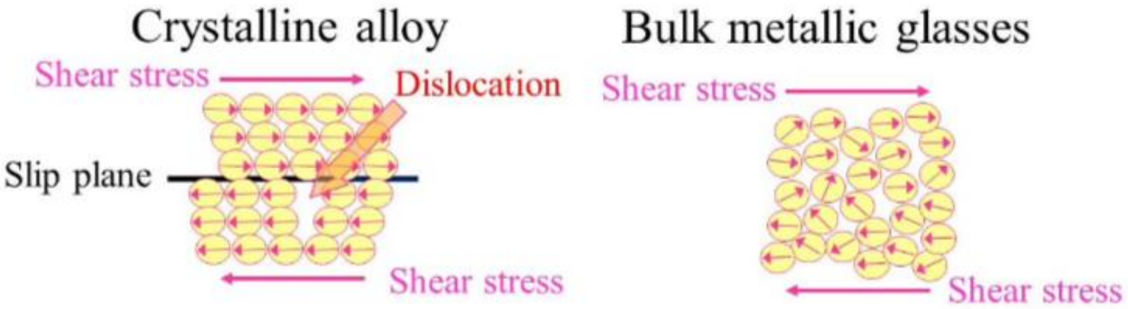
Some alloy elements have relatively high solid solubility in Mg, such as Y (12 wt.% limit), Sc (25.9 wt.% limit). It can exist in the form of solid solutions, thus achieving solid solution strengthening and improve corrosion resistance by reducing internal galvanic corrosion between the second phase and Mg matrix. (28)

Amorphous alloys[31]

Amorphous metals have glass like non crystalline structure. Prepared by extremely rapid cooling and solidification of molten alloys. By which the nucleation is suppressed without a long-range of atomic order.

Amorphous solids show unique mechanical & chemical properties that is superior to the conventional alloys.

Amorphous metals are formed as **an alloy** rather than a pure metal. The alloy constituents are made of at least three components. The components' atomic radii are significantly different to achieve **low free volume** and **high packing density**. Thus attributing to the superior properties.



Titanium based amorphous alloys and zirconium based amorphous alloys are examples for amorphous alloys that showed superior properties when compared with their crystalline alloys. Titanium based amorphous alloy has yield strength 2000 MPa which is more than twice that of pure titanium (800 MPa) or titanium alloy (853 MPa).

Moreover, Titanium based amorphous alloy and zirconium based amorphous alloy surfaces showed prevention against bacterial adhesion more than bovine enamel for both Streptococcus mutans and Prevotilla gingivalis. Accordingly, Zr-based and Ti-based amorphous alloys are good candidates for dental implant abutment surfaces.

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Polymers Degradation

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Abstract: Degradation is usually an unwanted process. But, in some cases, controlled polymer degradation is useful. As it can improve the processability of the polymer or it can be used in the recycling or natural decomposition of waste polymer. Polymeric degradation is a physico-chemical process, that involves physical and chemical phenomena. This differs from the metallic corrosion reactions which are electrochemical.

Keywords: *Polymers, physico-chemical failure, degradation, biodegradation.*

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Introduction

Generally, degradation is the act of reducing something or someone to a less respected state. Degradation in polymer science is “a complex process by which a polymeric material exposed to the environment and workload loses its original properties”. Degradation occurs by the action of heat, stress, radiation, oxidation, hydrolysis or chemical and biological agents to an extent that alter the material’s properties and compromise its function. In most of the cases, the cleavage of macromolecules is a basic part of the polymer degradation. Therefore, the breakage macromolecules into fragments of several structures and sizes is often referred to as polymer degradation. However, if monomer(s) are the final product, then the process is called depolymerization, since it is the opposite of polymerization [1, 2]. Biodegradation is the change in the polymer’s physical and chemical properties induced by organisms, isolated enzymes or by the action of the oral environment [2].

