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Imperfections in solids

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Nature is not perfect and so are the crystals, they may contain various types of imperfections and defects that influence many of their physical and mechanical properties. This influence could be beneficial as different types of defects can be intentionally introduced to produce specific characteristics within the material. (1)

Defects in Metals

Since crystallization does not occur in a regular perfect fashion, metals can have various types of defects which can be classified into 4 main categories: point, linear, interfacial and volume defects. (2)

1. Point defects (0-dimensional)

Point defects are zero-dimensional defects which occur when there is a missing, displaced, or extra atom. (2)

i. Vacancy defect

Vacancy is the simplest point defect where an atom is missing from one of the lattice sites (Figure 1). It may result from imperfect packing during crystallization, or due to increased thermal vibrations of the atoms at elevated temperature. Vacancies are important in determining the rate at which atoms or ions can move around (atomic diffusion). All crystalline solids have vacancies as it is impossible to create a material that is free of vacancies. The equilibrium number of vacancies $N\upsilon$ can be calculated through this equation: (1,2)

$$N\upsilon = N \exp(-\frac{Q\upsilon}{kT})$$

Where N is the total number of atomic sites, Q_υ is the energy required to form a vacancy, K is the Boltzmann's constant which is equal to 1.38 × 10−23 J/atom·K and T is the temperature in kelvins, therefore when temperature increase, the number of vacancies increase exponentially with temperature. (1,2)

ii. Self-interstitial defect

It is a type of point defects where the atom leaves it normal lattice site and occupies an interstitial site (Figure 1). In metal, self-interstitial defects produce large distortion in the surrounding lattice as the atom is much larger than the interstitial site it occupies, as a result, the probability of formation of this defect is low and much lower than vacancies. (2)

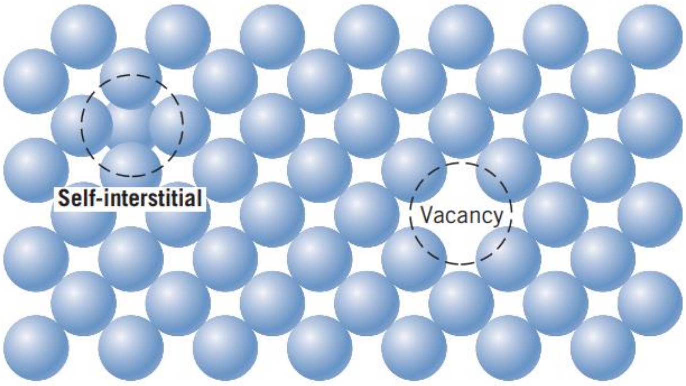


Figure 1: Two-dimensional representations of a vacancy and a self-interstitial.

iii. Impurities

Pure metals containing one type of atom does not exist, impurities will always be present. Impurities can be added intentionally to give specific properties to the material. (2)

The addition of impurity atoms to a metal could result in the formation of a **solid solution**. Solid solutions are made up of two components: a **solvent** which is the compound found in largest amount and a **solute** which presents in minor concentration. (2)

There are two types of solid solutions: *substitutional* and *interstitial*. (2)

In substitutional solid solution, the impurity atom replaces the original host atom (Figure 2), there are four rules that determine the degree of solubility of the solute in solvent, known as the ***Hume–Rothery rules***. According to these rules, substitutional solid solutions may form if the solute and solvent have: (2)

1. *Atomic radii difference less than 15%.* If more, the solute atoms will create substantial lattice distortions and a new phase will form.
2. *Same crystal structure.*
3. *Similar electronegativities,* if there is a large difference in electronegativity, the metals tend to form intermetallic compounds instead of solid solutions.
4. *Similar valency,* if all other factors are equal, A metal will have greater tendency to dissolve a metal with higher valency than one with lower valency. (2)

Figure 3: *Substitutional solid solution of copper in nickel.*

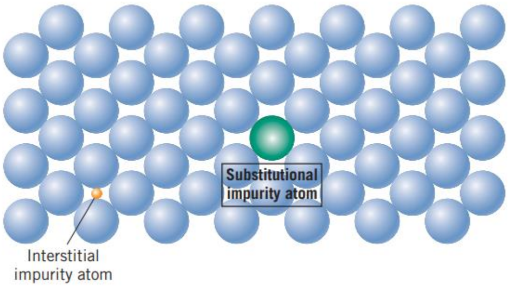
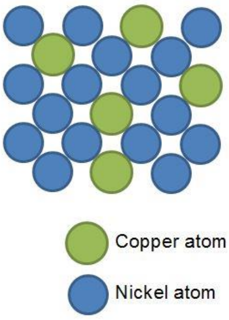


Figure 3: Substitutional solid solution of copper in nickel.



In interstitial solid solution, the impurity atoms fill the interstitial spaces between the host atoms (Figure 2). Metals have relatively high atomic packing factor, so their interstitial spaces are relatively small. Even if the impurity atom is very small, it would still be larger than the interstitial site causing lattice distortion (Figure 4). **Steel** is an example of interstitial solid solution where carbon atoms, *in maximum concentration of 2%,* occupy interstitial sites in the iron crystal structure since they are small enough to occupy these spaces with some strain (Figure 5). (2,3)

Figure 4: Lattice distortion by interstitial impurity atom.

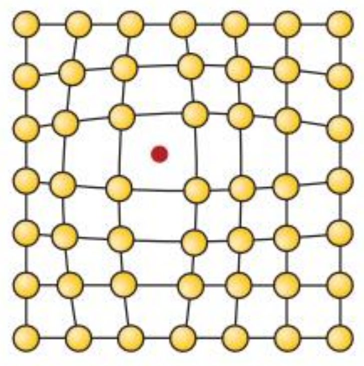
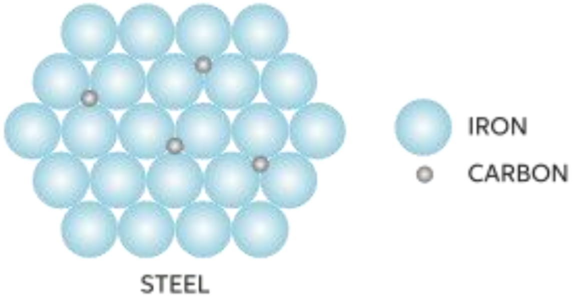


Figure 5: Interstitial solid solution of carbon in iron.



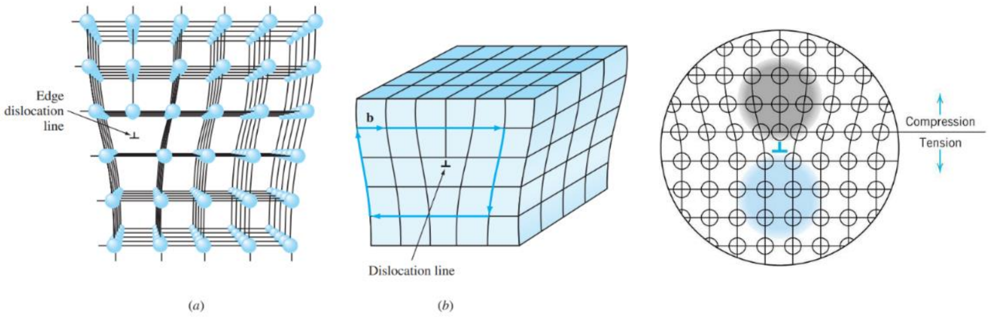
2. Linear defects (1-dimensional)

Linear defects, *also known as* ***dislocations***, are one-dimensional defect around which some of the atoms are misaligned. They are introduced into the material during solidification or when the material is permanently deformed. These defects cause distortion centered around a line. There are three types of dislocations: edge, screw and mixed dislocation. (2,5)

i. Edge dislocation

Edge dislocation is created when an extra half plane of atoms is inserted in the middle of the crystal, The bottom edge of this inserted half plane represents the edge dislocation. The dislocation line is indicated by the symbol ⊥. The atoms above the dislocation line are squeezed together (region of compressive strain), and those below are pulled apart (region of tensile strain). The lattice distortion around the dislocation is expressed in terms of the **Burgers vector b** which is **perpendicular** to the edge-dislocation line. (Figure 6) (3,5)

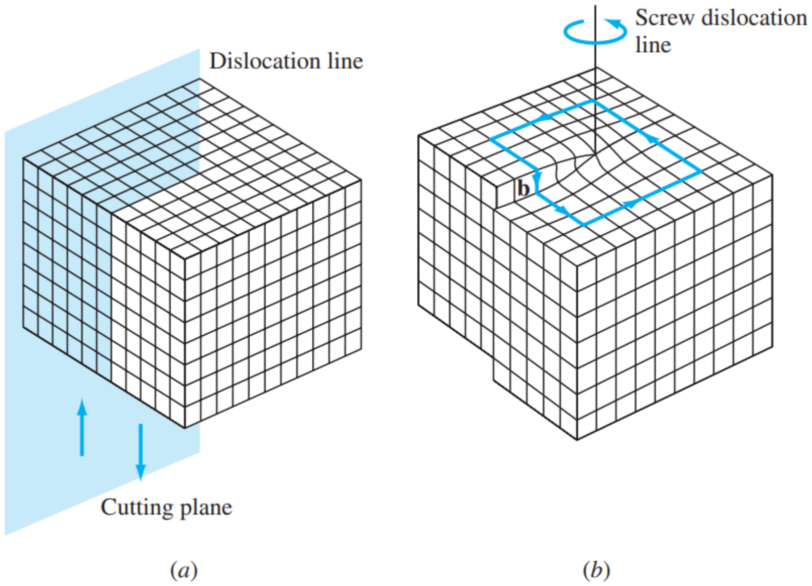
Figure 6: (a) Edge dislocation in a crystalline lattice. (b) Edge dislocation that indicates the orientation of its Burgers vector b. (c) Strain fields surrounding an edge dislocation.



ii. Screw dislocation

Screw dislocation is formed by a shear stress that is applied to produce the distortion. It is called a screw dislocation because the planes of atoms in the crystal lattice trace a helical path around the dislocation line. The vector required to complete the loop, ***Burgers vector b***, is parallel to the screw dislocation. (5) (Figure 7)

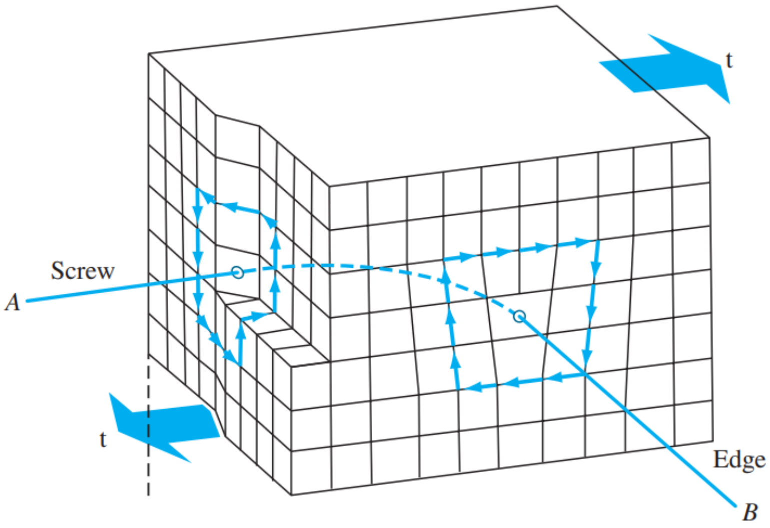
Figure 7: Formation of a screw dislocation. (a) A perfect crystal is sliced by a cutting plane, and up and down shear stresses are applied parallel to the cutting plane to form the screw dislocation in (b). (b) A screw dislocation is shown with its slip or Burgers vector b parallel to the dislocation line.



iii. Mixed dislocation

Most metals have large number of mixed dislocations, which have both **edge** and **screw** components with a transition region between them. Burgers vector is neither perpendicular nor parallel to the dislocation line. The Burgers vector remains the same for all portions of the mixed dislocation even though there is a change in the direction and nature of the dislocation within the crystal (e.g., from edge to mixed to screw). (Figure 8) (2)

Figure 8: Mixed dislocation in a crystal. Dislocation line AB is pure screw type where it enters the crystal on the left and pure edge type where it leaves the crystal on the right, For regions in between where there is curvature in the dislocation line, the character is mixed edge and screw.



C. Interfacial defects (2-dimensional)

Those are surface defects that separate regions of material with different crystalline structure or orientation. Interfacial imperfections include external surfaces, grain boundaries, phase boundaries, twin boundaries, and stacking faults.(2)

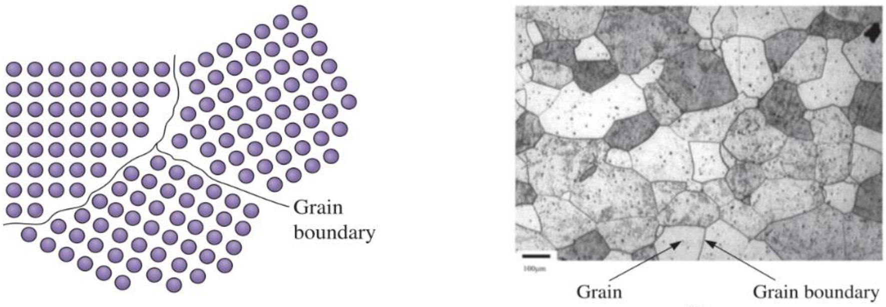
i. External Surface

It is the surface along which the crystal structure terminates. It is considered a defect because the atoms at the surface are not equally bonded from all sides, they have higher surface energy when compared to the atoms at the bulk of the crystal. The higher energy makes the atoms at the surface of the material susceptible to erosion and reaction with elements in the environment. (5)

ii. Grain boundaries

Most metals are polycrystalline, consisting of many grains with different orientation. The grains are separated from each other by **grain boundaries** (Figure 9)**.** They are created during solidification when crystals formed from different nuclei grow simultaneously and meet each other. The grain boundary is a very narrow zone probably just several atom distances wide. Within this region, there is an atomic mismatch due to the transition from the crystalline orientation of one grain to that of an adjacent one. (2)

Figure 9: (a) Diagram showing the grains orientation and grain boundaries. (b) Grains and grain boundaries in a stainless-steel sample.



(a) (b)

Atoms at the grain boundaries have irregular arrangement, as a result, they have higher energy. This higher energy state makes the grain boundaries more chemically reactive than the grains themselves. Since grain boundaries are regions of atomic mismatch and less dense atomic packing, Impurities tend to segregate at these regions. (3,6)

Depending on the degree of crystallographic misalignment between adjacent grains, grain boundaries are classified into *low-angle grain boundaries* and *high-angle boundaries* (Figure 10). Low-angle grain boundaries can be viewed as an array of dislocations, giving two types of grain boundaries: tilt and twist boundaries. *Tilt boundary* can be viewed as a series of parallel edge dislocations. It occurs when the axis of rotation is parallel to the plane of the grain boundary (Figure 11). *Twist boundary* can be viewed as an array of screw dislocations, it occurs when the axis of rotation is perpendicular to the plane of the grain boundary. (2)

Figure 10: Schematic diagram showing low and high-angle grain boundaries.

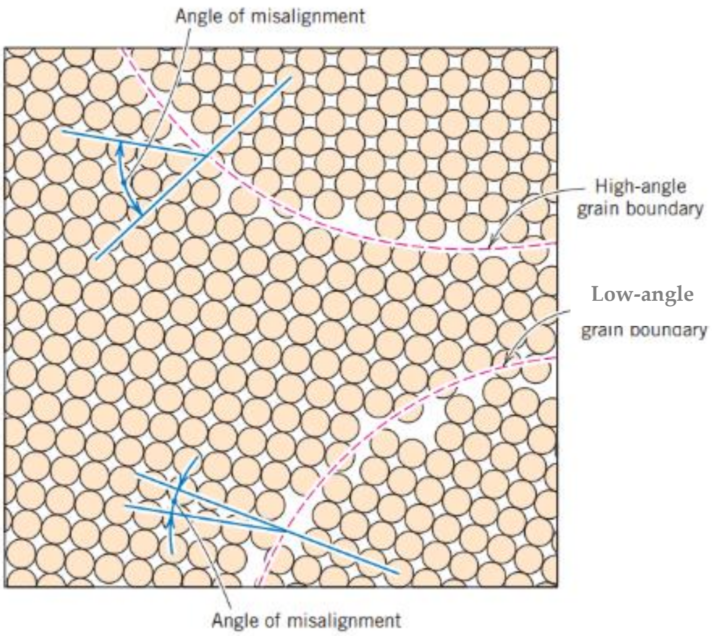
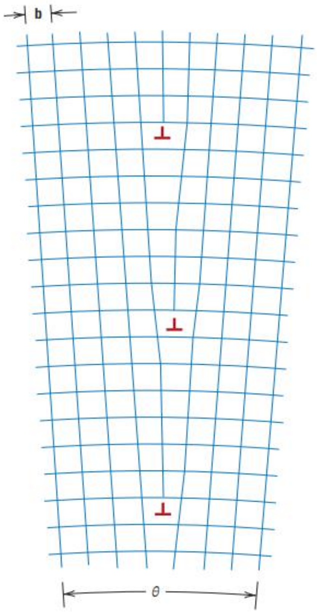


Figure 11: Demonstration of how a tilt boundary having an angle of misorientation θ results from an alignment of edge dislocations.



iii. Phase boundaries

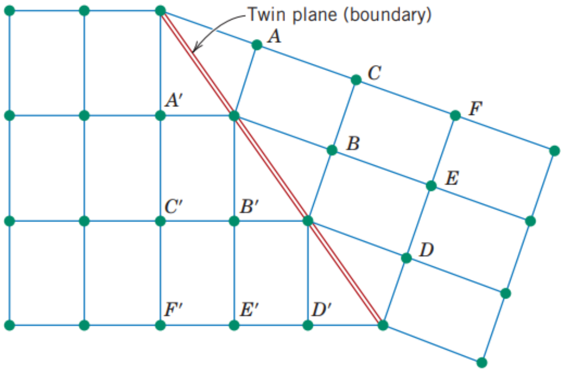
They are the boundaries that exist in multi-phase materials, in which there is a different phase on each side of this boundary and each phase has its own physical and chemical properties. (2)

iv. Twin boundaries

They are a special type of grain boundaries at which the atomic arrangement on one side of the boundary is a mirror image of the arrangement of atoms of the other side (Figure 12). The region of material between these boundaries called a twin. They are produced either by applied mechanical shear forces (mechanical twins) or by annealing heat treatments (annealing twins). (2,3)

Other possible interfacial defects include stacking faults and domain walls. Stacking faults occur when there is an interruption in the stacking sequence of the atomic layers in a crystal. Domain wall is a boundary that separates regions having different directions of magnetization in magnetic materials. (2)

Figure 12: Diagram showing a twin plane or boundary.