Degradation Mechanism of Polymers

Several polymer networks are known to have a moderately high chemical and thermal stability due to its large insoluble structures. Despite of this, these networks have the ability of absorbing water and chemicals from the environment, resulting in the dissolution of these networks. The occurrences of sorption and solubility act as forerunners to chemical and physical changes that has a permanent negative effect on the the structure and function of the polymers, in addition it shows some biological concerns. As a results, volumetric changes such as swelling, physical changes such as plasticization and softening, and chemical changes such as oxidation and hydrolysis may occur, which compromise the function of these polymers. [3]

a. Sorption

1. Quantity

Dimethacrylate monomers form a dental polymer network that has the ability to absorb aqueous solvents to certain percentage of their total weight. Water sorption is proved to follow Fickian diffusion kinetics. Sorption was found to be greater in ethanol/water solutions than that of water. However, water sorption was lower in materials which highly filled, with a rate of uptake and time to reach saturation almost equal to those unfilled. When comparing the water sorption of resin-modified glass ionomers, compomer and composite after 9 months in artificial saliva, the results revealed that the resin-modified glass ionomers showed the higher water sorption of 7.0%, followed by compomer 1.2% and composite showed the least by 0.17%. The process of water uptake of composites and resin cements may continue up to 6 months, however most materials reach the saturation leave after 7–60 days. As a conclusion, water sorption depends mainly on the chemistry and nature of the monomers. Therefore, water sorption was greater for Bis- GMA-based resins compared to ethoxylated Bis-GMA (Bis-EMA) resins that showed the lowest due to the absences of the hydroxyl groups of Bis-GMA. Additionally, higher concentrations of TEGMDA in Bis-GMA resins lead to higher water uptake due to the hydrophilic ether linkages of TEGDMA.[7]

2. Swelling

This type of degradation occurs when the polymers are subjected to liquids. The liquid starts to diffuse and be absorbed into the polymer. Swelling occurs when the polymer is partial soluble in the solvent, whereas dissolution is the complete dissolution process, or in other words the swelling continuation. The small liquid molecules squeeze themselves between the polymer molecules, that force the macromolecules to be pushed apart. That leads to the expansion or the swelling of the polymer. [3] Nevertheless, the presences of porosity and free volume between chains, especially in the region near crosslinks within the polymer network, may lead to the absorption of water without volumetric change theoretically. However, decrease in volumetric change may occur as a result of the leaching out of unreacted components. Therefore, the dimensional changes depend on the materials structure. [7] In addition, the polymer becomes softer and more ductile due to the increase in the chain separation that decreased the secondary intermolecular bond. The solute also influences the glass transition temperature of the polymer to the extent that it can change a once strong polymer into a rubbery and weak especially when placed at temperature lower than its ambient temperature. [7]

Factors that affect swelling and dissolution:

a. The chemical the structure:

The more the polymers and solvent chemical structures are similar to each other, the more it expected for this polymer to swell and/or dissolute.

b. Temperature & molecular structure:

As the molecular weight increases, the degree of crosslinking and crystallinity increases and therefore the resulting degradation will be decreased as the temperature is lowered. For example, in a study that compared the volumetric change after water storage after 2 months between composite core material and resin – modified and glass ionomers, revealed that composite core showed an increase in volume by 0.4–1.0% which was less than resin – modified and glass ionomers which showed 5 or 8% increase. In another study, also showed an increase in volume after 2 years in water by 0.5% in dental composite when compared to composite cement and compomer, 1.1% and 2.26% respectively. This volumetric expansion may lead to the development of stresses on the interfacial bonds with the cavity wall in rigid material, that may eventually lead to the falling of the restoration from the cavity. [7]

3. Plasticization

The solvent effect on the polymer network is known as plasticizing. The solvent molecule acts as a space occupier, which prevent the formation of primary bonds between the chains and decrease the interchain interactions such as entanglements and secondary bonding. As a result, separation of the chains will occur, leading to the decrease of hardness and other properties. The effect of softening will begin at the surface, which will significantly affect the hardness and wear and will then progress into the bulk networks at the slower rate affecting the bulk properties. The rate of softening depends on the rate of solvent uptake, which starts immediately, and it might take up to one to 2 months to reach the maximum when the polymer network is completely saturated. [7]

b. Solubility

1. Species

The dimethacrylate monomers form a crosslinked polymer network through free radical polymerization, yet unreacted monomers such as polymerization promoters and oligomers exist. Also, ions from the filler particles may be leached out in filled polymers. These unreacted monomers and ion can be degraded from the network and cause a biological drawback. Examples of leachable by-products from dental resin are methacrylic acid, formaldehyde, and specific methacrylate molecules. Therefore, as a conclusion any set material such as composite and adhesive resin can undergo degradation and elution of its components such as the photo-initiators. They can undergo degradation in alcohol or organic solvents and water; however, water shows lower values of leached components. Also, it was found that monomers and plasticizers were released from uncross- linked polymers such in denture base, reline, soft liner and tissue conditioning materials. [7]

2. Quantity

As the unreacted methacrylate groups is reacted on one end of dimethacrylate molecules, which is covalently bonded to the main polymer chain in dental restorative resins, sealants, and adhesives, therefore they will not leach out in aqueous environments. However, unreacted monomer and small chain polymer was found significantly leached. Amounts of released components vary from 0.05% to 2.0% of the weight of the specimen and even higher when placed in alcohol and other organic solvents, 2–6%. Other studies also revealed higher percentages of elution up to 10% of the unreacted monomer in dental composite. The leaching out process is rapid for most species that may take 1–3 days to be completed from set resins. On the other hand, leaching of very small concentrations may take 1 week as in case of Bis-GMA. The rate of elution depends on the surface area and the light-curing process. However, the monomer elution does not continue for a long period due to presences of small concentrations and the rapid rate of release. [7]

Polymer Erosion

Polymer erosion indicates the loss of material due to the release of the monomers and oligomers from the polymer. The erosion of a degradable polymer is considered a complicated process, as it depends on several processes, such as degradation, swelling, the dissolution and diffusion of oligomers and monomers, in addition to morphological changes. However, degradation is considered the most important process of erosion. Molecular weight loss, weight loss and geometric changes all are indication of erosion.Therefore, the mechanism of erosion degradable polymers should be understood to be able to use these materials successfully, such as in tissue engineering and drug delivery. [5]

Types of erosion:

1. Surface (or heterogeneous) erosion

This occurs when the degradation of the polymer bonds is faster than the diffusion of water, it will be consumed by the hydrolysis of bonds on the polymer surface, preventing diffusion into the bulk. [4, 5] In this type of erosion, the polymers get smaller due to the loss of the surface material only, while maintain its original geometric shape. [5] Erosion occurs at a constant rate throughout the process. [4, 5] One of its advantages is that the erosion process is predictable. Therefore, this can be useful in case of drug delivery, where the rate of erosion can indicate release of drugs. [5]

2. Bulk (or homogeneous) erosion

This occurs when the diffusion of water into the polymer is faster than the degradation of polymer bonds, as the degradation is not restricted to the polymer surface. [4, 5] In bulk erosion, the polymers erosion is not just limited to the surface. As a result, the size will not change for a significant period during its application. The situation is more changeling for bulk eroding polymers since their erosion velocity is not constant. [5]

Morphological changes during erosion

The morphological changes during erosion were first limited on the surface of the polymer, revealing cracks and surface roughness. As the erosion process continues, the polymers become a more porous structure. There are two types of pores: macropores with a diameter of approximately 100 ~m which originate because of the crack formation and micropores with a diameter of approximately 0.1~m which originate because of polymer bulk erosion was observed in poly(anhydrides). The crystallinity of the polymer has an effect on the rate of erosion. Where, the crystalline skeleton of an eroded spherulitic skeleton shows regions of erosion at the amorphous parts of the spherulite and the crystalline skeleton is still retained. [5]

Types of polymer degradation

Polymers start to degrade when active centres are formed in it. The dominant active centres of degradation are radicals that are created in a polymer thermally, photochemically, mechanochemically or by any oxidation process. Therefore, the type of initiation is used as an adjective denoting the type of polymer degradation [2]. Polymers may show two types of degradation, either (i) hygroscopic degradation by absorption of a liquid solvent followed by dimensional changes, or (ii) covalent bond rupture induced by heat, electromagnetic radiation (mainly ultraviolet), chemical dissolution into a solvent (hydrolytic) or oxidation reactions [6]. In hydrolytic degradation, there are two principal ways by which polymer bonds can be cleaved: passively by hydrolysis or actively by enzymatic reaction [4]. Enzymatic degradation is only available for naturally occurring biopolymers like polysaccharides, proteins (gelatin and collagen) where appropriate enzymes are available [5]. Passive hydrolysis is the most important mode of degradation for most artificial polymers [5].

i. Hygroscopic degradation

Regarding water diffusion in polymers, two main models have been discussed. The first one is the free volume theory which assumes that water penetrates resin matrix through nanopores and remains as unbound water between the chains without any chemical reaction. The second model is the interaction theory which suggests that water diffuses through the material and binds to hydrophilic groups by Vander Waals or hydrogen bonds. The absorbed water is found as bound water, which is attached to polymer chains [3, 6]. The water uptake and swelling is encouraged by the presence of hydrophilic groups such as (ether linkages in TEGDMA, hydroxyl groups in Bis-GMA, urethane linkages in UDMA, and the presence of ester groups in all) [3].