4. Volume defects (3-dimensional)

Volume defects or bulk defects are clusters of point defects. They include discontinuities such as pores, microcracks, inclusions, and other phases. These defects can be introduced during processing and fabrication steps. (2,5)

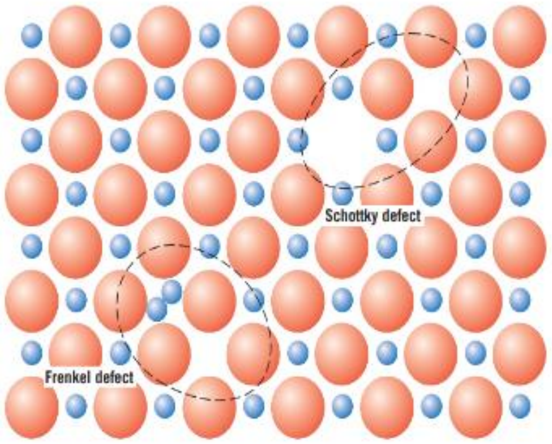
III. Defects in Ceramics

Ceramic materials are inorganic and nonmetallic materials, they are composed of metallic and non-metallic elements. So, their crystal structure is more complex than metals. Their atomic bonding ranges from purely ionic to totally covalent. Regarding ceramic materials with predominantly ionic atomic bonding, the crystal structure is composed of electrically charged ions; positively charged cations and negatively charged anion. The cations are normally smaller than anions as they lost their valence electrons when ionized. The crystal must be electrically neutral; the cation positive charges must be equal to the anion negative charges. When atomic defects occur, the electroneutrality state must be maintained, because of that, defects in ceramic do not occur alone, they usually come in pairs. Frenkel and Schottky defects are two of the most common defects that occurs in ceramic materials. (7)

i. Frenkel defect

It is a type of point defect where a positive cation leaves its normal position and move to an interstitial site. It is a combination of both cation vacancy and cation interstitial type of defects. It occurs when there is a large difference in the size between the anion and cation where the cation is much smaller and will fit better in the interstitial sites. The number of cations and anions remain equal, as a result, charge neutrality is maintained. Frenkel defect does not have any impact on the density of the crystal (Figure 13). (7,8)

Figure 13: Schematic diagram showing Frenkel and Schottky defects in ionic solids.



ii. Schottky defect

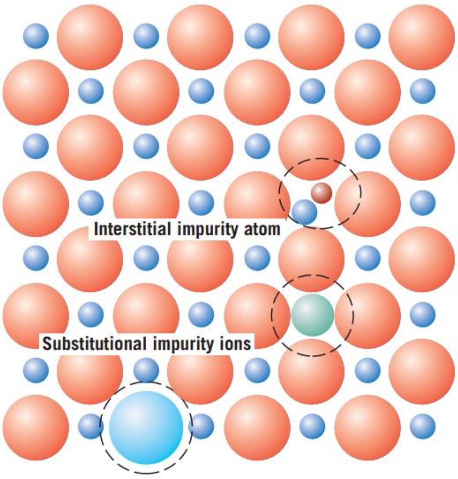
It is another type of point defect where an anion and a cation are removed from the interior of the crystal and placed at an external surface. It is a combination of both cation and anion vacancies, it occurs when the anion and cation have similar size. Since they carry opposite charges, charge neutrality is maintained. However, there is a decrease in the density of the crystal since a fraction of ions leave the crystal (Figure 14). (7,9)

In both, Frenkel and Schottky defects, the ratio of anions to cations is not changed by the defect, so the ceramic compound is said to be stoichiometric. However, if there is any deviation from the ratio of anions to cations as predicted by the chemical formula, the ceramic compound is said to be nonstoichiometric. (7)

iii. Impurities

Impurity atoms can form substitutional and interstitial solid solutions in ceramics as they do in metals. For an interstitial solid solution to occur, the radius of the impurity ion must be relatively small in comparison to the anion. However, for a substitutional solid solution to occur, the size and charge of the impurity ion must be nearly the same as one of the host ions whether a cation or an anion. If the impurity ion has a different charge than that of the host ion, crystal must compensate for this difference in charge by the formation of lattice defects so that the electroneutrality is maintained (Figure 14). (7)

Figure 14: Schematic representations of interstitial, anion-substitutional and cation-substitutional impurity atoms in an ionic compound.



Note: Common ceramic materials include Silica. Silica can be crystalline or amorphous. In amorphous silica, the atoms have a short-range order. It is made up of continuous network of connected structured tetrahedral units consisting of one silicon surrounded by four oxygen (Figure 15). Coordination defects are the main type of defects found in these amorphous solids. They are a kind of defect when the atom has different coordination compared to the atoms of similar type in the structure. A coordination defect can occur in silica due to oxygen vacancy; the neighboring silicon will have coordination number of three instead of the typical four (Figure 16). (10)

Figure 15: (a) Structural Unit of Silica, (b) Amorphous Silica.

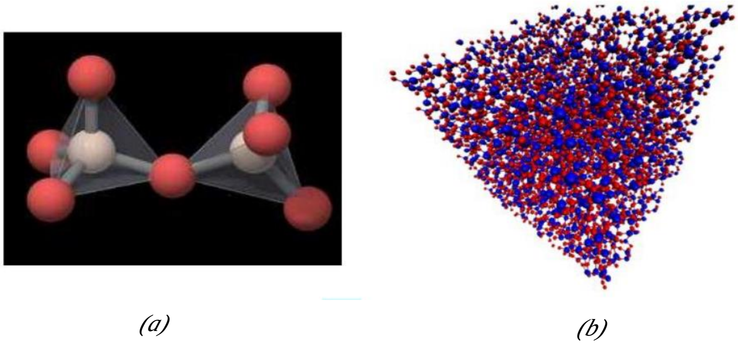
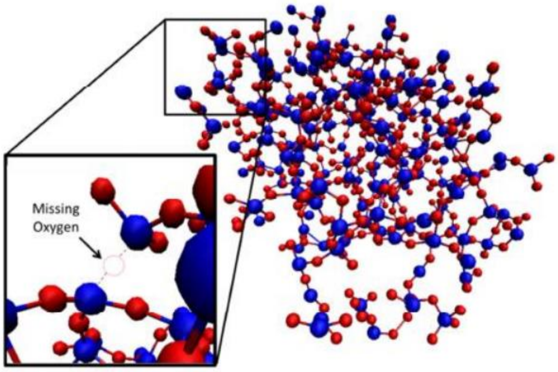


Figure 16: Diagram showing coordination defect in an amorphous structure where silica is surrounded by three oxygen atoms instead of four.



IV. Defects in Polymers

Polymers are high molecular weight long-chain macromolecules. Generally, polymers are amorphous structure with randomly coiled and entangled chains. However, some chains align themselves to form crystalline regions within the remaining amorphous material (Figure 17). ⁽¹¹⁾

Defects in the polymer structure are due to the chain-like macromolecules and the nature of the crystalline state for polymers. The crystalline regions may have point defects like vacancies, interstitial atoms and impurity atoms similar to those found in metals. Chain ends are considered defects as they are chemically different from normal chains units. Vacancies are also associated with chain ends. Defects can also result from branches in the polymer chain, dangling chains, loose chains, and dislocations (Figure 18). ⁽¹²⁾

Figure 17: Diagram of polymers a) Polymer containing only amorphous structure (b) Polymer containing amorphous and crystalline regions.

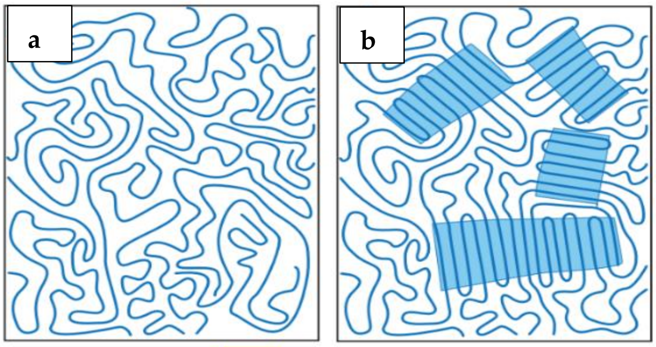
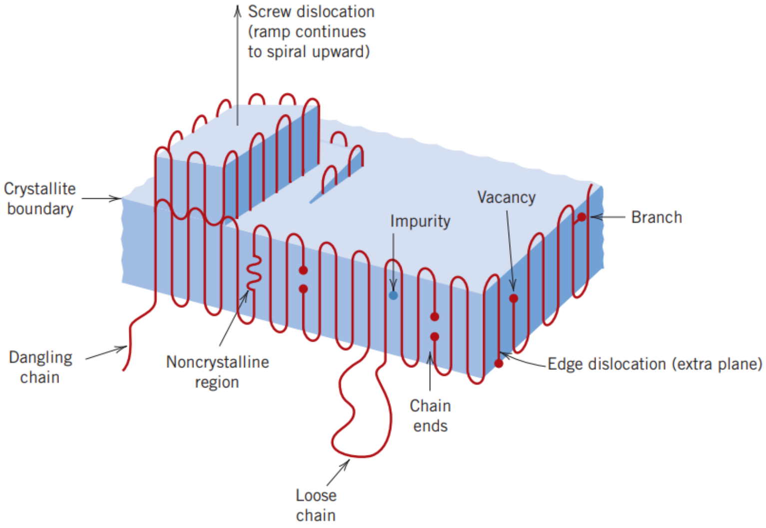


Figure 18: Schematic representation of defects in polymer crystallites.



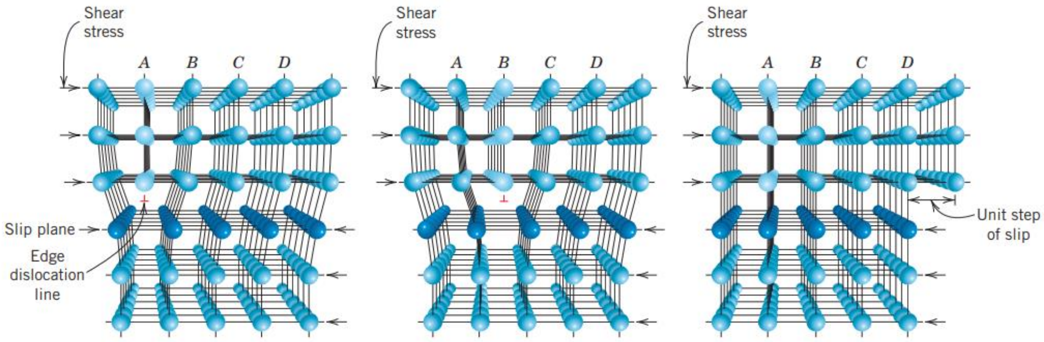
V. Effect of defects on the properties of the material

Defects play an important role in influencing the properties of the materials, Dislocations are especially important in metals and alloys as they provide a mechanism for *plastic deformation*. When the applied stress is above the yield strength, it will cause bond breakage, dislocation movement and permanent deformation. This must be distinguished from *elastic deformation* where only stretching of the inter-atomic bonds occurs and no dislocation movement. The dislocation movement occurs through a process known as slip (Figure 19). (3)

The slip process is important in understanding the mechanical behavior of metals:

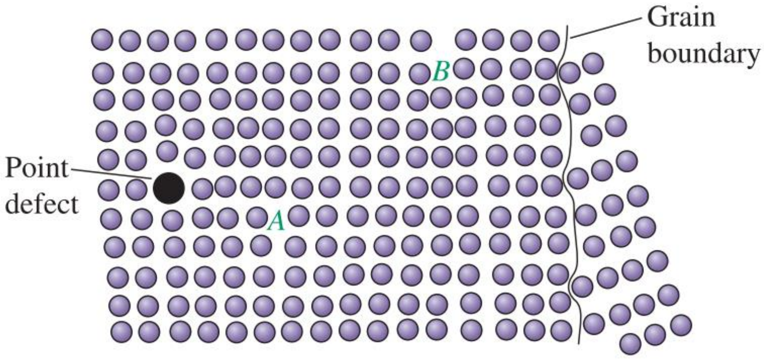
1. It explains why the strength of metals is much lower than the value predicted from the metallic bond because only a tiny fraction of metallic bonds is being broken at any one time, rather than the whole row at once. So, the force required to deform a material is lower than expected.
2. It provides ductility in metals, if there are no dislocations, the metal would be brittle.
3. Controlling the mechanical properties of metals or alloys can be done by interfering with dislocation movement. Any obstacle that prevents dislocation movement will increase the strength since higher forces are needed to overcome this obstacle. (3)

Figure 19: Diagram showing motion of an edge dislocation as it moves in response to an applied shear stress.



Defects as point defects, dislocations, and grain boundaries act as "*stop signs*" for dislocations; they obstruct dislocation movement, As a result, higher stresses are needed to overcome these obstacles, therefore, the strength of the material is increased (Figure 20).(3)

Figure 20: *If the dislocation at point A moves to the left, its motion is hindered by the point defect. If the dislocation moves to the right, it interacts with the distorted lattice near the second dislocation at point B. If the dislocation moves farther to the right, its motion is obstructed by a grain boundary.*



Three common strengthening mechanisms are based on the three categories of defects in crystals: Strain Hardening, Solid-Solution Strengthening and Grain-Size Strengthening. These mechanisms work best for metallic materials because dislocation movement is easier in metals and alloys. (3)

Strain Hardening: By increasing the number of dislocations by cold working. since increasing the dislocation density causes more stop signs for dislocation motion. (3)

Solid-Solution Strengthening: By intentionally introducing substitutional or interstitial impurity atoms, solid-solution strengthening occurs. (3)

In both types of solid solutions, the impurity atoms will distort the lattice due to the difference in atomic size between solute and solvent. As a result, dislocation movement is inhibited which will lead to strengthening of the material, the degree of strengthening depends on: (4)

The difference in atomic size between solute and solvent, the larger the difference, the greater the strengthening.

The concentration of solute atoms, the higher the concentration, the greater the strengthening effect.

Grain-Size Strengthening: By reducing the grain size, the number of grains increase. Thus, the amount of grain boundary area increases, as a result, the strength of the material will increase. (3)

Other effects on the properties of materials:

Twin boundaries interfere with the slip process; thus, the strength of the material increases. (3)

Crystalline defects serve as scattering centers for electrons conduction in metals, increasing the number of defects, will decrease the electric conductivity. (3)

Cracks and pores have undesirable effects as they decrease the strength and fracture resistance of the materials. (3)

VI. Microscopic Examination

Structural elements and defects have a large influence on the properties of the materials. Some of these structural elements are of macroscopic dimensions which can be seen by naked eye. However, in most materials, they are in microscopic dimensions. As a result, they must be investigated using microscope. Microscopic examination is very useful in the study and characterization of materials. The common types of microscopes are optical, electron, and scanning probe microscopes. (2)

A. Optical Microscopy

Optical or light microscopy involves passage of visible light transmitted through or reflected from the sample through a single lens or multiple lenses to allow a magnified view of the sample. Surface preparation of the sample must be done first to reveal the microstructure details, this involves polishing and etching of the specimen surface in order to achieve a smooth and mirror-like finish. (2,5)

In polycrystalline materials, etching characteristics and resulting surface texture vary from grain to another due to different crystallographic orientation (Figure 21). Also, upon etching, atoms along grain boundaries are more chemically active and therefore dissolve faster than those within the grains, forming small grooves along the grain boundaries, these grooves are detectable under microscope as they reflect light at a different angle than the atoms within the grain, so they appear under microscope as dark lines (Figure 22). (2)

Figure 21: (a) How polished and etched grains might appear when viewed with an optical microscope. (b) Grains with different crystallographic orientation have different etching characteristics and resulting surface texture.

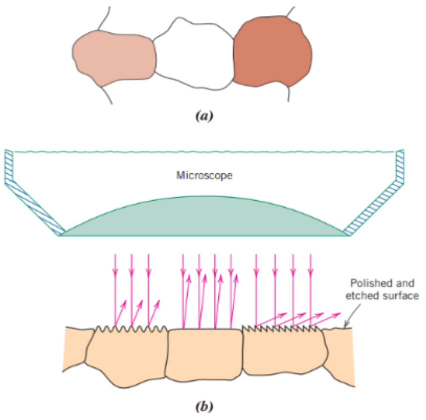
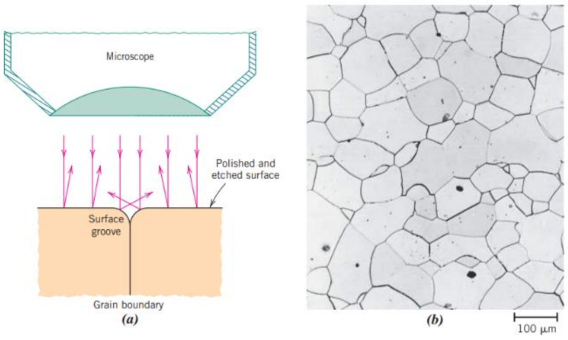


Figure 22: (a) Section of a grain boundary and its surface groove produced by etching, the light reflection characteristics are also shown. (b) Photomicrograph of the surface of a polished and etched polycrystalline specimen in which the grain boundaries appear dark.



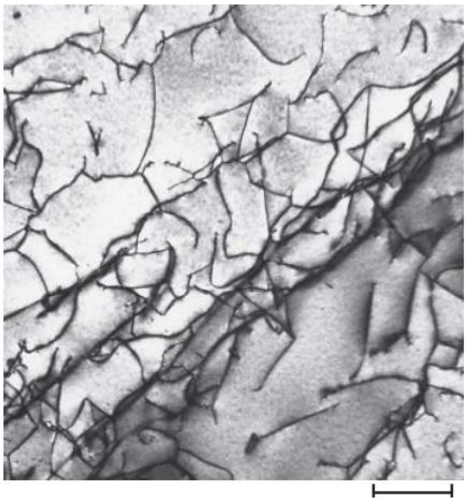
B. Electron Microscopy

The magnification of optical microscope is limited to 2000X which is insufficient for observation of very fine structural elements, in such cases, the electron microscope can be used. It uses a **beam of electrons** instead of light to form the image. It is characterized by **high magnification and resolving power** because of the short wavelengths of electron beams. The two types of electron microscopes are Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). (2)

Transmission Electron Microscopy (TEM)

TEM allows magnification up to 1,000,000× therefore it is commonly used to study dislocations (Figure 23). The image is formed by passing an electron beam through the specimen. The specimen preparation for TEM analysis is complex and requires highly specialized instruments. It should be very thin to allow transmission of electron through the specimen. The transmitted beam is then projected onto a fluorescent screen or photographic film. (2,5)

Figure 23: A transmission electron micrograph of a titanium alloy in which the dark lines are dislocations.