Consequences of hygroscopic degradation

1. Plasticization because water molecules penetrate into the spaced between chains and the macromolecules are forced apart reducing secondary intermolecular bonding forces and entanglements, therefore, the polymer becomes softer and more ductile. This, in turn, increases the probability of polymer fatigue failure because crack growth becomes easier [3].

2. Extrinsic discoloration and aesthetic failure due to ingress of stains with water molecules [3].

3. Changes on the physical and mechanical properties such as decreasing the glass transition temperature, flexure strength, hardness and fatigue limit [3].

4. Dimensional changes (usually swelling) accompany water sorption. This results in stress build-up at the bond interface between denture base resin and relining materials decreasing the bond strength between them [3].

N.B: The dimensional change of a polymer network in a solvent is difficult to predict, and is very material dependent because: i. The polymer network contains porosity and free volume between chains, so, it is theoretically possible for water to be absorbed without creating a change in volume. ii. Water uptake is accompanied by a loss of unreacted components that would cause a reduction in volume [7].

5. Biological failure due to leaching out of unreacted components and residual monomers that may elicit inflammatory reactions, chemical irritation to the oral mucosa, labial oedema, ulcerations or burning mouth syndrome and denture stomatitis [6].

ii. Covalent bond rupture (Scission)

Chain scission is a term used in polymer chemistry describing the degradation of a polymer main chain. It is often caused by thermal stress (heat) or ionizing radiation (e.g. light, UV radiation or gamma radiation), hydrolysis or enzymes. During chain cleavage, the polymer chain is broken at a random point in the backbone to form two highly molecular fragments to some extent [8].

Mechanisms of Covalent bond rupture [8]

1. β-chain scission:

It is the rupture of the carbon-carbon bond at a molecular chain end and accompanied by free radical release.

2. α-chain scission:

It is the breakage of the bond between a carbon and a functional group along the chain backbone.

3. Oxidation:

It is the breakage of the double bond along the polymer chain.

N.B: The mechanism of chain attack or bond rupture depends on several factors as; presence of impurities which may be catalyst, solvent or any incorporation during the polymerization reaction. Or a result of physical or chemical treatment.

Consequences of covalent bond rupture

1. Reduction in the molecular weight due to chain separation at the point of bond breakage, subsequently, decreases the mechanical strength and resistance to chemical attack (because many polymer properties depend on the molecular weight of polymer chain) [3,8].

2. Oxidative degradation by ultraviolet rays may cause chain crosslinking and embrittlement [3].

3. Change in polymer properties for specific use, such as hardening and rigidity of soft liners and tissue conditioning materials due to leaching out of plasticizers from denture base (clinical failure) [3, 7].

4. Intrinsic discoloration and aesthetic failure.

There are many types of degradation by covalent bond breakage depending on the cause or the initiating factor, which are:

1. Thermal degradation.

2. Chemical degradation.

3. Mechanochemical degradation.

4. Photo-chemical/photo-oxidative degradation.

5. Enzymatic (biological) degradation.

ii.1. Thermal degradation

Thermal degradation corresponds to the scission of molecular chains at elevated temperatures [3]. The increase in temperature amplifies intramolecular vibrations and accelerates cleavage of macromolecules. The intra-chain chemical bonds that are sufficiently stressed by these motions dissociate giving rise to polymer fragments of lower molecular weight [2]. The way in which a polymer degrades under the influence of thermal energy in an inert atmosphere is determined, on the one hand, by the chemical structure of the polymer itself, on the other hand by the presence of traces of unstable structures (impurities or additions) [9]. Thermal degradation does not occur until the temperature is so high that primary chemical bonds are separated. It begins typically at temperatures around 150–200 °C and the rate of degradation increases as the temperature increases [9]. Thermal stability is related primarily to the magnitude of the bonding energies between the various atomic constituents of the polymer: higher bonding energies result in more thermally stable materials [3]. For example, the magnitude of the C—F bond is greater than that of the C—H bond, which in turn is greater than that of the C—Cl bond [3]. The fluorocarbons, having C—F bonds, are among the most thermally resistant polymeric materials and may be used at relatively high temperatures. However, because of the weak C—Cl bond, when polyvinyl chloride is heated to 200 °C for even a few minutes it discolours and gives off large amounts of HCl [3].