Scanning Electron Microscopy (SEM)

SEM allows magnification from 10× to 50,000×. The surface of the specimen is scanned with ***electron beam***, the reflected beam is collected and then displayed on a screen. The surface of the specimen must be electrically conductive. If the material is nonconductive, it must be covered with a thin layer of conductive material, most commonly gold. This is done by using a device called a "sputter coater." (2,5)

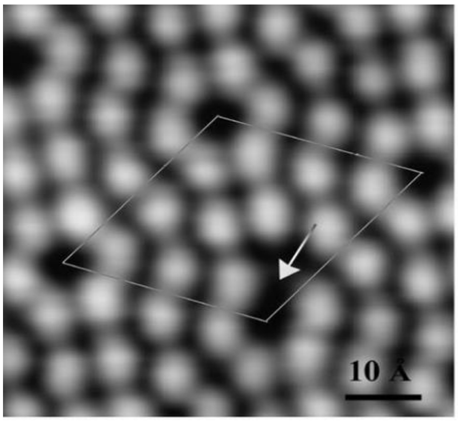
The main difference between SEM and TEM is that SEM creates an image by detecting reflected electrons, while TEM uses transmitted electrons (electrons that are passing through the sample) to create an image. As a result, TEM offers valuable information on the inner structure of the sample, while SEM provides information on the sample's surface. (2)

C. Scanning Probe Microscopy

A scanning probe microscope (SPM) is used for studying surfaces at the *nanoscale* level. It allows magnification up to 10^9x which provides much better resolution than other microscopic techniques. SPMs use a tiny probe with a very sharp tip to scan the specimen's surface, the probe does not touch the surface but traces the specimen nanometers above the surface. The movement of the probe allow generation of a 3D topographic image of the surface at the atomic scale (Figure 24).(2)

Scanning Tunneling Microscopes (STMs) and Atomic Force Microscopes (AFMs) are examples.

Figure 24: Scanning probe micrograph showing vacancy defect.



CONCLUSION

Materials are rarely perfect; they usually contain defects or imperfections that affect their properties either in a positive or a negative way. Several microscopes are used for examining such defects.

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The relation between Interatomic bonding and thermal energy

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Abstract: The bonding energy determines many physical and mechanical properties of the materials. Different atomic orbitals will overlap in different ways, so different amounts of energy will be released upon their formation.

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Introduction

An understanding of many of the physical and mechanical properties of materials is enhanced by a knowledge of the interactions that exist among constituent atoms or molecules, and the geometric atomic arrangement.

Electrons in atoms

Atomic models

The atom is the smallest part of any matter. In the center of each atom, a nucleus is present which is composed of positively charged protons and neutral neutrons. The nucleus is encircled by moving negatively charged electrons.

The first successful theory of atomic structure, the **Bohr atomic model** was proposed by Niel Bohr. He used the concept of quantized energy to propose that electrons moved around the nucleus in fixed orbits or shells. Bohr's atomic model represents that each orbit can have a specific number of electrons, which correlates to the energy levels. The shell closer to the nucleus has lower energy while the one farthest away has the highest energy. If an electron jumps to a lower energy orbit, it will give out the extra energy, thereby maintaining the atomic stability (1). (Figure1)

With the establishment of the quantum behavior of entities like electrons, it became quite clear that Bohr's atomic model didn't satisfy the Heisenberg uncertainty principle (2). According to this principle, it is impossible to know the exact position of electrons in an atom, which means they can't exist in fixed orbits, as Bohr hypothesized. In **the quantum mechanical model**, an electron is no longer described as a particle moving in a discrete orbit; rather, the arrangement of electrons could only be described in terms of probability, in other words, there are certain regions where electrons are much more likely to be found. We call these regions "orbital" (1). (Figure2)

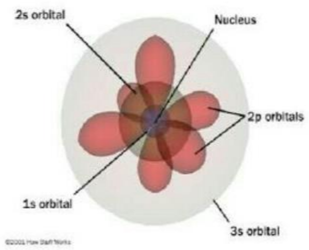


Figure 1: Bohr's atomic model

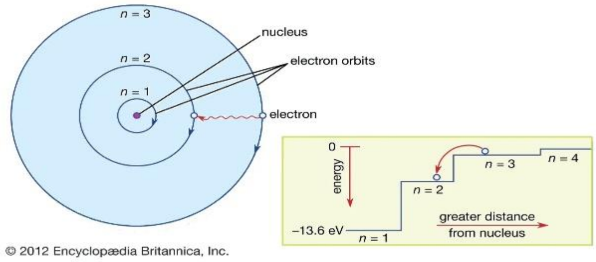


Figure 2: The quantum mechanical model

Quantum numbers

There are four quantum numbers used to specify each orbital in an atom (1).

- The principal quantum number, n, is the same quantum number that Bohr introduced. n labels the shell of the atom, these shells are sometimes denoted by letters K, L, M, N, O, and so on, which corresponds to $n=1, 2, 3, 4, 5$, respectively. This quantum number is related to the size of an electron's orbital. The maximum number of electrons in the shell can be represented by $2n^2$.
- The second quantum number is the angular momentum quantum number, ℓ.
  ℓ represents the subshell. ℓ can have any value from 0 to $n-1$, for example, if an electron has an n value of 3, it can have an ℓ value of either 0, 1, 2. The subshells are labeled s, p, d, and f.
  ℓ also describes the shape of the orbital. When $\ell=0$, we are describing s orbitals which are spherical and centered on the nucleus. When $\ell=1$, we are describing p orbitals which are 3 in number oriented perpendicular to each other and each one has a nodal surface in the shape of a dumbbell. When $\ell=2$, we are describing d orbitals. (Figure 3)
- The third quantum number, the magnetic quantum number, m_ℓ, represents the number of electron orbitals for each subshell. m_ℓ can have values between $-\ell$ and ℓ including 0. When $\ell=2$, m_ℓ can have a value of -2, -1, 0, 1, 2 which corresponds to the d subshell having 5 orbitals. (Figure 3)
- The fourth quantum number is the spin quantum number, m_s, this one will be either + ½ (spin up) or - ½ (spin down).

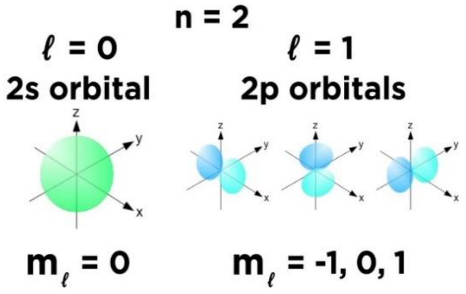


Figure 3: The second and third quantum numbers.

A complete energy level diagram for the different shells, subshells, and orbitals using the wave mechanical model is shown in figure 4.

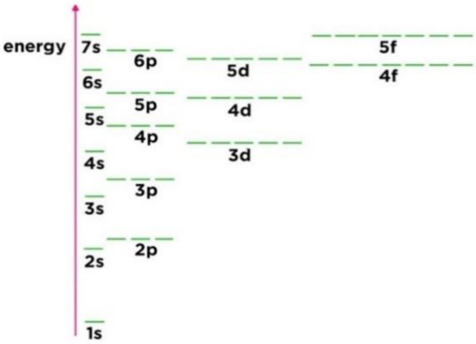


Figure 4: Energy level diagram.

The smaller the principal quantum number, the lower the energy level; for example, the 3p state has higher energy than the 2p state. The energy of the subshell level increases within each shell; for example, the 3d state has higher energy than the 3p state which is higher than 3s. There may be an overlap in electrons of a state in one shell with states in an adjacent shell, this can be found in d and f states as the energy of the 3d state is usually greater than that of a 4s (1).

Electrons configurations

Pauli exclusion principle states that any orbital can only hold up to 2 electrons and the two electrons in the same exact orbital will have opposite spin values, thus s, p, d, and f subshells may each accommodate respectively 2, 6, 10, and 14 electrons (Figure 5) (Table 1).

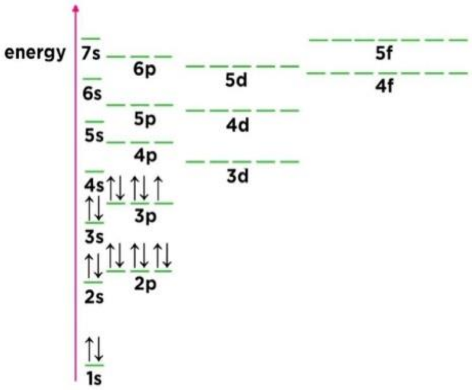
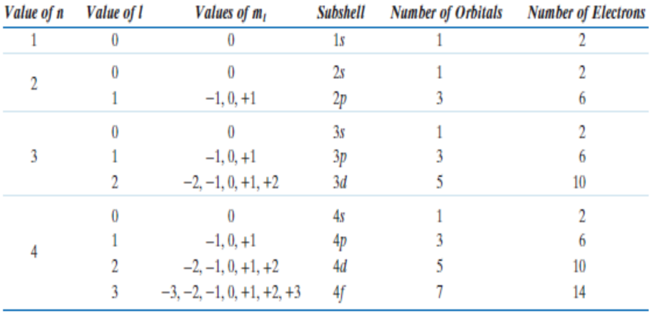


Figure 5: Electrons distribution in Cl.

Table 1: The relationships among the quantum numbers n, ℓ, m_ℓ, numbers of orbitals and electrons.



Value of n	Value of l	Values of m_l	Subshell	Number of Orbitals	Number of Electrons
1	0	0	1s	1	2
2	0	0	2s	1	2
	1	−1, 0, +1	2p	3	6
3	0	0	3s	1	2
	1	−1, 0, +1	3p	3	6
	2	−2, −1, 0, +1, +2	3d	5	10
4	0	0	4s	1	2
	1	−1, 0, +1	4p	3	6
	2	−2, −1, 0, +1, +2	4d	5	10
	3	−3, −2, −1, 0, +1, +2, +3	4f	7	14

At this point, it is important to know what valence electrons are. Valence electrons are those occupying the outermost shell. They determine which type of interatomic bonding will occur between atoms to form a molecule. When the valence shell is filled with 8 electrons except for helium which contains 2 1s electrons, the atom will have what is termed stable electron configuration as in neon and argon, so they are called noble gases or inert, which are unreactive chemically. Some atoms have unfilled valence shells, so they will gain, lose, or share electrons to reach the stable configuration (1).

Interatomic bonds

The process of gaining, losing, or sharing electrons forms strong primary atomic bonds, also called chemical bonds. The formation of primary bonds depends on the atomic structures and their tendency to reach a stable configuration. The molecules are held together by weak forces called secondary bonds.

Primary interatomic bonds

1- Ionic bonds

Ionic bonding is always formed between metals on the left side of the periodic table and non-metals on the right side of the periodic table (Figure 6). Metallic atoms lose their valence electrons to the non-metallic atoms so that all the atoms reach a stable configuration. The metal will acquire a positive charge and the non-metal will acquire a negative charge (Figure 7). The net energy of the formation of positive ions and negative ions is the sum of three terms. First, the energy needed to ionize the metal atoms. Second, the energy released when the metal loses the electrons to the non-metal. Third, the energy released due to attraction between the positive and negative ions (3).

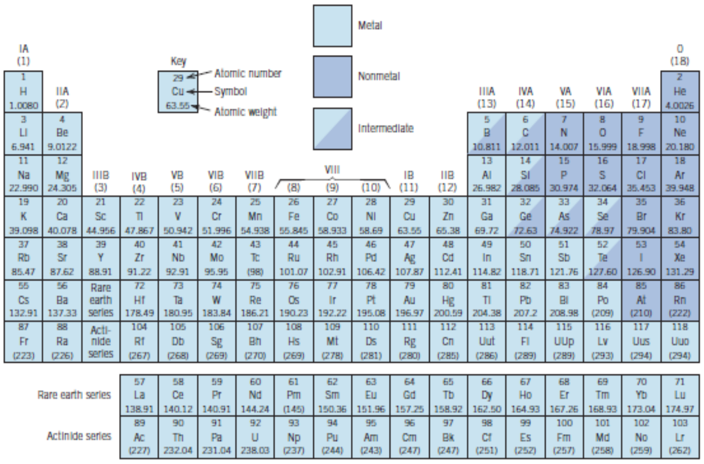


Figure 6: Periodic table of elements.

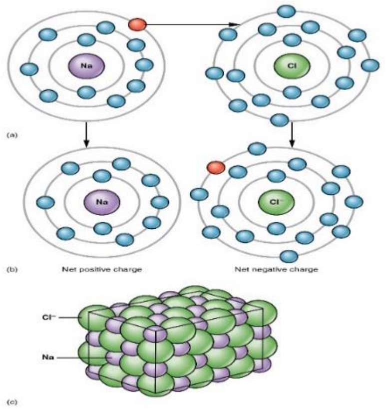


Figure 7: Ionic bonding in sodium chloride and formation of Na+ and Cl− ions.

Ionic bonding is considered nondirectional as the magnitude of the bond is equal in all directions around the ion. They have high bonding energies, reflected in their high melting temperature. Bonding energies range between 600 and 1500 KJ/mol (1) (Table 2). Ceramic materials are ionic bonded materials characterized by being hard, electrically, and thermally insulators due to the absence of free electrons or ions. Ceramic materials have high melting temperatures due to the presence of strong electrostatic force so a large amount of thermal energy is required to separate the ions. Ionic solids can conduct electricity in a liquid state.

Examples in dentistry: Ionic bonds exist in some dental materials such as gypsum structures, phosphate-based cement, and ceramics (4).

2- Covalent bonds

Although ionic bond occurs between atoms having a large difference in electronegativity, covalent bonding, is found between atoms having a small difference in electronegativity. For these materials, a stable state is reached by sharing electrons between adjacent atoms. A covalent bond is formed between two non-metallic atoms on the right side of the periodic table (Figure 6) (Figure 8).

A covalent bond is directional as it occurs between specific atoms and electrons are present in the direction between the two adjacent atoms. There is an overlapping of electron orbitals between the two adjacent bonding atoms. Bonding energies and melting temperatures for a few covalent bonded materials are presented in table 2.

Examples in dentistry: Covalent bonds exist in dental resin, where they link to form the backbone of hydrocarbon chains ⁽⁴⁾. Silica used in ceramics and investment materials is formed from covalent bonds.

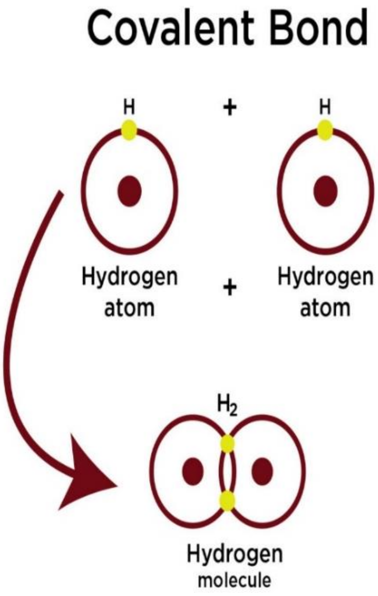
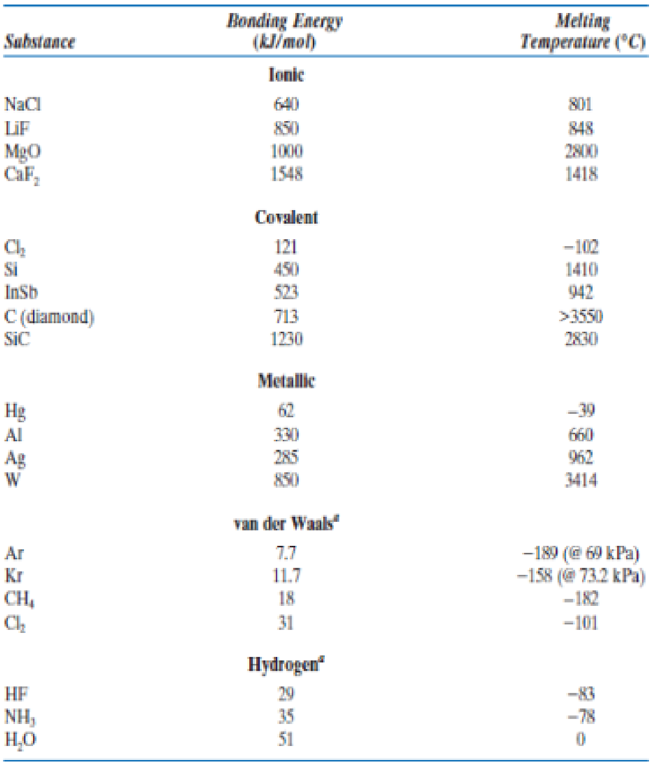


Figure 8: Example of a covalent bond in hydrogen molecule.

Table 2: Bonding Energies and melting temperature for various substances.



Substance	*Bonding Energy (kJ/mol)*	*Melting Temperature (°C)*
	Ionic	
NaCl	640	801
LiF	850	848
MgO	1000	2800
CaF_2	1548	1418
	Covalent	
Cl_2	121	−102
Si	450	1410
InSb	523	942
C (diamond)	713	>3550
SiC	1230	2830
	Metallic	
Hg	62	−39
Al	330	660
Ag	285	962
W	850	3414
	van der Waals^a	
Ar	7.7	−189 (@ 69 kPa)
Kr	11.7	−158 (@ 73.2 kPa)
CH_4	18	−182
Cl_2	31	−101
	Hydrogen^a	
HF	29	−83
NH_3	35	−78
H_2O	51	0

Bond hybridization in carbon

The covalent bonding of carbon and other non-metallic substances is associated with hybridization of two or more atomic orbitals so that more overlapping during bonding results.

When a carbon atom finds itself in a bonding situation, its bonding electrons themselves will exist at equivalent energies which requires that they hybridize to an energy that is intermediate between the 2s and 2p energies (Figure 9), and since the energy of these electrons is now changed, the shape of the orbitals they occupy are different as well which is called hybrid orbitals.

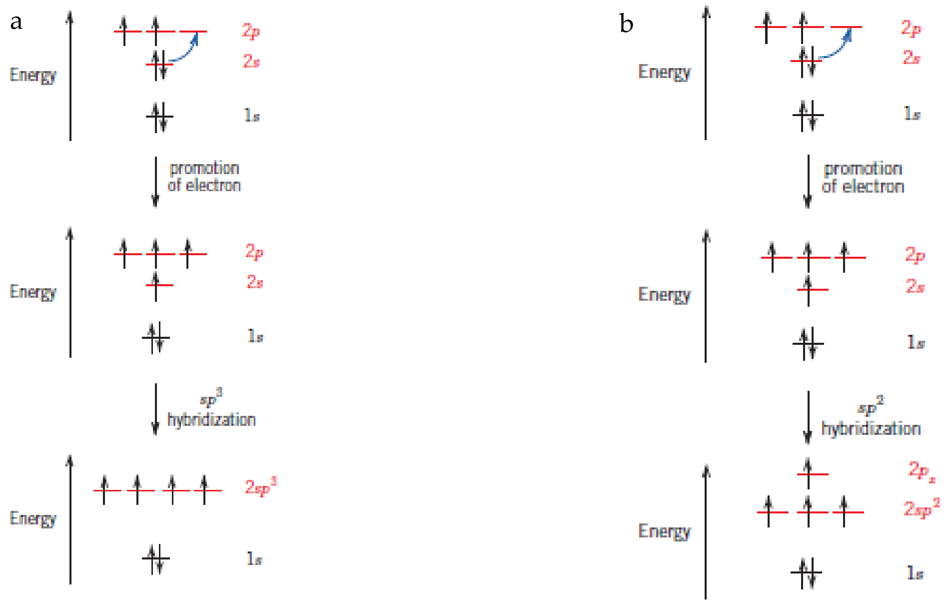


Figure 9: (a)The formation of $2sp^3$ hybrid orbitals and (b) $2sp^2$ hybrid orbitals.