Types of thermal degradation

There are three types of thermal decomposition: chain depolymerisation, random degradation and degradation by substituents reactions.

1. Chain depolymerization [9]

Chain depolymerisation is the successive release of monomer units from a chain end or at a weak link. It is the reverse of chain polymerisation; it is often called depropagation or unzippering. A “weak link” may be a chain defect, such as an initiator fragment, a peroxide or an ether linkage arising as impurities from polymerisation. Depolymerisation is characterised by:

a) the major product is monomer

b) the decrease of degree of polymerisation is initially negligible, and accordingly the mechanical properties do not deteriorate fast.

Example is liberation of monomer from polymethyl methacrylate when a sample is hold close to a burning candle.

2. Random degradation [9]

Occurs by chain rupture at random points along the chain, giving a disperse mixture of fragments which are usually large compared with the monomer unit. The probabilities of breaking any bond in the polymer chain are equal. Random scission is characterised by a) the major products are typically fragments with molecular weights up to several hundred (monomers, dimers, trimers, etc.), b) the decrease of molecular weight is initially significant; therefore, the mechanical properties decrease fast and c) the rate of degradation is initially rapid and gradually decrease (when reaching a maximum).

3. Degradation by substituent reactions [9]

Occurs by modification or elimination of substituents attached to the polymer backbone. Volatile products are not monomers. Example is hydrogen chloride elimination in the case of Polyvinyl chloride. This polymer undergoes degradation reactions, where it looses HCl quite easily, due to polymer backbones with conjugated double bonds.

ii.2. Chemical (hydrolytic) degradation

Water is responsible for the chemical hydrolysis of polymers. Normally hydrolysis proceeds slowly in the neutral conditions of the oral cavity, however, it may be catalysed by acids, bases, or enzymes [3]. Polymer dissolution is directly proportional to the similarity of chemical structure between the solvent and polymer [3]. For example, many hydrocarbon rubbers readily absorb hydrocarbon liquids as gasoline. On the other hand, hydrofluoric acid (HF) that corrode many metals and dissolve glass, is stored in plastic bottles [3].

ii.3. Mechano-chemical degradation

A linear polymer macromolecule can be mechanically broken to two fragments if sufficient mechanical work is applied to it under flow shear stress [2]. Mechano-chemical degradation is only possible on long molecules. Accordingly, the mid-chain cleavage mode is typical of this degradation [2]. Shear degradation is desired in preparation of rubber mixtures before vulcanization. Where some rubbers contain large portions of macromolecules with the relative molecular weight (more than one million). So, cleavage significantly reduces the viscosity of the vulcanization mixture, thus achieving faster and better homogenization of the mixture [2].

N.B: Combined corrosive environment (as water) and mechanical stresses lead to stress corrosion cracking (SCC). SCC often progresses rapidly and can lead to sudden failure of polymer [3].

ii.4. photo-chemical/photo-oxidative degradation

It is well known that all existing organic polymers degrade if they are subjected to ionising radiation (as ultraviolet radiation) with high dose [3]. In photochemical degradation, depending on the photon energy, radiation may excite and activate reactive groups in the polymer, or dissociate some of its bonds to radicals [2]. One of its reactions is ionization, in which the radiation removes an orbital electron from a specific atom, converting that atom into a positively charged ion. Consequently, one of the covalent bonds associated with the specific atom is broken and there is a rearrangement of atoms or groups of atoms at that point. This bond breaking leads to either chain scission or crosslinking at the ionization site, depending on the chemical structure of the polymer and the dose of radiation [3]. Crosslinking may result in limiting chain mobility, increased embrittlement of the polymer and microcracks formation. The greatest radiation damage to polymers is caused by UV irradiation. After prolonged exposure, most polymer films become brittle, discolour, crack, and fail. For example, camping tents begin to tear and plastic windows become cloudy [3]. Not all consequences of radiation exposure are deleterious. Crosslinking may be induced by irradiation to improve the mechanical behaviour and degradation characteristics. For example, γ-radiation is used commercially to crosslink polyethylene to enhance its resistance to softening and flow at elevated temperatures [3]. When it occurs in air, photochemical initiation is followed by oxidation of the polymer and the overall complex process is called photooxidative degradation [2].

ii.5. Biological (enzymatic) degradation [10]

Polymeric materials can be degraded by microorganisms in the environment by their secreted enzymes. Enzymatic attacks on the polymer side chains results in, reduces hardness and wear resistance of the polymer and producing harmful by-products. The extent of the enzymatic degradation is related to the extent of cure of the resin, because ester groups may be more available for attack in more loosely crosslinked networks. However, the composition of the monomers producing the network is of primary importance in determining the extent of degradation, TEGDMA has been shown to be more susceptible to enzymatic hydrolysis than Bis-GMA or Bis-EMA [11, 12].

Factors affecting polymers degradation

Polymers used in dentistry in the fabrication of dental composite restorative and prosthetic materials are typically composed of mono- or di-methacrylates. Because their chemical structure is nearly identical, the reaction of prosthetic polymers to an aqueous environment is like that of the composite restoratives. The other commonly used polymeric networks are made from polyacrylic acid and its copolymers, which are used in glass ionomers and adhesives, and from polydimethylsiloxane, which is used in soft denture liners. Dental restorative materials are exposed to a service environment, saliva, containing water and different enzymes and a variety of chemicals, including acids, bases, salts, alcohols and oxygen that enter the oral environment during eating and drinking. The chemistry and duration of exposure are important determinants of polymer network degradation. Several factors relating to the chemistry and structure of the polymer network are important in determining the extent to which the material will be affected by an aqueous environment [7, 13].

1. Polymer structure and composition

1.a. Polymer network characteristics and cross linking

The quality of the network that forms during polymerization will affect the extent to which molecular uptake and swelling occur when a polymer is submerged in a solvent [7]. Networks with high cross-linking density have reduced solvent uptake and swelling due to the reduced free volume in the network, as well as to the covalent cross-links that maintain the close proximity of the polymer chains [7]. Generally, highly crosslinked polymers are more resistant to degradative reactions, based on the more limited space and pathways available for solvent molecules to diffuse within the structure [7]. Arima et al. [14] has shown a strong correlation between increasing the concentration of cross-linking agents and the reduced degradation of polyethylmethacrylate polymers. However, their study also showed that when the cross-linker contained hydrophilic ether linkages, water sorption increased with cross-linker concentration. Cheng et al. [15] studied the effect of addition of glutaraldehyde as a cross linking agent on the degradation rate and drug release of gelatin. It was found that the degradation rate and drug release are inversely proportional to the glutaraldehyde concentration.

1.b. Molecular weight

The molecular weight and molecular weight distribution of polymers affects the volume fraction of chain ends and hence the free volume of the polymer and determines the chain mobility and crystallisation. It also determines the number of acidic end groups that can participate in hydrolysis and their possible catalytic effect. Overall, the molecular weight affects both the chemical and physical properties of a polymer and polymer degradation [16]. Zhu et al. [17] and Park [18] both correlated the faster degradation of PGA, PLA and their copolymers with decreasing molecular weight. This is attributed to an increase in the free volume and number of acidic reactive end groups.

1.c. Hydrophilicity [7]

The hydrophilic nature of a polymer is a function of the chemistry of its monomers and its polymerization linkages. The three most common monomers used in dental composites are Bis-GMA, UDMA (urethane dimethacrylate), and TEGDMA (triethyleneglycoldimethacrylate). An examination of the structure of the most popular monomers reveals that they are heteroatom polymers, having carbon and oxygen or nitrogen in their backbones. In addition, their structure shows the presence of hydrolytically susceptible groups, such as ester, urethane, ether linkages and hydroxyl groups. These monomers and their resultant polymers certainly absorb water to a damaging extent. Venz and Dickens [19] correlated the differences in long term water sorption (6 months) for polymer networks composed of various monomers, showing sorption to be in the following order: TEGDMA>Bis-GMA>UDMA>HMDMA. This difference was explained by the presence of hydrophilic ether linkages in TEGDMA, hydroxyl groups in Bis-GMA, urethane linkages in UDMA, and the presence of ester groups in all, including the HMDMA. Park et al. [20] correlated the relation between the hydrophilicity of amide units in polyesteramide and the degradation rate. It was found that the introduction of amide groups to the aliphatic polyester increased the biodegradability owing to its increased hydrophilicity.