Four $2sp^3$ hybrid orbitals are derived from combining the energies of one 2s orbital and three 2p orbitals (Figure 9 a). When hybridization occurs, the s and p orbitals cease to exist and $2sp^3$ orbitals exist having an entirely different shape, tetrahedral shape since all four $2sp^3$ orbitals are equivalent, each $2sp^3$ orbital repels the other with equal force, resulting in identical bond angles = 109.5° (1) (Figure 10).

In methane CH_4, when hydrogen atoms bind to carbon, each 1s orbital of hydrogen atom binds with carbon hybrid orbitals sp^3 (1) forming a sigma bond which represents the single covalent bond (Figure 11).

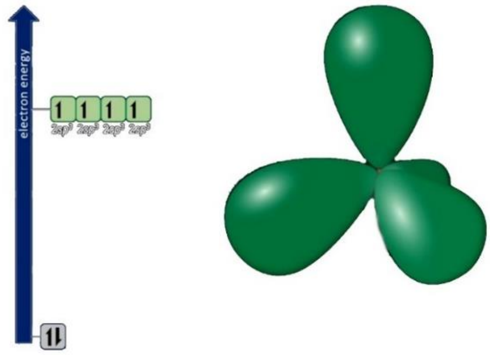


Figure 10: Four *sp*3 hybrid orbitals that point to the corners of a tetrahedron, the angle between orbitals is 109.5°.

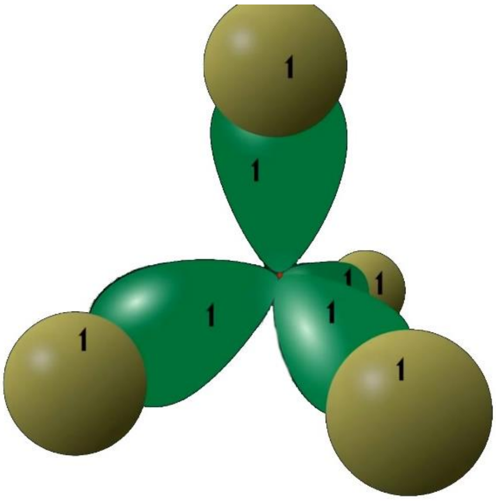


Figure 11: Schematic diagram that shows the bonding of carbon sp3 hybrid orbitals to the 1s orbitals of four hydrogen atoms in a molecule of methane (CH4).

In ethane C_2H_4, the C atom hybridizes one 2s orbital with two 2p orbitals forming 2 sp2 orbitals and one unhybridized 2p orbital. A pi bond will come from the side-to-side overlap of the unhybridized p orbitals, and a sigma bond will come from the head-to-head overlap of the $2sp^2$ hybrid orbitals, so double bonds contain sigma and pi bond (5) (Figure 12).

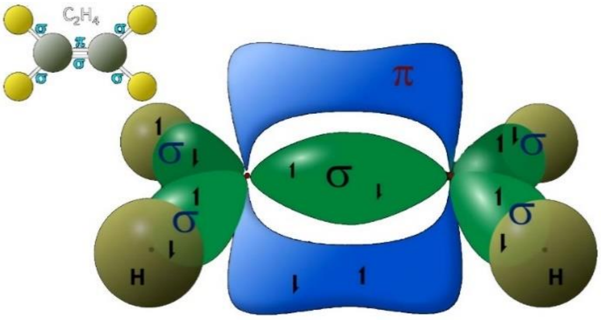


Figure 12: Schematic diagram that shows the bonding of carbon sp^2 hybrid orbitals to the 1s orbitals of four hydrogen atoms in a molecule of ethane (C_2H_4).

Sigma and pi bonds

A sigma bond is formed by the head-to-head overlap of bonding orbitals along the internuclear axis. This can be formed by any one of the following types of combination of atomic orbitals s-s, s-p, p-p (5).

During the formation of pi bonds, atomic orbitals overlap in such a way that their axis remains parallel to each other and perpendicular to the internuclear axis (5) (Figure 13).

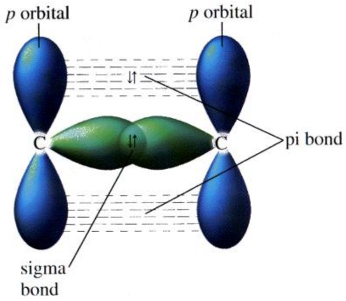


Figure 13: Sigma and pi bonds.

All single bonds are sigma bonds, while multiple bonds contain one sigma and the rest are pi bonds. The strength of a bond depends on the extent of overlapping of orbitals, so sigma bonds are stronger than pi bonds since maximum overlapping is formed along the internuclear axis and this will lead to higher bonding energy (5).

Diamond and graphite are both allotropic forms of carbon and are formed of inter-atomic covalent bonds. Although diamond is one of the hardest-known materials in nature, graphite is relatively soft. In addition, diamond is a poor conductor of electricity, but graphite is a reasonably good conductor. In diamond, each carbon atom has undergone sp^3 hybridization so that it bonds to four other carbon atoms by strong single covalent bonds (sigma bonds) forming a tetrahedral crystal that can be destroyed only by the rupture of many strong bonds. Thus, the extreme hardness, the high melting temperature, and the insulating properties are all consequences of the crystal structure of the diamond (1) (Figure 14).

For the graphite structure, sp^2 hybrid orbitals bond each carbon atom to three other adjacent and coplanar carbon atoms in a hexagonal crystal, inter-layer bonds are perpendicular to these planes and are weak van der Waal forces which give the graphite its slippery property. The unhybridized $2p_z$ orbital is oriented perpendicular to the plane containing sp^2 hybrid orbitals and forms a pi bond with the adjacent $2p_z$ orbital of another carbon atom. The electrons in the pi bond of the un-hybridized orbitals are delocalized (1), they are free to move through the carbon atoms of graphite, thus graphite is considered a semi-conductor material (Figure 15).

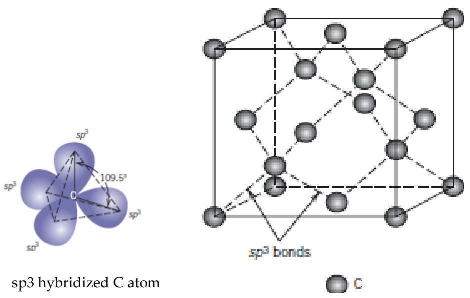


Figure 14: A unit cell for the diamond cubic crystal.

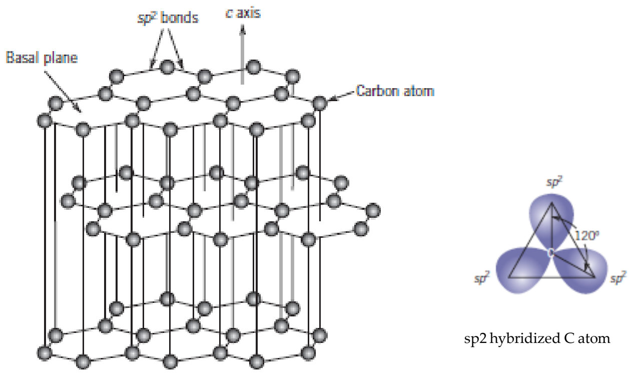


Figure 15: The structure of graphite.

Metallic bonds

The third type of primary atomic bonding is the metallic bond. The valence electrons in metals can be removed easily forming positive ions and the electron cloud. The electrostatic attraction between the electron cloud and positive ions will form the metallic bond (Figure 16).

The properties of metals occur as a consequence of the presence of free electrons. The free electrons make the metal highly thermal and electrically conductive. Metals are opaque and lustrous. The metallic bonds are responsible for the ability of metals to deform plastically. Bonding energies and melting temperatures for several metals are listed in table 2.

Examples in dentistry: Metallic bonds exist in amalgam restorations and dental implants.

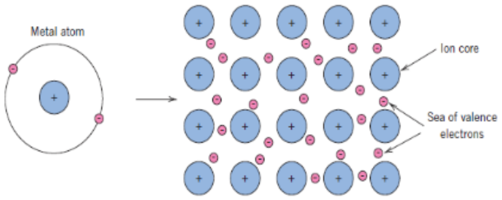


Figure 16: Metallic bonding.

Mixed bonding

The mixed bonds are illustrated in a bonding tetrahedron as shown in figure 17. Actually, for many real materials, more than one type of bond is present.

1- Mixed covalent-ionic bonds show some of the ionic characters to the covalent bond and some of the covalent characters to the ionic bond. The degree of each bond type depends on the difference in their electronegativities, the greater the difference in electronegativity, the more ionic is the bond. The smaller the difference in electronegativity, the greater is the degree of covalent bond. Percent ionic character of a bond between element A and B where A has higher electronegativity may be expressed by the following equation:

$$\%IC = \{1 - \exp[-(0.25)(X_A - X_B)2]\} \times 100 \qquad (1)$$

Where X_A and X_B are the electronegativities for the respective elements.

2- Mixed covalent-metallic bond is called metalloids and their properties are intermediate between metals and non-metals.

3- Mixed metallic-ionic bonds present in compounds composed of metals having a large difference in electronegativity. The larger the difference in electronegativity, the greater the degree of ionic characters.

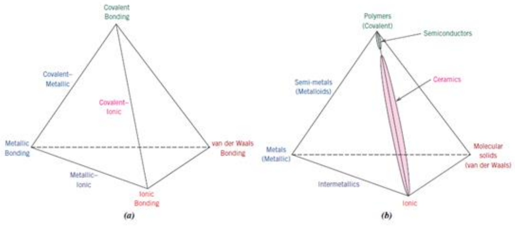
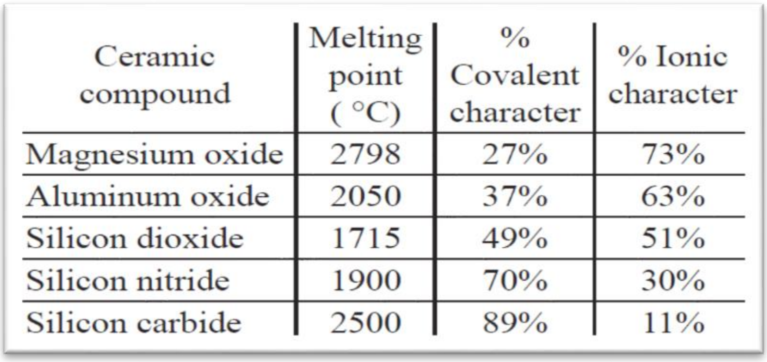


Figure 17: Bonding tetrahedron, each bond is located at one corner and three mixed bonding types are located along tetrahedron edges.

Examples in dentistry:

- Dental ceramics is a mixed ionic and covalent bond. The degree of presence of each bond depends on ionic character %. If there is an increase in ionic character %, the bond will be more ionic and if there is a decrease in ionic character %, the bond will be more covalent (6) (Table 3).
- Calcium sulfate, present in gypsum products is a mixture of both ionic and covalent bonds. The sulfur and oxygen atoms in sulfate ion(SO_4^{2-}) bonded covalently but they need two electrons to be stable, so they react with calcium which contains two electrons that can be easily removed, so an ionic bond is formed between Ca^{+2} ion and SO_4^{2-} ion (4).

Table 3: ionic character % of dental ceramic material.



Ceramic compound	Melting point (°C)	% Covalent character	% Ionic character
Magnesium oxide	2798	27%	73%
Aluminum oxide	2050	37%	63%
Silicon dioxide	1715	49%	51%
Silicon nitride	1900	70%	30%
Silicon carbide	2500	89%	11%

Secondary bonds

There are two types of molecules according to the difference in electronegativity of the constituent atoms; polar molecules where the unequal sharing of electrons induces permanent dipoles as in HCl and nonpolar molecules where there is an equal sharing of electrons as in methane. The random movement of electrons within the nonpolar molecule creates fluctuating dipoles.

Secondary bonds are intermolecular physical bonds. They arise from atomic or molecular dipoles either fluctuating induced dipole bonds (Van der Waals forces) or polar molecule-induced dipole bonds, permanent dipole bonds, and hydrogen bonds.

Secondary bonds are weak bonds in comparison to primary bonds but influence the physical properties of some materials. Bonding energies range between 4 & 30 KJ/mole (1). The magnitude of the hydrogen bond is generally greater than that of the other types of secondary bonds and may be as high as 51 kJ/mol. Bonding energies and melting temperatures of various molecular solids are present in table 2.

In dentistry, all polymer-based materials contain secondary bonds such as acrylic resin denture bases, artificial teeth, endodontic fillings, and resin composite restorative materials.

Interatomic bond distance and thermal energy

Bonding Force

Between any two atoms, two types of forces exist; forces of attraction drawing the two atoms together and forces of repulsion pushing them apart. Attraction forces (F_A) depend on the particular type of bonding that exists between the two atoms. Repulsive forces (F_R) occur due to interaction between negatively charged electron clouds for the two atoms when their orbitals begin to overlap.

At large distances, the atoms are too far apart to have an influence on each other, so interactions are negligible. However, at small separation distances, both attraction and repulsive forces increase. The sum of both attraction and repulsive forces will give the net force (F_N) acting on the two atoms.

$$F_N = F_A + F_R \qquad (1)$$

When the two atoms are far apart, F_A will exceed F_R so the net force will be an attraction force. However, when the two atoms are much closer, F_R will exceed F_A and the net force will be a repulsion force (4).

Interatomic bond distance

When F_A and F_R are equal in magnitude and opposite in sign, the net force will be zero and a state of equilibrium will exist. The interatomic distance at equilibrium (r_0) represents the distance between the centers of two adjacent atoms (Figure 18). For many atoms, r_0 is approximately 0.3nm (1). consequently, as atomic bonds are stretched, atoms tend to attract each other, and as the bonds are compressed, atoms tend to repel each other (7).

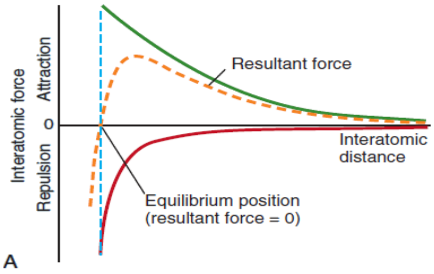


Figure 18: Relation of interatomic forces to interatomic bond distance.

<u>The correlation between the shape of the force-interatomic distance curve and the modulus of elasticity</u>:

The slope for a relatively stiff material at the $r = r_0$ position on the curve will be quite steep; however, the slopes are shallower for more flexible materials (1) (Figure 19).

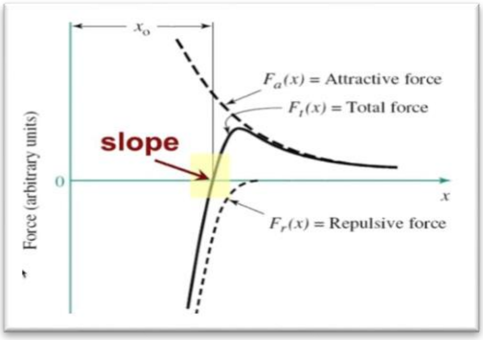


Figure 19: The slope at r = r_0 indicates the material's modulus of elasticity.

Bonding energy

The conditions of equilibrium are more related to energy factor than to interatomic distance. Mathematically, energy (E) and force (F) are related where the integration of the interatomic force over the interatomic distance yield the interatomic energy.

$$E = \int F \, dr \qquad (1)$$

And, for atomic systems,

$$\begin{aligned} E_N &= \int_r^{\infty} F_N \, dr \\ &= \int_r^{\infty} F_A \, dr + \int_r^{\infty} F_R \, dr \\ &= E_A + E_R \end{aligned} \qquad (1)$$

in which E_N, E_A, and E_R are, respectively, the net, attractive, and repulsive energies for two isolated and adjacent atoms.

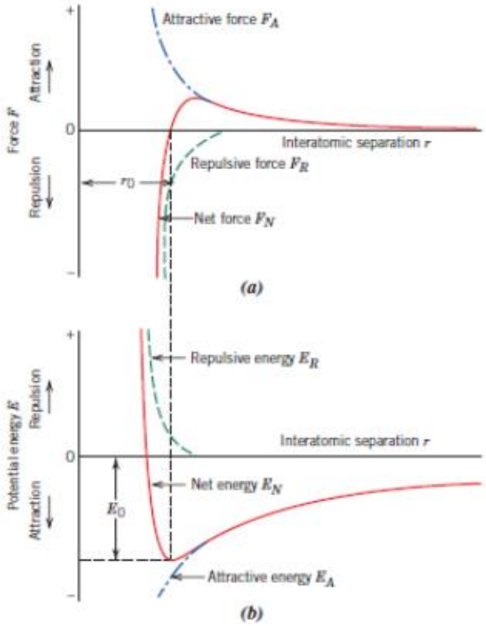


Figure 20: (*a*) The dependence of forces on interatomic separation for two isolated atoms.
(*b*) The dependence of potential energies on interatomic separation for two isolated atoms.

Figure(20 b) describes the attractive, repulsive, and net potential energies in relation to the atomic distance between two atoms. The net curve is the sum of attractive and repulsive curves. Beginning at the right edge of the curve, the atoms are far apart, the interactions are negligible, so potential energy = 0. As they move closer to each other, their 1s orbitals begin to overlap allowing each electron to interact with the proton of the other atom, and energy decreases until an ideal inter-nuclear distance is reached. This decrease in potential energy occurs because each electron is interacting with the protons of the two nuclei. As the potential energy decreases, the stability increases. Bonding energy at E_0 corresponds to energy at r_0, this is a stabilizing and energetically favorable situation. E_0 represents the energy required to separate these two atoms to an infinite separation, E_0 also shows why bond formation is an exothermic reaction because there will always be a decrease in potential energy as a result of orbital overlap and that difference in energy must be released to the environment, so the energy is absorbed to break the bond, and energy is evolved as bonds are made (8).