1.d. Fillers effect [7]

The presence of fillers in a polymer network can affect solvent uptake, dissolution and degradation in direct relation to its percentage as it reduces the overall volume of the absorbing polymer [21]. Water also serves as a weak acid and may cause the erosion of the surface of filler particles. Composites with pure silica or quartz fillers are inert in water. While, composites containing radiopaque glasses undergo greater dissolution in water and saline solutions [22]. The deterioration of the glass is one of the reasons that it is so important to form an organic layer, typically of silane molecules, on the surface of the filler to protect it from the environment [23]. The quality of this interface influences the extent to which the composite material degrades. Poor, nonbonded interface may provide a low energy pathway for solvent molecules and dissolution [24].

1.e. Porosity [7]

High level of porosity or microvoids facilitates fluid transport into and out of the polymer, leading to enhanced solvent uptake and degradation.

1.f. Copolymerization [5]

By introducing a second monomer into the polymer chain, many properties of the original polymer can be influenced, such as crystallinity or glass transition temperature [25]. Poly(anhydrides) degradation depends on the copolymer composition. It was shown for poly(1,3-bis-p-carboxyphenoxypropane-co-sebacic acid) (p(CPP-SA)) that degradation depends on the CPP content. Increasing the content of the aromatic monomer from 50 to 100% was reported to increase the time of erosion substantially [26]. Other examples are poly(lactic-co-glycolic acid) copolymers, where the decrease of molecular weight during degradation was found to be accelerated with increasing glycolic acid content [27]. Other factors that depend on the copolymer composition, such as the glass transition temperature and the crystallinity of a polymer, can have additional indirect effects on degradation rates.

1.g. Polymer Crystallinity [28]

Crystallinity has a significant effect on the degradation rate of polyesters because it determines how easily water molecules can access the ester linkages to cause chain cleavage and degradation. Studies by (proton-based nuclear magnetic resonance spectroscopy) suggested that PLA and PLA/PGA copolymers all degrade via the same mechanism but that the GA units on PLA/GA copolymers constitute vulnerable points on the macromolecular chains, so that degradation occurs preferentially on the GA bonds. Hurrell and Cameron [29] reported that removal of amorphous material from the polymer structure would result in a significant loss of mass and degradation. Further analysis using small-angle x-ray diffraction (SAXS) deduced that insertion of secondary crystals within the amorphous region was the cause of the increase in crystallinity and decrease in degradation.

2. Solvents, Enzymes & Saliva components [37]

The chemistry of the environment surrounding a polymer network, influences the nature of the interaction between them [7]. Studies of the effect of storage conditions on the stability of dental polymer networks have exposed the materials to water, artificial saliva, alcohol, and acidic or basic solvents to study the degradation process [7]. The effect of these chemicals is varied, but typically involves an elution of unreacted components and some degradative effect on the polymer network. Solutions of 50–75% ethyl alcohol in water have been shown to be among the best solvents for dental composite networks [30]. Interaction between oral microbes and the polymer network also may occur. Bacteria can colonize on compomer surfaces causing degradative effect as a result of acids produced by the bacteria. Another very important aspect of the interaction between the polymer network and its environment is the presence of enzymes that can degrade the polymer through attacks on the side chains, producing both potentially harmful by-products as well as a deterioration of the properties of the network [31].

Numerous studies have shown the effect of esterases on dental composites [32, 33]. These studies have shown a reduction in wear resistance as well as the loss of molecules from the surface of the composite. Due to the large size of the proteins and their limited mobility within a polymer network, it is unlikely that the effects of enzymes would be experienced deep within the structure of the polymer, away from the surface.The chemistry of the polymer will influence the enzymatic degradation of the material, for example, urethane modified bis-GMA/TEGDMA networks have been shown to be more stable in the presence of cholesterol esterase than unmodified bis-GMA/ TEGDMA networks [34]. Water is the most abundant component of saliva and one of the main factors to cause biodegradation. The oral environment necessarily facilitates water sorption from the saliva to the resin. There are two conditions that influence the amount of water diffusion to denture resins. One is the water diffusion coefficient of the material that affects the time needed for its saturation with water. The other one is the amount of residual components that are release for the medium and replaced by water molecules 38. Polymeric structures and dental materials may be chemically degraded in saliva through two mechanisms: hydrolysis and enzymatic reaction. Salivary enzymes can degrade polymers through attacks on the side chains, producing by-products as well as a deterioration of the properties of the network [38].