If we continue to push the protons together, the situation becomes less favorable due to cumulative proton-proton repulsion and electron-electron repulsion which will quickly begin to outweigh any attraction and the curve will rise steeply to the left.

Thermal energy

The atoms at a temperature above zero are in a constant state of vibration. The vibration of the atoms occurs between two positions and the mean interatomic distance is calculated (Figure 21).

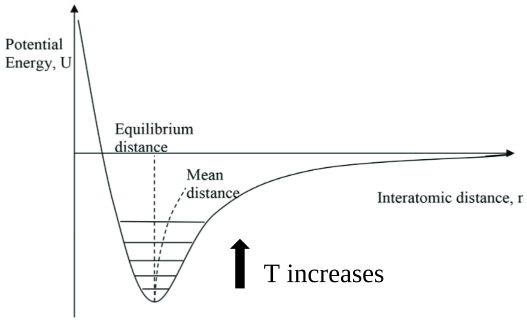


Figure 21: The mean interatomic distance.

As the temperature increases, the mean interatomic distance increases due to the asymmetry of the energy-interatomic distance curve, if the curve was symmetrical, there would be no change in the mean interatomic distance and this increase in mean interatomic distance is less with deeper energy trough than that in shallower energy trough (4) (Figure 23).

The correlation between the energy-interatomic distance curve and the melting temperature of the materials:

The magnitude of the bonding energy and the shape of the energy-interatomic separation curve varies from material to material. Many material properties depend on the curve shape and bonding type.

For example, materials having large bonding energy will have a high melting temperature (1) (table 2) (Figure 22). A greater slope of the force curve implies a narrower and deeper trough in the energy curve; Hence, a high melting point is usually associated with greater stiffness (4).

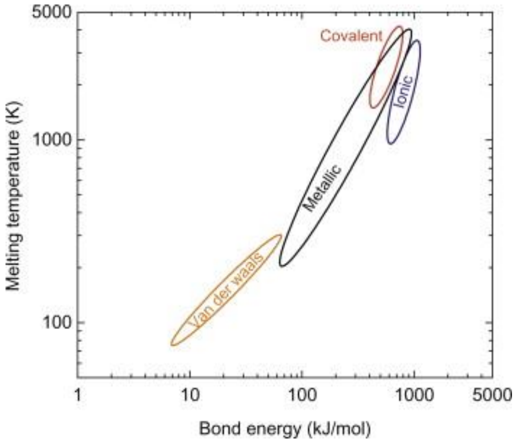


Figure 22: Melting temperature plotted against interatomic bond energy showing the ranges of different interatomic bonds.

The correlation between the energy-interatomic distance curve and coefficient of thermal expansion:

A deep and narrow trough which typically occurs for materials having large bonding energies normally correlates with less change in mean interatomic distance upon temperature changes than the shallow curve. The change in the interatomic distance will lead to thermal expansion. This means that the coefficient of thermal expansion in a deep and narrow trough is less than in a shallow trough, and the linear coefficient of thermal expansion for materials having similar atomic structures is inversely proportional to the melting temperature (4) (Figure 23).

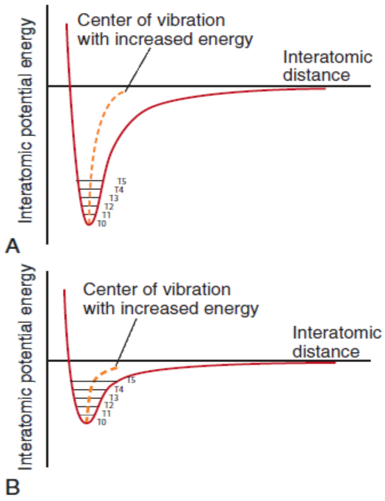


Figure 23: A represents a deep energy trough. B represents a shallow energy trough.

If the temperature continues to increase, the increase of interatomic distance will result in a change in the state of the material from solid to liquid and then to gas. There is a correlation between the magnitude of bonding energy and the state of materials; solids have large bonding energy (deeper trough depth) which corresponds to higher melting and boiling temperatures, while gases have small energies, and liquids tend to have intermediate energies (4) (7).

Conclusion

The bonding energy determines many physical and mechanical properties of the materials. Different atomic orbitals will overlap in different ways, so different amounts of energy will be released upon their formation. The greater the orbitals overlap, the stronger the bond between the two atoms, and the greater is the minimum potential energy (E_0).

A deep and narrow energy trough occurs in materials having large bonding energies, high melting temperatures, high stiffness, and a low coefficient of thermal expansion (Figure 24).

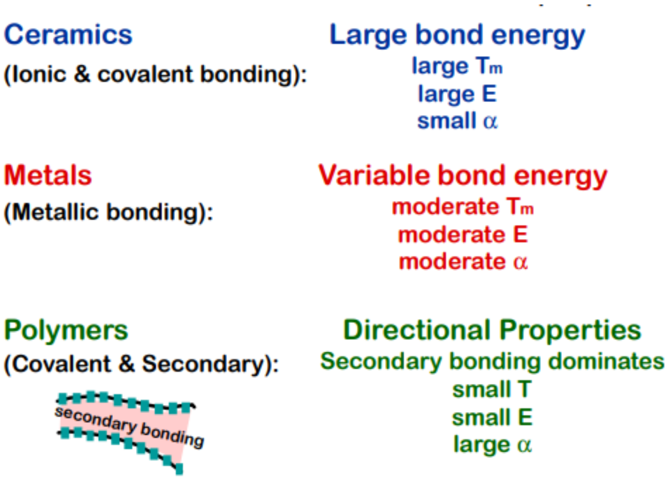


Figure 24: Interatomic bonding and materials properties where Tm is melting temperature, E is the modulus of elasticity, and α is coefficient of thermal expansion.

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Hot Isostatic Pressing technology for dental ceramics

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Abstract: The microstructure of ceramics can be defined as the arrangement of grains (individual crystals) and pores of different size and shape and occasionally of a crystalline or vitreous intergranular phase. This microstructure is generated at the end of the densification process from a powder compact following heat treatment. No microstructure is perfect and homogeneous and it is strongly dependent on powder characteristics and sintering mechanism.

Keywords: *hot isostatic pressing,dental ceramics,fabrication techniques of ceramics.*

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The matter transport to reduce the porosity of a powder compact occurs at high temperature by: (1) diffusion of atoms through the crystal lattice (Dl), along the surface (Ds) or the grain boundaries (Db) in the absence of liquid phase, (2) dissolution-diffusion-precipitation mechanisms in the presence of a liquid phase, or (3) by viscous flow in the case of a large amount of liquid phase. In all cases, there is a competition between the densification phenomenon and grain growth which strongly impacts the final grain size.

As most of the ceramic properties, such as mechanical properties, optical properties or electric conductivity depend on microstructure, it is therefore crucial to control all the steps leading to the microstructural development. Microstructure can be controlled by optimization of each of the fabrication process steps:

(1) Careful choice of raw materials particularly taking into account the chemical purity and particle size and shape

(2) Selection of the appropriate shaping technology with optimized parameters, and (3) Optimization of the temperature–time schedule and furnace atmosphere during sintering (air, O2–Ar, Ar, N2, water).

In addition, the thermal treatment can be modified, for example using:

Pressure assisted methods such as Hot Pressing, HIP, Post-sintering HIP treatments, where the driving force includes an extra parameter related to external pressure, (2) Methods such as Spark Plasma Sintering and Flash Sintering where the application of an electrical field induces increases in densification rates, and (3) Microwaves, a process which involves more homogeneous heat source distribution. [1]

I.Definition:

Hot Isostatic Pressing (HIP) is one of material processing methods, which compresses materials by applying high temperature of several hundreds to 2000 °C and isostatic pressure of several tens to 200MPa at the same time. It was invented in 1955 for diffusion-bonding applications in the nuclear industry and has since found numerous applications in other fields. Argon is the most commonly used pressure medium. Since the applied load (gas pressure) is hydrostatic, deformation of the porous body is supposed to be isotropic. The workpiece is usually encapsulated in an evacuated capsule of **sheet metal,** ceramic or glass. [2] [3]

II. Difference between HIP and Hot Pressing

HIP applies isostatic pressure to materials using gas pressure, while hot pressing applies only uniaxial pressure. To explain the difference of HIP and hot pressing clearly, suppose that HIP or hot pressing is applied to Material A (metal with pores inside) and Material B (metal with uneven ends).

In case of HIP, Material A, as shown in Figure 1, will contract keeping its initial shape until pores inside disappear, and bond together due to diffusion effects. On the other hand, Material B undergoes no shape change at all because uniform pressure is applied to the uneven edges.

In case of hot pressing, Material B, however, can't keep its initial uneven shape because pressure is applied only to the convex portions. Both Material A and Material B will have different final shapes after hot pressing depending on shapes of a mold and a punch used. Fabrication of large products and moldings under high temperature might be difficult because of ununiformity due to friction force with a mold and constraints due to temperature and dimensions during the deformation. [3]

Compared to hot pressing, HIP can provide material shapes not much different from the initial one after pressure. A material even after changing its shape can keep its initial shape, and will be relatively less restricted by processing of products. By making full use of these features, HIP has been applied in various fields. [3]

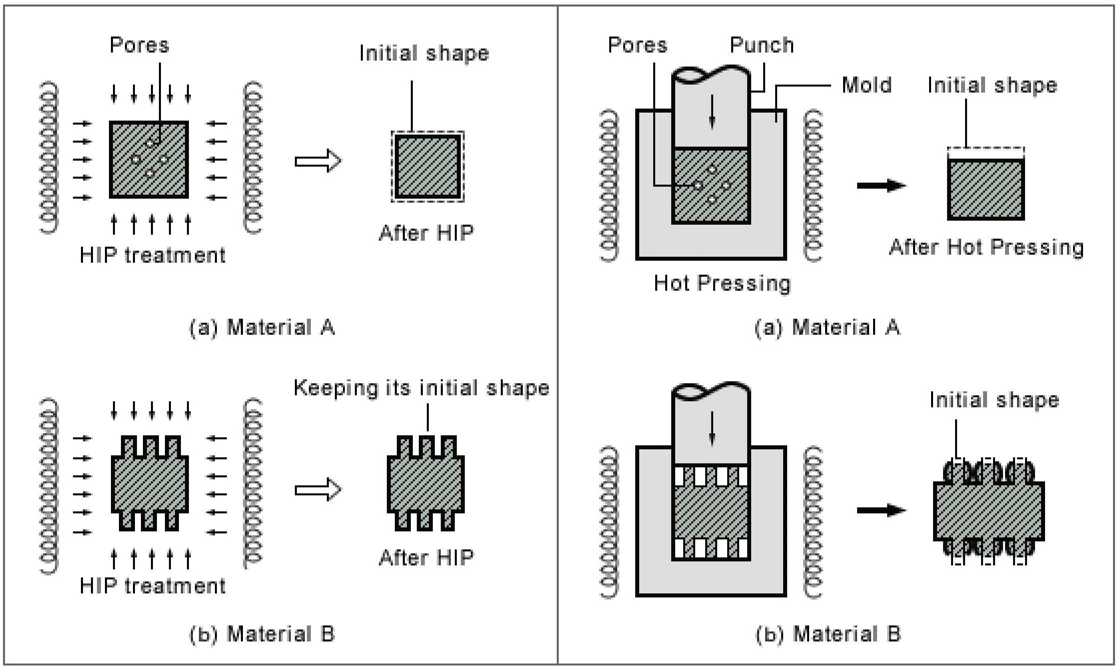

Figure 1: difference between hot pressing and isostatic hot pressing

III. Difference between HIP and Sintering:

Sintering occurs when heat is applied to a powder or to a body containing pores. Grain boundaries and dislocations are also regions of disorder and, therefore, are zones of high energy relative to the perfect crystal in the bulk. All systems try to achieve their minimum energy configuration and, in the limit, for a crystalline material, this is a single crystal containing no defects (pores, grain boundaries, dislocations). [4]

From a thermodynamic standpoint, the first step toward the goal of reduced energy is for pores to be eliminated from the system (the specific surface energy of pores is greater than the grain-boundary energy). However, during any sintering activity, the process of grain-boundary elimination (grain growth) often begins before the process of pore elimination has been completed. This state can then inhibit further pore removal for mechanistic reasons.[4]

While isostatic hot pressing, the combination of pressure and temperature can be used to achieve a particular density at a lower temperature than would be required for sintering alone. The effect of the lower temperature is that unacceptable grain growth can be avoided. In addition, the methods identified previously for enhancing densification of powders by introducing additives such as low-melting-point constituents (which may have deleterious effects on mechanical properties) are not needed.[5]

IV.Advantages of HIP:

HIP removes the impurities (pores) out of materials creating a product with an homogenous microstructure (compact solid) with minimal or no impurities in the material.HIP gives the manufacturer and ultimate user a number of unique benefits:

- Reduced porosity
- Higher Density
- Higher uniform strength in all directions (isotropic properties)
- No segregation or grain growth during manufacture
- Higher yield and tensile strength
- Homogeneous microstructure
- Maximum abrasion resistance
- Near-Net shaped parts
- Shape flexibility: Isostatic pressing makes it practical to produce shapes and dimensions that are difficult or impossible to produce by other methods. [5]

V.Limitations of HIP:

The tooling cost and complexity of the process are higher than for uniaxial hot pressing.

VI.HIP equipment and HIP process:

The HIP process uses the combination of elevated temperatures and high pressure to form, densify, or bond raw materials or preformed components. The application of the pressure is carried out inside a pressure vessel, typically utilizing an inert gas as the pressure-transmitting media. A furnace located inside the vessel is the temperature source. Parts are loaded into the vessel, and pressurization occurs usually simultaneously with the heating. Parts are then cooled inside the vessel and removed.[5]

A hot isostatic pressing system usually consists of five major components: pressure vessel, internal furnace, gas handling, electrical, and auxiliary systems. Hot isostatic pressing systems currently range in size from 1 to 80 in. (25 to 2000 mm) diameter. The **smaller** units usually are used for research. It is common practice to design one unit universally for research processes such as: densification of ceramics at (2,000°C). This can be accomplished with one basic system but with various plug-in furnaces and a versatile control system. Larger size production units are usually designed for handling a specific process but can also accept various plug in furnace types. [5]

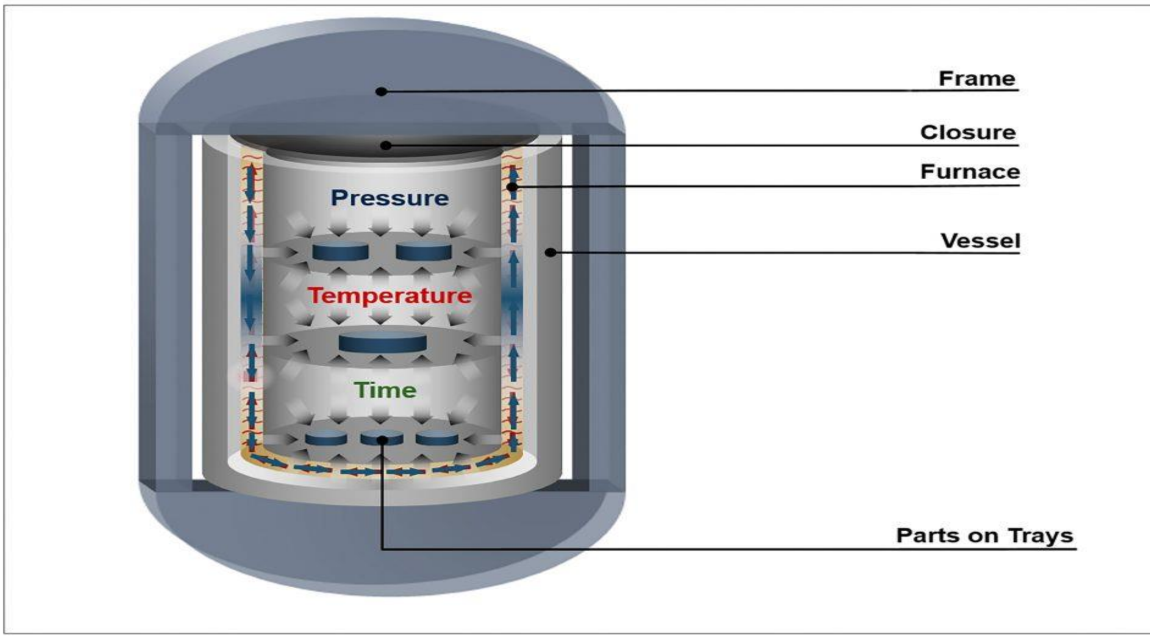

Figure 2: HIP equipment

A.Pressure Vessel

The pressure vessel in a HIP system contains the high-temperature furnace and retains the high-pressure gas. Utility connections to the furnace typically extend through the bottom cover and require a reliable pressure seal as well as electrical isolation from the vessel. Elastomer O-rings seal the gas in the vessel since the vessel temperature is kept below (250°C). The design of any pressure vessel must meet two essential requirements. They are the minimum dimensions based on allowable stress and fatigue life.[5]

B.Furnaces

The hot isostatic pressing furnace, contained within the pressure vessel, provides the heat required either from direct radiation, gas convection, or forced-gas convection. Within the furnace are electrical resistance heating elements and a space for placing the work piece (tooling and components to be HIPed). The pressure vessel is designed as a "cold wall vessel" and is protected by a thermal barrier that prevents hot gas penetration to the inside of the vessel wall. Furnaces can be constructed to "plug-in" with the work piece in place. Direct thermocouple attachment takes place outside the vessel. [5]

A.Radiation furnaces are typically multi-level, multi-zone styles with the heating elements surrounding the work piece. There are two types of radiation furnaces used; the cold load system where the element and work piece start at room temperature and are heated together, or the hot load system where the work piece is preheated outside the vessel then loaded into the hot furnace cavity.

B.Natural convection furnaces are common for many sizes of HIP units. They work by heating the dense gas in the furnace element area and conveying it to the work piece above by the buoyancy of the hot gas molecules. In this type of furnace, a convection liner creates a path for the gas flow as its energy dissipates to the work piece and as more hot gas molecules move upward from the element. This gas circulation continues until the temperature is equalized throughout the work area. [5]

C. Forced convection furnaces are also of single or multi-level construction but have a fan to circulate the gas. Heat transfer to the work piece is a function of the full coefficient of heat transfer of the gas. By increasing the gas velocity the final coefficient is increased to provide high heating/cooling rates.

There are several advantages to using convection furnaces. The work piece is not exposed to direct radiation from heater elements. There is a larger work cavity available for a given vessel diameter. Heating elements are not susceptible to damage by the load/unload process, and construction is much simpler than that for multi-level radiation furnaces.

Many different furnace element materials are available for hot isostatic pressing furnaces. Each element material has characteristics that affect its capability in HIP applications. The three most common element materials are graphite, molybdenum, and nickel/chrome. [5]

C.Gas Handling

Hot isostatic pressing processing requires an inert gas to apply an equal (iso) force to the part for densification. Most systems use argon as the pressurizing medium. HIP systems often require pressures to 15,000 psi and sometimes even up to 45,000 psi (N/mm^2) depending on the material being processed. Gas pressures can be achieved with a compressor and/or by thermal expansion.

Gas purity is very important when processing parts which are susceptible to oxygen, hydrogen, carbon monoxide, carbon dioxide, water vapor, and hydrocarbons contamination. [5]

D.Controls

The control system for a hot isostatic pressing unit is the subsystem that links the vessel/furnace, gas handling, and auxiliaries into a functioning production tool. Computer control ensures repeatability of these parameters to maintain consistency of operation.

E.Auxiliary Systems

A HIP system is supported by a number of important subsystems classified as auxiliaries. These include cooling and vacuum systems, material handling with work piece fixtures and facilities subsystems including exhaust fans, oxygen monitoring equipment, and cranes. [5]

1. The cooling system keeps the pressure vessel temperature below its design limits.

2. The vacuum system provides a means of removing the atmospheric contaminants from the furnace/vessel. Commonly a mechanical pump with a blower is used for handling high flow rates at low pressure. Isolation is provided by a high-capacity high-pressure vacuum valve. System interlocks ensure safety and prevent exposure of the vacuum components to high pressure.

3. Work piece fixturing is determined by the material being processed as well as by the operating temperature. Carbon steel has a relatively high melting temperature and is used.

Materials such as nickel/chrome alloys or a combination ceramic and graphite fixture can be used also for work piece fixtures. [5]

4. Oxygen monitoring equipment are essential for the safety of personnel. The monitoring equipment can be set up to automatically start exhaust fans and give warnings of an oxygen deficiency.

VII. Applications of hot isostatic pressing:

HIP is widely used during the manufacturing of high integrity and precise components for a diverse range of applications and industries from Aerospace and Medicine to Automotive; Composites, dental Implants, Sintering (Powder metallurgy), Coatings, Ceramic parts, Titanium Castings and diffusion bonding.

VIII. Effect of hot isostatic pressing on ceramics properties:

A. The influence of HIP conditions on densification, mechanical properties and biocompatibility of zirconia ceramics was investigated. Compressive strength increased considerably after HIP treatment, from approx.101 MPa (for pre-sintered samples) to at least approx. 602 MPa. All samples presented high Young's modulus values between 1739 MPa and 4372 MPa. Dental zirconia ceramics have proved a good biocompatibility. The results reported in this work showed that ZrO_2–CaO dental ceramics manufactured by hot isostatic pressing presented high density and compressive strength, elastic behavior and a good biocompatibility with human cells. [6]

B. High transparency: vacuum sintering to closed porosity with a subsequent HIP'ing step provides an alternate processing route to fully dense Lu2O3:Eu. It has been shown that evolution of porosity and microstructure during sintering and densification must be optimized to achieve fully dense transparent ceramics. Over-sintering led to rapid grain growth at high temperatures and the grain boundary motion was faster than pore mobility, resulting in entrapped pores in the interior of grains. During the subsequent HIP stage, closed porosity was achieved while maintaining the minimal grain size and the maximum grain boundary area during the vacuum sintering step. This enabled the pore mobility to be fast enough to keep up with the grain boundary motion during HIPping, and the pores were completely annihilated forming fully dense Lu2O3:Eu. By this method, highly transparent Lu2O3:Eu was formed.[7] [8]

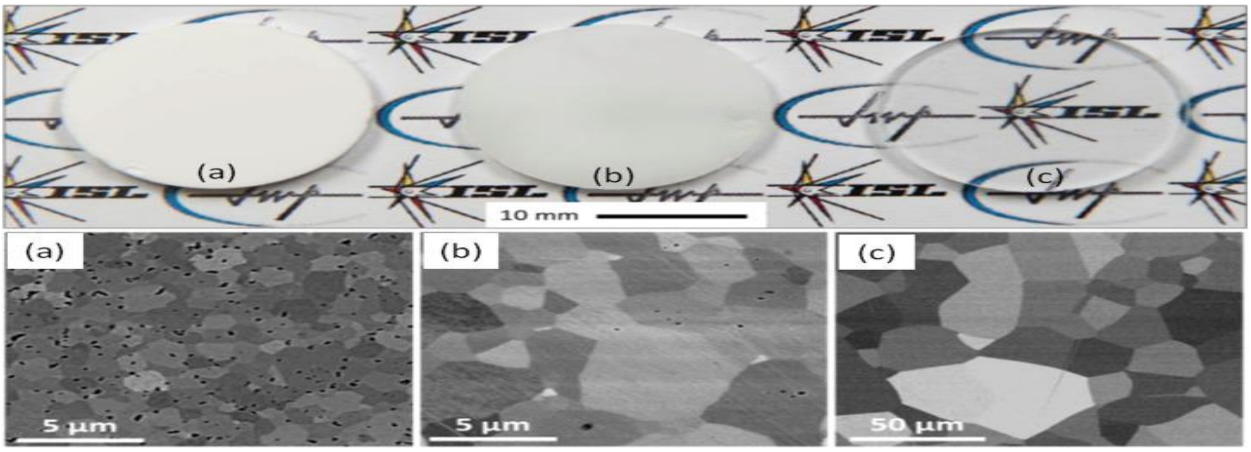

Figure 3: Transparency after hot isostatic pressing

C. High cyclic fatigue: the cyclic fatigue strength (888 MPa) of HIP Y-TZP with sandblasting and acid-etching was more than twice that of Y-TZP as specified in ISO 13356 for surgical implants (320 MPa), indicating the clinical potential of this material.[9]

D. However, HIP nano zirconia exhibited inferior strength, surface polishability and behaviour to loading.[10]

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Recent Advances in Contemporary Dental Adhesives

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Abstract: Dental adhesives are solutions of resin monomers that can make the resin/ tooth structure interaction achievable. Adhesive systems are composed of monomers with both hydrophilic groups that enhance wettability to the dental hard tissues and hydrophobic groups that allow the interaction and co-polymerization with the restorative material. Modification of adhesive materials is necessary to improve the longevity of resinous restorations and to obtain more stable resin-dentin bond through incorporation of active components into the adhesive system, treatment of the dentin surface prior to adhesive application, and modification of the bonding protocol.

Keywords: *Collagen crosslinking; MMPs; Hybrid layer; Dental adhesives; Adhesive degeadation.*

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I. Introduction:

Contemporary adhesive systems are unable to completely infiltrate the collagen network with resin monomers. The presence of water-rich spaces and unprotected collagen fibrils are responsible for nano-leakage within hybrid layers. Moreover, the unprotected collagen fibrils network will be subjected to enzymatic degradation. Therefore, modification of adhesive materials is necessary to improve the longevity of resinous restorations and to obtain more stable resin-dentin bond (1-4).

II. Classification of dental adhesives:

II.1. Classification according to generation:

1st generation: Etching dentin with 7% hydrochloric acid and GPDM (Glycerophosphoric acid dimethacrylate) was used for bonding to dentin.

2nd generation: The bonding adhesives were composed of BisGMA (bisphenol-glycidyl-methacrylate) and HEMA (hydroxyethyl methacrylate).

The 1st and 2nd generation dentin bonding agents chemically bonded to the smear layer rather than to the dentin tissue. Therefore, the bond strength was too weak leading to the poor clinical performance(1, 4).

3rd generation: Incorporation of hydrophilic primer that infiltrate and modify the smear layer. However, these adhesives do not eliminate marginal leakage (1, 4).

4th generation: Total-etch technique was introduced. Total-etch technique permits simultaneous etching of enamel and dentin(1, 4).

5th generation: The total-etch technique was simplified into two steps by combining primer and bonding resin into one application(1, 4).

6th generation: Self-etch adhesives two-step systems composed of self-etching primer solution and bonding agent (1, 4).

7th Generation: One bottle system contains etch, primer and bond (1, 4).

8th generation in 2010, voco America introduced voco futurabond DC, which may be used either as etch-and-rinse or as self-etch adhesives(1, 4).

II.2. Classification by mechanism of adhesion/clinical step:

II.2.1. Three-steps: These bonding systems are supplied as three bottles (etchant, primer, and bonding agent).

II.2.2. Two-steps 1: Bonding systems are supplied in two bottles, one consisting of etchant, and the other of the combined prime and bond formulation.

II.2.3. Two-steps 2: Bonding systems are supplied in two bottles, one containing a self-etching primer and the second the bonding agent.

II.2.4. One-step: Single bottle containing self-etching primer and bonding agent(4).

II.3. Classification according to adhesion strategy:

II.3.1. Smear layer removing adhesive systems:

These bonding agents completely remove the smear layer. Enamel and dentin are etched simultaneously using 37% phosphoric acid. After washing and drying the tooth surface, primer and bonding agent are applied either separately or in combination(5).

II.3.2. Smear layer modifying adhesive systems:

The bonding agents modify the smear layer and incorporate it in the bonding process. Enamel is selectively etched with 37 % phosphoric acid. After washing and drying the tooth, primer and adhesive are applied separately or in combination(5).

II.3.3. Smear layer dissolving adhesive systems (self-etch approach):

These agents partially demineralize the smear layer and the superficial dentin surface without removing the remnants of smear layer or the smear plugs. They use acidic primers which provide simultaneous conditioning and priming of both enamel and dentin. After this, adhesive is applied without washing the tooth surface(5).

II.4. Classification based on etching pattern:

II.4.1. Total etching technique:

The concept of total etching is the simultaneous etching of enamel and dentin. Total etching technique may either be as follows:

II.4.2. Self-etch system:

No separate etching and rinsing. The residual smear layer remnants remain within the bond. Depending on etching aggressiveness they are divided into:

- Strong Self-etch Adhesives ($pH<1$).
- Intermediate Self-etch Adhesives ($pH \approx 1.5$).
- Mild Self-etch Adhesives ($pH \approx 2$).
- Ultra Mild Self-etch Adhesives ($pH\geq 2.5$)(6).

III. Composition of dental adhesive:

a) Etchant:

In total-etch technique the etchant used is 35–37% phosphoric acid. The etchant in self-etch bonding agents is an acidic monomer that also serves as the primer.

b) Primer:

Primer is composed of hydrophilic monomers such as HEMA in a water-soluble solvent (acetone, ethanol, water) to promote good flow and penetration into hydrophilic dentin. Self-etch bonding agents utilize acidic primers.

c) Adhesive resin composed of two types of monomers:

Crosslinking hydrophobic monomers: Bis-GMA, TEGDMA, and UDMA.

Functional monomers:

10-MDP, phenyl-P and 4-META monomers with carboxylic and phosphate groups. These functional groups can ionically bond with calcium in hydroxyapatite providing satisfactory chemical bonding to dentin.

Meth acrylamides: Meth acrylamides have an amide (–CO–NH– or –CO–N–) group instead of an ester group (–CO–O–R–) as in conventional acrylates and methacrylates which promotes the formation of hydrogen bonds between the carboxyl and amide groups of the monomer with the carboxyl groups of collagen.

d) Fillers:

Recently nanofillers 0.5% to 40% by weight in the 8th generation adhesive systems. Fillers control handling, improve strength, and increase film thickness of the adhesive layer.

e) Solvent:

Solvents include acetone, ethanol, and water. Their main function is to promote good penetration of the monomers in the collagen network of the demineralized dentin, thus improve the diffusion ability of resin. Acetone evaporates quickly and requires the shortest drying time in the mouth. Ethanol evaporates more slowly and requires moderate drying time. Water evaporates very slowly and requires longest drying time. Bonding agents should be dispensed immediately before use to prevent premature evaporation of the solvent.

f) Photo-initiators:

Compounds that dissociate into free radicals upon absorption of light energy, such as camphorquinone (CQ) and 1-phenyl-1,2 propanedione (PPD).

g) Inhibitors:

Inhibitors (butylated hydroxytoluene) added to dental resins to scavenge free radicals originating from prematurely reacted initiators.

h) Modifiers:

Such as glutaraldehyde, (MDPB) monomer for antibacterial effect, and fluorine compounds(4, 5).

IV. Failure of Resin-Dentin Bonding:

IV.1. Degradation of Resin-Dentin Bonding Interface:

IV.1.1. Degradation of Adhesive Resins:

Water within the hybrid layer and oral fluids (dentinal fluids and saliva) serves as a medium for the hydrolysis and leaching of resin adhesives leading to resin degradation and reduction of bond strength through different mechanisms(7, 8) :

- Water acts as a plasticizer between the polymer chains of the adhesives leading to the acceleration of matrix degradation(9).
- Human saliva contains cholesterol esterase and pseudocholinesterase, which act synergistically to degrade dimethacrylates(1).
- Methacrylate adhesives containing ester bonds are subject to chemical hydrolysis(1).
- Dental adhesive systems comprise both hydrophilic and hydrophobic components undergo phase separation phenomenon.

Phase separation phenomenon:

The hydrophobic monomers stay on the surface while the hydrophilic components infiltrate the interior of the hybrid layer producing heterogeneous resin layers. The hydrophilic domains have a limited degree of polymerization. Therefore, the poorly polymerized hydrophilic phase undergoes degradation more quickly(9, 10).

IV.1.2. Degradation of Collagen:

Degradation of collagen matrix by matrix metalloproteinases (MMPs) and cysteine cathepsins are among the major reasons for the failure of resin- dentin bond(1, 9).

- Matrix Metalloproteinase (MMP):

MMPs are produced by odontoblasts as they play an important role during dentine maturation, then they become inactive after the collagen matrix mineralization is completed. MMPs are Zn^{2+} and Ca^{2+} dependent endogenous proteases, Ca^{2+} ions preserve the structure of MMPs and Zn^{2+} ions are responsible for the enzyme activation. Acid-etching during dentin bonding and weak acids released by cariogenic bacteria can uncover and activate matrix-bound MMPs (2, 11).

- Cysteine Cathepsins:

Cysteine cathepsins (CTs) are expressed by mature human odontoblasts cells and pulpal tissues. There is synergistic activity between MMPs and CTs and they regulate the activities of each other. MMPs and CTs can attack type I collagen, the most abundant organic component of dentin matrix(1, 2).

IV.2. Incomplete Infiltration of the Resin Adhesives:

Incomplete infiltration of the adhesive in the collagen network is a result of the difference between penetration of the adhesive and action of the etching acidic agents leading to nano-leakage(9). Moreover, incomplete resin infiltration leads to the activation of MMPs and CTs because the exposed dentin collagen becomes recognizable and available to MMPs and CTs(1).

IV.3. Mechanical Loading:

Masticatory forces can adversely affect the bonding interface leading to gap formation and marginal leakage around restorations. Moreover, exposed collagen fibrils due to incomplete infiltration of bonding resin are susceptible to creep or cycling fatigue during function. Additionally, surface strains of the adhesive layer facilitate the absorption of fluids and accelerates degradation of the adhesive(1).

IV.4. Microleakage:

When polymerization shrinkage and the associated contraction stresses of composite resins are higher than the bond strength, marginal gaps would form at the interface, resulting in microleakage. Bacteria and oral fluids can penetrate the tooth-composite interface. Bacterial collagenases may cause degradation of the hybrid layer and increase nanoleakage. Lactic acid produced by cariogenic bacteria can activate MMPs impairing resin-dentin bond durability(1).

V. Recent Advances in contemporary adhesives:

V.1. Incorporation of agents with anti-MMPs, remineralization, antibacterial, or reinforcing functions into adhesive systems.

V.2. Treatment of the dentin surface prior to adhesive application.

V.3. Modification of the Bonding Protocol.

V.1. Incorporation of agents with anti-MMPs, collagen crosslinking, remineralization, or antibacterial functions into adhesive systems.

V.1.1. Adhesives modified with anti-MMPs and collagen crosslinking Functions:

Applying MMPs inhibitors as a component of the adhesives may help to improve durability of adhesive restorations because they have the potential to decrease the degradation of the collagen fibrils within(1). Several crosslinking agents have been suggested for protecting collagen fibers which were used as primers or incorporated into the adhesive formulation(12).

➢ Mechanism of action:

- Cationic-anionic reaction, cationic agents electrostatically bind to negatively charged catalytic sites of MMPs, blocking the active site.

- Chelating or formation of covalent bonds with zinc or calcium which leads to loss of catalytic activities of MMPs.

- Protein cross-linkers can induce changes in MMPs 3D structure and hinder molecular mobility which is essential for their enzyme activity. Moreover, they may stabilize collagen matrix and improve the mechanical properties of the hybrid layer, thus strengthening the resin-dentin bond.

- Crosslinking agents can crosslink proteases which interferes with their molecular mobility(1, 12).

V.1.1.1. Adhesives modified with synthetic anti-MMPs and collagen crosslinking Functions:

a) Glutaraldehyde:

Glutaraldehyde is a crosslinking agent with strong antibacterial activity. It contains two aldehyde groups at each end of the chain able to react with the amino groups of the collagen fibrils. Therefore, it stabilizes the collagen fibers in the hybrid layer and preserves the adhesive interfaces. Glutaraldehyde-containing bonding agents was introduced as a desensitizing agent for hypersensitivity treatment through denaturation of collagen in dentin, occlusion of dentinal tubules, and prevention of post-operative pain (2, 12, 13).

However, Glutaraldehyde has toxic, allergenic, and mutagenic effects. Direct incidental contact with mucous tissues, inhalation of glutaraldehyde evaporated from the adhesive should be considered as a source of irritation and allergic asthma both for dentist and patient(13).

Commercial Products:

- Gluma 2Bond bonding systems that contained 5% glutaraldehyde were the first adhesives that contained glutaraldehyde.

- Several other manufacturers also added glutaraldehyde to their adhesive formulation (Syntac, Vivadent; ProBond, DENTSPLY Caulk) (2, 13, 14).

b) Chlorhexidine (CHX):

CHX inhibits MMP and CTs proteolytic enzymes through cationic-anionic reaction of CHX which deforms MMPs molecules and prevents them from binding to substrates. In addition, CHX could bind Ca^{2+} and Zn^{2+} ions resulting in loss of catalytic activities of MMPs. Moreover, CHX is an antimicrobial agent that can inhibit bacterial proteolytic enzymes and can electrostatically bind to demineralized dentin(1, 2, 7). Adhesive systems modified with CHX diacetate showed enhanced long-term stability of resin–dentine interfaces without affecting the bond strength(15).

Commercial product: Peak Universal Bond contains 0.2% chlorhexidine diacetate(14).

c) Zinc-Doped Adhesives:

MMPs-mediated collagen degradation activity is dependent on calcium (Ca^{2+}) and zinc (Zn^{2+}) ions concentrations and the Zn^{2+}/ Ca^{2+} ratio. Therefore, a relatively high concentration of Zn^{2+} may interfere with the MMP-mediated collagen degradation. The Zn^{2+} liberation from Zinc-doped adhesives will facilitate the formation of a ZnO rich layer that permits Ca and P deposits and further remineralization. For self-etching adhesives, Zn should be added into the bonding resins, and never in the primer containing MDP, as it forms Zn-MPD complexes that may interfere with chemical interaction of calcium/dentine and MPD dentin infiltration(1, 16, 17).