3. Media Ph

Media pH can affect polymer degradation, either directly, by altering the polymer chemistry or indirectly, by interacting with degradation products and affecting degradation kinetics. Chu [35] found there was a greater loss in the mechanical properties of PGA sutures in buffered than unbuffered solutions. Also, the presence of buffer ions increases the degradation rate of poly(a-hydroxy acid) copolymers. Ginde and Gupta [36] also observed alkaline media (pH 9.2 and 10.6) to have a more severe effect on the degradation and mechanical properties of PGA fibres than acidic or neutral media. This is due to the enhanced removal of degradation products that diffuse out, creating space for water ingress in the structure, thus increasing the degradation kinetics.

4. Chewing forces [37]

Biodegradation of the materials in the oral cavity can also be induced by fatigue, which is caused by repetitive loads such as chewing force. A continuous application of mechanical and environmental loads leads to progressive degradation and crack initiation and growth, resulting in catastrophic failure of the resins. This process is further assisted by pre-existing voids introduced during the material processing and residual stresses. Chewing can also apply shear and compression forces on denture teeth causing wear [38, 39].

5. Dietary changes [37]

Intraoral temperature changes may be induced by routine eating and drinking. These temperature changes affect the polymeric materials as they have a different coefficient of thermal expansion compared to natural tooth. Thermal fluctuations will induce surface stresses that can directly cause crack propagation [40]. Foods and drinks can also affect dental materials by the direct effect of their additives, like ethanol, and their capacity of changing the intraoral pH values [41].

Biodegradable

Biodegradable polymers are a special class of polymer that breaks down after its planned purpose by bacterial decomposition process to result in natural by-products such as gases (CO2, N2), water, and inorganic salts [42]. These polymers are found both naturally and synthetically made, and largely consist of ester, amide, and ether functional groups. Biodegradable polymers, have extremely strong carbon backbones that are difficult to break, so the degradation often starts from the end-groups. Since the degradation begins at the end, a high surface area is exposed to chemicals, light, or organisms easily [43].

Properties of biodegradable polymers [43, 44]

1. Biodegradable polymers should be stable and durable enough for use in their particular application, but upon removal they should easily break down.

2. Hydrophillicity, because hydrophobic polymers and end groups will prevent the water-soluble enzymes from interacting with the polymer.

3. Non-toxic, non-irritant, with no inflammatory tissue response.

4. Maintain good mechanical integrity until degraded.

5. Controlled rates of degradation which match that of the healing or regeneration process.

Applications of biodegradable polymers [44] One of the most active areas of research in biodegradable polymer is in controlled drug delivery and release and tissue engineering. Also it is used widely in resorbable surgical sutures.

Protection of polymers against degradation [2]

Polymer degradation is a complex process by which the polymer loses its original functional properties owing to irreversible changes in its structure. All types of polymer reactions take part in corrosion:

i. chemical transformation of functional groups.

ii. cleavage of polymer molecules by oxidation, hydrolysis, photochemical and other chemical reactions, mechanochemical processes and by depolymerization.

iii. crosslinking of polymer molecules as well as their fragments.

Crosslinking makes the aged polymer brittle while cleavage processes makes it waxy or sticky. Undesirable degradation processes are significantly reduced by stabilizers admixed into the polymeric material. A single stabilizer is usually not enough; a mixture of a few stabilizers mostly must be used. According to the function, stabilizers are divided to photostabilizers, antioxidants, antiozonants, radical scavengers, peroxide scavengers, acid scavengers, fire retardants and biocides. Because the stabilizer is only admixed into a polymer, not bound to it, its second key property is a good compatibility with the polymer. When the compatibility is poor, the stabilizer is spontaneously displaced to the polymer surface by the thermal motion, from where it is removed by external influences. As a result, the polymer becomes unprotected.

Degradation processes can be reduced also by:

1. Increasing the polymer crosslinking.

2. Decreasing the hydrophilic groups or hydrophilic crosslinking agents in the polymer structure.

3. Increasing the polymer molecular weight.

4. Increasing the fillers content in the polymeric structure.

5. Decreasing the porosity.

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