V.1.1.2. Adhesives modified with natural anti-MMPs and collagen crosslinking Functions:

a) Grape seed extract (GSE):

GSE is composed of proanthocyanidins (PA) which is a natural collagen cross-linker derived from polyphenols. PA can create hydrogen bonds between collagen fibrils. Moreover, electrostatic interactions occur between the amide carbonyl group of collagens and the phenolic hydroxyl group of PA. This will increase the mechanical stability of the collagen matrix and improve the quality of the hybrid layer.

The incorporation of PA to an experimental adhesive did not show adverse effects on the immediate resin-dentin bond strength when its concentration was less than or equal to 2%. In addition, PA was incorporated into the etching solution and experimental primer to enhance the stability of bonding. However, there is a lack of long-term in vitro and in vivo studies on its stability; it may also stain the dentin brown (7, 12, 18).

b) Hesperidin (HPN):

HPN is a protein cross-linking flavonoid extract of citrus fruits. HPN has the capability of enhancing dentin remineralization. The effect of HPN on remineralization is related to its interaction with collagen providing stable collagen matrix for the remineralization process, since it acts as a scaffold for mineral deposition. HPN has been incorporated in Clearfil SE primer. Incorporation of HPN into Clearfil SE primer had a positive influence on the immediate resin-dentin bond strength, the hardness and elastic modulus of the interface(19, 20).

c) Quercetin:

Quercetin is a polyphenol abundantly found in in many plants and foods, such as onions, green tea, apples, and berries. Quercetin can inhibit MMP activity by zinc chelation because it has high affinity to metal ions. Quercetin increases the expressions of tissue inhibitor of metalloproteinase (TIMP). Quercetin suppresses prostaglandin-E synthesis by inhibiting the activity of cyclooxygenase-2 enzyme (COX-2) because the over-production of the COX-2 induces MMP release(2, 7, 21). Quercetin has a crosslinks collagen by formation of hydrogen bonds, van der Waals forces, and electrostatic forces. Quercetin can induce dentinogenic differentiation of dental pulp cells and has an antibacterial effect by inhibiting the metabolic activity of *S. mutans*. Quercetin was incorporated into adhesive and used as pretreatment of etched dentin to improve the bond strength (22).

V.1.2. Adhesives with Remineralization Functions:

Remineralization of resin-dentin interfaces aims to replace water from water-rich resin-sparse regions of the hybrid layer with apatite crystallites. Moreover, cariogenic bacteria produce acids causing demineralization of the tooth structure and the tooth-restoration margins. Therefore, a new approach to stabilize resin-dentin bonding is to remineralize the hybrid layer to increase the mechanical properties of the dentin-resin interphase and protect the exposed collagen leading to inactivation of MMPs and CTs (1, 3).

The local alkalinization promoted by ion release (Ca^{2+}, Na^{+}) downregulates MMP activity that normally triggered in acidic conditions. In addition, Electrostatic interactions between MMP and CaP precipitates form high molecular weight, low-mobility aggregates, reducing enzymatic activity (3).

Dentin remineralization could be obtained through two approaches:

- Top-down remineralization (ion-based crystallization concept): In case of partially demineralized carious dentin, apatite crystallites left in the intrafibrillar regions serve as nucleation sites for calcium and phosphate ions precipitation, followed by epitaxial crystal growth. However, this approach may not be applicable for remineralization of completely demineralized dentin where seed crystallites are absent, e.g., in hybrid layers created by phosphoric acid etching or aggressive self-etch adhesives.

- Bottom-up (biomimetic) remineralization: Apatite precipitation in completely demineralized dentin is assisted by biomimetic analogs of non-collagenous proteins. These molecules serve as stabilizers for the mineral precursors and as templates to guide apatite growth in an oriented and hierarchically organized manner within collagen matrix. This strategy inhibits MMPs through biomimetic remineralization and prevents collagen degradation(3, 23-25).

V.1.2.1. Bioactive glass (BAG):

BAG could be used as a source of calcium and phosphate ions that will subsequently crystallize into hydroxyapatite and induce remineralization of the resin-dentin interface. BAG has anti-microbial activity due to high pH in their environment due to the release of alkaline elements Na^+ or K^+ (1, 14). The bioactivity of such BAG could be potentiated by doping with specific ions, such as Sr, Ag, F, and Cu. Fluoride (F)-doped BAG incorporated into adhesive resin have been demonstrated to have greater remineralization properties and MMP inhibition ability(3, 26).

Copper (Cu^{2+}) ions are considered a potent inhibitor of MMPs in human dentin. Cu doped BAG added to adhesive showed MMP deactivation and remineralization properties at the resin-dentin interface(1, 12). Adhesives modified by Cu doped BAG are able to release Ca, Si, and Cu ions, which induce remineralization at adhesive resin-dentin interface, bind to specific sites on the exposed collagen fibrils and modify its spatial configuration protecting them from MMPs action, reduce the MMP enzyme activity, and induce formation of tertiary dentin or osteodentin structures along the walls of the pulp chamber (3, 26).

V.1.2.2. Amorphous Calcium phosphate nanoparticles (NACP):

NACP modified adhesives release Ca^{2+} and P^{3-} ions inside the water-filled voids in the hybrid layer which re-precipitate to form hydroxyapatite to mineralize the dentine and enamel and cause calcification of MMPs (1). When collagen fibrils are completely demineralized, NACP could be used to achieve the biomimetic remineralization of adhesive resins. NACP bind with collagen and serve as a template when polyanions are incorporated around the NACP. This in vitro concept is not translated into clinical trials yet(25).

V.1.2.3. Hydroxyapatite:

HA nanorods in adhesives may biomineralize with the collagen network of tooth through hydrogen bonding between $COOH^-$, OH^-, and NH_2^- of the collagen network and OH^- group of the hydroxyapatite particles, achieving remineralization of the dentin at resin-dentin interface(1).

V.1.2.4. Dentin phosphoproteins Analogues:

Mineralization of dentin is a complex process regulated by the collagenous matrix mainly type I collagen, non-collagenous proteins (NCPs) such as dentin phosphoproteins (DPP), and minerals. Type I collagen defines the framework for mineral deposition and by itself is not sufficient to support nucleation of hydroxyapatite. DPP has a strong affinity for Ca^{2+} and are considered as nucleation sites within the collagen fibrils for mineral deposition initiation and propagation of hydroxyapatite crystals growth(27, 28).

Adhesives and primers modified with phosphoproteins analogues such as polyvinylphosphonic acid (PVPA), polyacrylic acid (PAA), polyaspartic acid, and sodium trimetaphosphate (TMP) show a promising potential for biomimetic remineralization of the hybrid layer through deposition of apatite crystals. Phosphoproteins analogues bind to collagen and serve as templates for specific calcium binding and apatite nucleation(25).

In biomimetic remineralization of resin–dentin bonds, a source of amorphous calcium phosphate (ACP) is required such as flowable composite or bonding agent containing (ACP)(25). ACP and phosphoproteins analogues can move into collagen fibrils and slowly diffuse through any water-filled porosities within adhesives and hybrid layers (i.e., residual water in un-infiltrated dentin) and ``back-fill'' such defects with apatite crystals and calcify all dentin proteases as the matrix collagen remineralizes(29, 30).

V.1.3. Antibacterial Adhesive Agents:

Antibacterial bonding agents could combat biofilms and recurrent caries at the tooth-composite margins.

V.1.3.1. Quaternary Ammonium Salts (QAS):

QAS is a potent antimicrobial agent due to presence of positive quaternary amine charge (N^+) that interact with the negatively charged bacterial cell membrane leading to alteration of membrane permeability, disturbance of the bacterial surface electrostatic balance, and cytoplasmic leakage. Moreover, positively charged QAS can interact with the negatively charged extracellular polymeric substances (EPS) changing its physicochemical properties leading to reduction of the bacterial adherence. Finally, QAMs electrostatically bind to negatively charged catalytic sites of MMPs and CTs leading to inhibition of their activity and reduction of the demineralized dentin collagen degradation(1, 7, 31).

Commercial Products:

✓ MDPB monomer (e.g. Adper prompt L pop and Clearfil SE Protect Bond):

MDPB (12-methacryloyloxydodecy l-pyridiniumbromide) is an antibacterial monomer based on quaternary ammonium salts which provides bonding agents with long lasting antibacterial activity without releasing the antibacterial agent. Before polymerization, MDPB in primer acts as cavity disinfection. After curing it becomes immobilized by polymerization in bonding agents and covalently bonded to the polymer network(1, 5, 14). Therefore, it is not leached from the hybrid layer and acts as a contact inhibitor against the bacteria that comes in direct contact with the polymer. MDPB-containing adhesive is promising to manage secondary caries, even root surface caries and active lesions. Clearfil SE Protect which contains 5% MDPB in the primer solution and fluoride in the adhesive resin, was the first antibacterial adhesive system to be commercialized (1, 5, 14).

✓ Benzalkonium chloride (BAC):

It is a cationic surface-acting agent with a quaternary ammonium group used as antimicrobial agent and surfactant. BAC-containing etchants can be used with E&R adhesives without affecting immediate bond strength to enamel or dentin. Bisco is already manufacturing the commercial 37% phosphoric acid with 1 wt% BAC(1, 7, 31).

V.1.3.2. Fluoride-releasing resin adhesives:

Fluoride-containing compounds are well known for their anti-caries effects because they enhance the formation of fluorapatite, accelerate remineralization, interfere the ionic bonds generated during biofilm formation, inhibit microbial growth and metabolism. Adhesives containing fluoride is superior for the hybrid layer strengthening and preservation of degradation of the resin dentine bond because F^- ions have been identified as MMP inhibitors through chelation of Ca^{2+} and Zn^{2+} and alteration of MMP structure(25, 32, 33).

Commercial Products:

Clearfil Protect Bond contains sodium fluoride (NaF) crystals which can release fluoride ions from the adhesive.

Clearfil Universal Bond Quick, Clearfil S3 Bond Plus, One Up F Bond Plus, Futurabond NR, OptiBond Solo and Reactmer Bond(14).

PEM-F in Xeno IV: PEM-F[1] is a monomer with a grafted fluoride functional group(5).

V.1.3.3. Surface pre-reacted glass ionomer (S-PRG) fillers:

Surface Pre-Reacted Glass-ionomer (S-PRG) fillers are synthesized by PRG (Pre-Reacted Glass) technology involving reaction between fluoroboroaluminosilicate glass and a polyacrylic acid solution. The S-PRG filler-containing adhesive can release various ions, such as aluminum (Al^{3+}), boron (BO_3^{3-}), fluoride (F-), sodium (Na+), silicon (SiO_3^{2-}

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[1] pentamethacryloyloxy-ethylcyclohexaphosphazene- monofluoride

), and strontium (Sr^{2+}) in both neutral and acidic conditions. These ions have antimicrobial activity against various oral bacteria such as *S. mutans*.

Commercial products: FL-Bond II(34).

V.1.3.4. Silver nanoparticles (AgNPs):

Silver ions are the most widely explored antimicrobial agents which exhibit antibacterial, antifungal, and antiviral activity, as well as low toxicity and biocompatibility with human cells(1). Polymers with Ag release a high number of ions initially losing their antibacterial activity in a short period. Thus, the synthesis and incorporation of nanometric Ag particles into the resin promoted polymers with a large reservoir of Ag ions, having ions releasing at a constant rate, allowing long-term antibacterial effects (24).

AgNPs cause rupture of cell membranes by contact with the silver metal surface leading to the uptake or ion penetration into the nucleus and formation of reactive oxygen species, and the inhibition of cell reproduction by interaction with DNA. Moreover, AgNPs inactivate the bacterial enzymes(14).

V.1.3.5. Chitosan:

Chitosan is known for being biocompatible and antibacterial agent that has several dental applications. The interaction between the positively charged chitosan and the negatively charged bacteria cell surface leads to the rupture of the cell membrane. Moreover, type I collagen has a capacity to form ionic complexes with chitosan, increasing the collagen strength. Chitosan was incorporated into dentin adhesives or used as a separate primer solution(14, 35). However, chitosan may increase the hydrophilicity of the adhesive systems leading to formation of nano leakage within the hybrid layer. In addition, undesirable interaction between the adhesive systems with chitosan may compromise the function of chitosan as a cross-linking agent(12, 36).

V.1.4. Resin Matrix Reinforcement with Fillers:

V.1.4.1. Silicon dioxide nanoparticles (SiO_2 NPs):

Incorporation of SiO_2 nanoparticles (20 nm) improves mechanical properties of dentin bonding agents and provide elastic resin–dentin interface which may help to counteract stress resulting from polymerization shrinkage of the resin composite. Commercial product: Futurabond DC(37).

V.1.4.2. Zirconia nanoparticles:

Incorporation silanized ZrO_2 nanofillers into the primer or adhesive could enhance the bonding integrity and mechanical properties at resin-dentin interface, increase durability of the of the dentine-resin bond, and improve resistance to the hydrolytic process(38).

V.1.4.3. Carbon nanotubes:

Carbon nanotubes are extremely strong which were incorporated as fillers to adhesives to reinforce the resin matrix and thus the resin-dentine bond strength. The cylindrical hollow structure of nanotubes can act as a medium for the encapsulation of therapeutic molecules such as doxycycline, biomimetic agents, antioxidants, and collagen crosslinkers and then incorporated into an adhesive resin(9, 39).

V.1.4.4. Titanium oxide nanoparticles (TiO_2 NPs):

TiO2 NPs are effective against Gram-negative and Gram-positive bacteria and enhance stability of resin- dentin bond(40).

V.2. Treatment of the dentin surface prior to adhesive application:

V.2.1. Ethylenediaminetetraacetic acid (EDTA):

EDTA contains 4 carboxylic acid groups and acts by chelation of Zn^{2+} and Ca^{2+} ions. Application of EDTA before bonding agent application inhibits MMP activity and improves the removal of the smear layer and resin infiltration into the collagen matrix(12). The benefits of EDTA pretreatment in dentin were also confirmed in a randomized clinical trial. A higher retention rate of composite resins was observed in non-carious cervical lesions bonded with a self-etch adhesive when the dentin was pretreated with EDTA 17% for two minutes(41, 42).

V.2.2. Tetracyclines:

Tetracyclines are antibiotics with cationic chelating properties. Chemically modified tetracyclines (minocycline and doxycycline) are considered broad-spectrum MMP inhibitors. Minocycline and doxycycline chelate Ca^{2+} and Zn^{2+} ions which play an important role in maintaining MMP structure and functional active sites. By binding to the zinc ion present on catalytic domain of the enzyme, modified tetracyclines can inhibit the MMPs by altering their conformation at the molecular level and thus blocking their catalytic activity in the extracellular matrix. The application of 2% MI, as dentin pre-treatment prevented the decrease in bond strength after storage for 6 months in artificial saliva(1, 7, 43).

V.2.3. Galardin:

Galardin is a synthetic MMP inhibitor which has a collagen-like backbone that facilitates its binding to the active site of MMPs and makes the antiproteolytic activity effective against MMPs. Pretreatment of dentin surface with Galardin resulted in high bond strength for a period of 12 months, even when used in low concentrations (7, 25, 44).

V.2.4. Carbodiimides:

Carbodiimides is a biocompatible synthetic crosslinking agent that can be easily rinsed from collagen without leaving any residual chemicals. They inhibit MMPs by inactivating the active sites and reducing their molecular mobility by creating a new peptide bond across adjacent peptides (MMPs crosslinking). Carbodiimides crosslink collagen without introducing additional linking groups as they activate the carboxylic acid groups of glutamic and aspartic acids that react with lysine or hydroxylysine to form amide crosslinking. Therefore, the resistance of cross-linked collagen matrices to degradation is improved. Carbodiimides' MMP inhibitory effect is much faster than its collagen cross-linking effect. This could be explained by the better accessibility of carboxyl and amino groups in MMPs than in collagen(7, 12, 43).

V.2.5. Natural Agents:

a) Grape seed extract (GSE)

b) Quercetin

c) Epigallocatechin-3-gallate (EGCG):

EGCG is a major green tea polyphenol which is considered as a natural inhibitor of MMPs through downregulation of MMPs expression and prevention of MMPs access to collagen chains. In addition, it stabilizes the collagen chain stable and increase the number of collagen crosslinks through the interaction of hydrogen molecules of galloyl groups. Treatment of the dentin surface with 0.1% EGCG aqueous solution before bonding agent application maintained the stability of the adhesive interface. However, EGCG at higher concentrations could interrupt the adhesive polymerization as it could be entrapped within the linear chains after curing interfering with the monomer conversion thereby affecting the bond strength(7, 12, 45).

d) Riboflavin (Vitamin B2):

Riboflavin is a crosslinking agent that produces free radicals when photo-activated in a spectrum ranging from ultraviolet (UV) to visible light (270 nm, 366 nm, and 445 nm). The free radicals create a strong covalent bond between the collagen fibers. However, the use of UV in the clinic is a concern as its safety is questionable. Moreover, additional light-curing steps are time consuming (7, 12, 29).

e) Sodium ascorbate (SA):

Sodium ascorbate is a bioavailable form of vitamin C. It is an antioxidant agent and inhibitor of MMPs. It stabilizes collagen and promotes collagen biosynthesis, but it lacks the cross-linking ability. Application of SA to dentin following bleaching reverse the compromised bonding that results from bleaching and improves the bond strength restoration (21, 43, 46).

V.2.6. Laser Treatment Prior to Bonding:

Laser irradiation of enamel/dentine may contribute to the success of dental bonding. Laser application to acid-etched dentin cause melting and occlusion of dentinal tubules and further reduce dentin permeability prior to the application of adhesives(47). Laser irradiation after the application of bonding agent and before curing can cause fusion of adhesive and dentin. In addition, the increase in the temperature due to laser irradiation can result in enhanced penetration of adhesive, improved flow of adhesive on the surface and better evaporation of solvent(48).

V.2.7. Plasma Treatment Prior to Bonding:

Dentin treatment with non-thermal atmospheric plasma (NTAP) After acid etching improves bond strength and stability because carboxyl and carbonyl groups are grafted by the plasma application onto the dentinal substrate, which will enhance the chemical and mechanical interaction of the resin monomers through hydrogen bonding interaction between collagen fibrils and adhesive resins(9). NTAP can increase interfacial bond strength by increasing the surface contact area with the collagen fibers allowing a higher interaction with the adhesive and penetration into the substrate(49, 50).

V.3. **Modification of the Bonding Protocol.**

V.3.1. Ethanol Wet Bonding:

Wet bonding technique is technically sensitive because excessive wetting or drying may adversely affect the bonding. The presence of water in the wet-bonding techniques may cause phase separation. Moreover, the collagen fibril network becomes suspended in water and complete penetration of resin will be hindered. Therefore, the ethanol-wet bonding concept was developed in etch-and-rinse (E&R) adhesive system to replace water with ethanol before the application of the adhesive(7, 51).

The miscibility of adhesive resin monomers in the ethanol-saturated dentin matrices is better than those in the water-saturated dentin matrices which allows intimate encapsulations of collagen fibrils with adhesive resin monomers(51). Ethanol can inhibit MMPs by forming covalent bond between the MMP’s catalytic zinc and the oxygen atom of the alcohol’s hydroxyl group and denaturation of enzymes by removing water from the enzyme structure causing their denaturation(1, 7).

Disadvantages:

- Premature volatilization during clinical practice.

- Pretreatment with a series of increasing ethanol concentrations is time consuming and impractical for clinical operation.

V.3.2. DMSO Wet Bonding:

Dimethyl sulfoxide (DMSO) is an organic liquid that possesses stronger permeability and lower volatility than ethanol. The application of DMSO after acid-etching promotes formation of longer resin tags and increased infiltration depth into dentin improving the stability of the hybrid layer. This could be explained by the ability of DMSO to dissociate collagen fibrils into a sparser network, therefore; spaces occupied by resin monomer are increased. Moreover, hydrophilic, and hydrophobic monomers are dissolved in DMSO due to its amphiphilic nature, thereby reducing phase separation, and enhancing adhesive infiltration. DMSO blocks binding sites of MMPs with their substrate (dentin collagen) to hinder the interaction between them(10).

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Preparation of Bioactive Composite and Fibers for Dental Applications

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Abstract: The ultimate goal of restoring tooth structure and bone regeneration depends on using durable and biocompatible material. Recently, bioactive materials have been widely used in hard tissue repair and regeneration and recently gained interest in dental sciences. The term bioactive materials generally refers to biomaterials which have the capability to induce and conduct the response to the biological system upon interacting.

Keywords: *Bioactive; resin composite; fiber; reminerlization; fillers.*

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I. Introduction:

The ultimate goal of restoring tooth structure and bone regeneration depends on using durable and biocompatible material. Recently, bioactive materials have been widely used in hard tissue repair and regeneration and recently gained interest in dental sciences. The term bioactive materials generally refers to biomaterials which have the capability to induce and conduct the response to the biological system upon interacting (1).

There are two classes of bioactive materials; class B bioactive materials bond to hard tissue (bone) and stimulate bone growth along the surface of the bioactive material (osteo-conduction). Examples of class B bioactive materials are synthetic HA and tricalcium phosphate ceramics. Class A bioactive materials not only bond to bone and are osteoconductive but they are also osteo-inductive, that is, they stimulate the growth of new bone on the material away from the bone/implant interface by stimulating the differentiation of undifferentiated mesenchymal cells. Examples of class A bioactive materials are bioactive glasses (2). As a result of their valuable properties, bioactive materials have been introduced into various dental applications and there is extensive ongoing research to optimize and tailor their properties according to each specific use.

Applications of bioactive composites in dentistry:

Bioactive scaffold materials:

Synthetic bioactive and bioresorbable composite materials are becoming increasingly important as scaffolds for tissue engineering. Certain bioactive ceramics such as tricalcium phosphate and hydroxyapatite as well as bioactive glasses, react with physiologic fluids to form tenacious bonds with hard (and in some cases soft) tissue. However, these bioactive materials are relatively stiff, brittle, and difficult to form into complex shapes. Conversely, synthetic bioresorbable polymers are easily fabricated into complex structures, yet they are too weak to meet the demands of surgery and the in vivo physiologic environment. Composites of tailored physical, biologic, and mechanical properties as well as predictable degradation behavior can be produced combining bioresorbable polymers and bioactive inorganic phases (3).

Bioactive resin composite:

The incorporation of bioactive materials into resin composites is advantageous in many ways (4):

a) Remineralizing effect:

- Bioactive restorative materials can release calcium and phosphate ions to remineralize dental hard tissues (4).

b) Marginal gap sealing:

- The dissolution of bioactive materials provide nucleation sites for apatite formation, favoring its precipitation almost immediately after the start of dissolution (4).
- This feature can be used to form HA layer on the restoration surface which is thick enough to hinder bacterial penetration into the marginal gap (4).

c) Improving the longevity of the hybrid layer:

- By inhibiting the matrix metalloproteinase activity via the increase in the local pH and depositing the HA precipitate within the demineralized collagen network. This will result in decreasing the nanoleakage and protecting the hybrid layer from hydrolytic degradation (4).

d) Treatment of post operative sensitivity:

- Precipitation of HA can occlude Dentinal tubules and reduce dentinal fluid flow thus reducing dentin postoperative sensitivity after placing composite fillings (4).

Bioactive materials used in dental applications:

Calcium Orthophosphate materials:

Hydroxyapatite (HA):

HA is a highly crystalline form of calcium phosphates. It is classified as bioactive due to its osteoconductive ability and formation of hard tissues and remineralization of enamel and dentin. Since it is highly crystalline, it is highly stable and has low dissolution rates and high acid resistance (5).

Amorphous Calcium phosphates (ACP):

ACP [$Ca_9(PO4)_6$] is one of the calcium orthophosphate compounds. it has a much higher degradability than any other calcium phosphates. The ACP is readily converted into crystalline HA, which is desirable during hard tissue maturation. The crystalline HA is more acid-resistant and has better mechanical properties. ACP had shown better cell adhesion with hard and soft tissues, biocompatibility, bioactivity, and osteoconduction properties. Based on its bioactive properties, the ACP is applied as a transient phase that could be readily utilized as a precursor in apatite growth (6).

Tri Calcium Phosphates (TCP):

TCP exists in three polymorphic forms, the ultra-high temperature α'-TCP, high-temperature α- TCP, and the low-temperature ◎-TCP. The α-TCP only exists at very high temperatures (around 1500°C) and is not generally used. The ◎-TCP is unstable at high temperatures and changes into α-TCP (1125–1200°C) and reverts to the original single ◎ phase if it cools properly. The α-TCP is safe at high temperatures and single-phase powder can be achieved successfully. TCPs are bioactive, biocompatible, bioresorbable and osteo-inductive materials. TCPs had been used in dental surgery, however, due to their poor mechanical properties, low cohesion, brittleness, and no microporosity, their clinical applications were limited to non-load bearing areas (6).

As pure HA had a low dissolution rate and pure TCP had a very high dissolution rate. Therefore, biphasic apatites (HA/TCP) could affect the dissolution tendency and bone-bonding. The reported dissolution order of calcium phosphate members was: α -TCP > ◎-TCP > HA (1).

Bioactive glass:

1969, Larry Hench and co-workers laid the first stone of bioactive ceramics by bringing chemically bone-alike Hench's 45S5 Bioglass® into the market. This first Bioglass was based on 45% SiO_2, 24.5% Na_2O, 24.5% CaO, and 6% P_2O_5. The first generation of bioglass was biologically inert, while the second generation of bioglass concept changed from bioinert to bioactivity. The third generation led to the development of resorbable bioactive bioglass. Recently, bioactive glass particles, micro-, and nano-sizes had been introduced, combined with polymers, to form a composite for diverse applications (7).

Calcium Silicates:

Calcium silicate based bio-ceramics are commonly used in various load bearing biomedical applications. They also possess chemical similarities to bone with osteoconduction properties (1).

There were two crystalline modifications of stoichiometric calcium silicate ($CaSiO_3$), i.e., low-temperature (◎-$CaSiO_3$) and (α-$CaSiO_3$). Dicalcium silicate (Ca_2SiO_4) had four different modifications: γ phase, which was stable at room temperature; α' and α- phases, which were stable at high temperatures; and ◎ -phase, which was not thermodynamically stable. Tricalcium silicate (Ca_3SiO_5) was a phase stable between 1250°C and 1900°C (1).

With all the advantages of biocompatibility, limitations of CSs are high brittleness, and insufficient bioactivity compared to calcium phosphates-based materials. To overcome these limitations, other components such as magnesium (Mg), zinc (Zn), and zirconium (Zr) could be added to form ternary compounds (1).

Commercial calcium silicates based dental biomaterials include MTA and Biodentine.

Preparation methods of bioactive fillers:

Preparation of calcium phosphates (CP) materials.

Dry synthesis:

Stoichiometric and well-crystallized CP can be prepared by solid-state reactions of calcium orthophosphates with calcium oxide or related salts such as Ca $(OH)_2$ (e.g. $CaHPO_4 + CaO$). at a stoichiometric Ca/P mixing ratio for each CP material formation at high temperatures (typically above 700 $^{\circ}$C) (8).

Mechano-chemical processing (or mechanical alloying) through direct ball milling for the above mixtures (that is, calcium orthophosphates and calcium oxide) is another way to fabricate CP nanoparticles in a dry state (8)

These CPs materials are generally obtained in the bulk form, and therefore grinding or milling is necessary to obtain micro or nanoparticles (8).

Wet synthesis:

Calcium phosphates can be fabricated under milder conditions in solutions via several ways, such as wet chemical precipitation, sol–gel method, emulsion method. The morphology (shape and size) of HAp nanoparticles can be widely varied by adjusting the reaction conditions. However, highly crystallized HAp can be obtained only at elevated temperatures, by hydrothermal treatment in a wet condition or calcination in a dry state (8).

Wet chemical precipitation:

Wet chemical precipitation has been widely used because of its simplicity. Mixing of two aqueous solutions of calcium and orthophosphate (at pH > 7) results in the formation of highly supersaturated solutions for CP. The type of the formed CP compound is controlled by the reaction and precipitation conditions which induces a fast precipitation of nanoparticles according to the following reaction (8):

$$10\ Ca\ (OH)_2 + 6H_3PO_4 \rightarrow Ca10(PO_4)_6(OH)_2 + 18H_2O$$

The morphology (shape and size) of the nanoparticles depends on precipitation conditions such as concentration of reactants, ionic strength, pH and temperature. The mixing condition for two (calcium and orthophosphate) aqueous solutions is also important. A microreactor is a device that has microchannels on the order of micrometers and that enables chemical reactions to be performed in a space several orders of magnitude smaller than conventional batch reactors (8).

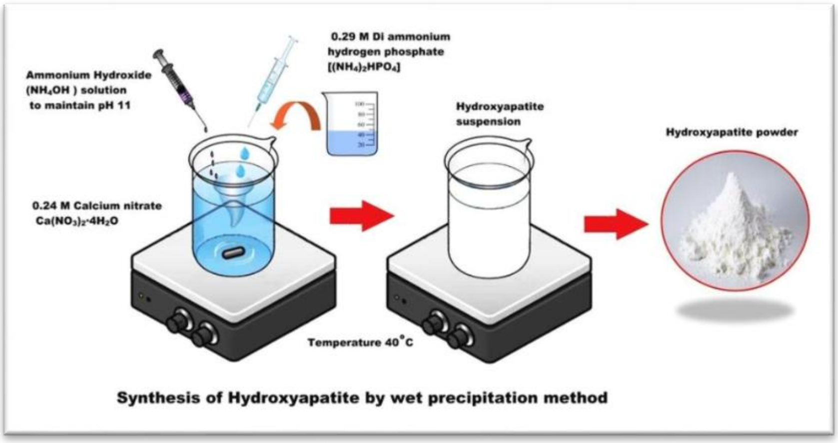

Figure (1) is a schematic representation for wet synthesis of HA.

Hydrothermal process:

Hydrothermal processes include several techniques for crystallizing materials in aqueous media at high temperatures (typically 100–250 ◦C, and hence under high vapor pressure when the temperature is above 100 ◦C). Microwave irradiation can be used instead of conventional heating in pressure-resistant vessels, shown in figure (2) (8).

The hydrothermal process usually produces particles with larger size (up to millimeter range), higher degree of crystallinity and a Ca/P ratio close to the stoichiometric value compared with those obtained by the precipitation processes at lower temperature. However, the size distribution of the produced particles is usually broad (8).

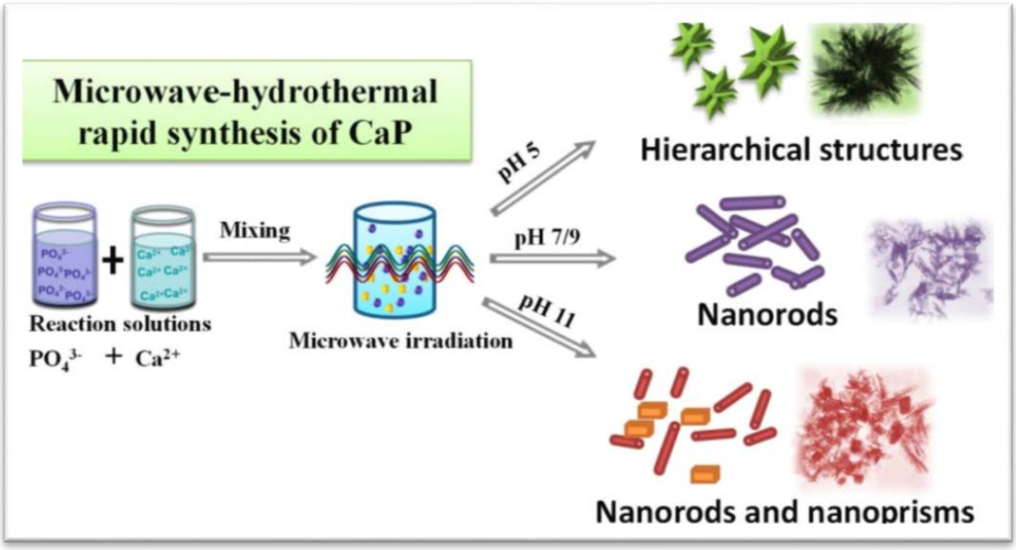

Figure (2) Schematic representation for hydrothermal process

Homogenous precipitation:

The homogeneous precipitation starts with a homogeneous, acidic calcium phosphate solution, and nucleation/growth of CP compound is induced by thermal decomposition (hydrolysis) of:

Urea: $((NH_2)2CO + H_2O \rightarrow CO_2 + {}_2NH_3)$

or acetamide $(CH_3CONH_2 + H_2O \rightarrow CH_3COOH + NH_3)$.

The resultant NH_3 raises the solution pH (and degree of supersaturation for CP), leading to the formation (precipitation) of CP particles. Slow hydrolysis of the molecules at a high temperature leads to the formation of large and well-crystallized particles (8).

Sol-Gel method:

The sol–gel method has been used for fabricating fine ceramics in wet conditions for a long time. The precursor combinations (calcium alkoxides and phosphorus alkoxides) undergoes hydrolysis and polycondensation reactions to form a solid phase. In this process, the sol (i.e., solution) dissolving precursors evolves gradually towards the formation of a gel-like network of the solid phase, as shown in figure (3). The solid phase can also be deposited on a substrate to form a film. By controlling the reaction parameters, the solid phase can also be obtained as nanoparticles dispersed in media (8).

In the sol-gel method for CP preparation, the as-obtained solid phase is generally amorphous Ca–P intermediates and hence a thermal treatment (typically at 400–500 ◦C, which is lower than the sintering temperature of CP powder, ~800–1000 ◦C) is necessary to obtain well-crystallized CP. The products are obtained in a sintered polycrystalline form and hence grinding or milling is usually necessary to obtain micro or nanoparticles (8).

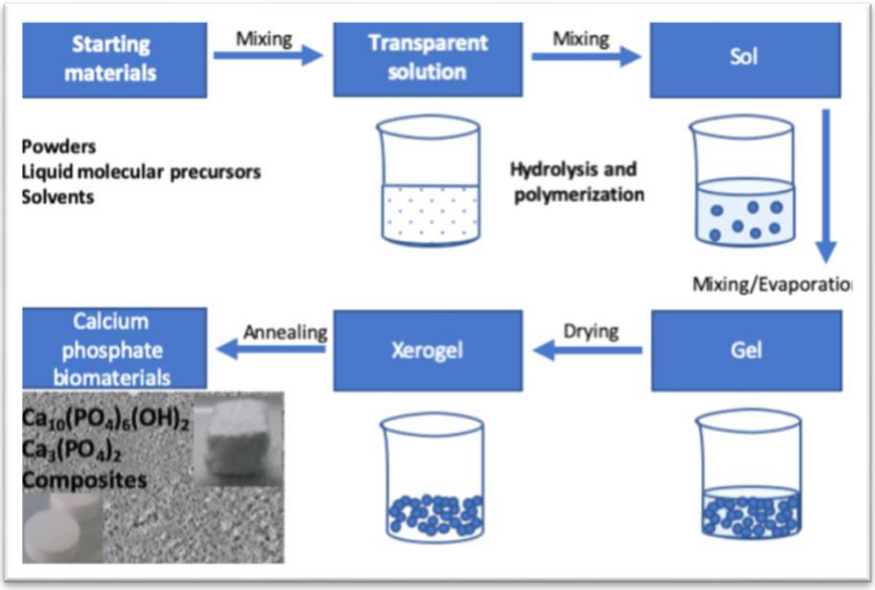

Figure (3) Schematic representation for Sol-Gel process

Preparation of calcium phosphates fibers:

CaP fibers can be produced through several routes including spinning, extrusion, sol–gel and pyrolysis, and electrospinning, shown in figure (4). Electrospinning is frequently used because it is a simple technology that allows the production of nano- and micro-fibers by applying a high voltage to a polymer solution. It has been used to produce different types of ceramic fibers using chemical precursors mixed to the polymer solution and by performing a thermal treatment on the resulting fibers (9).

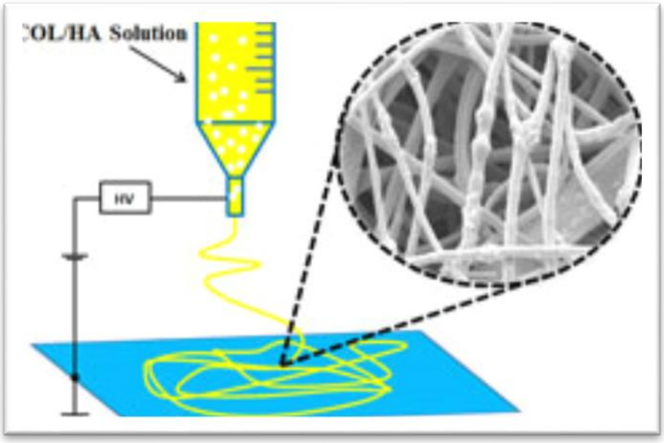

Figure (4) Schematic representation for preparation of HA fibers

Preparation of bioactive glass:

The most common techniques to produce bioactive glasses are traditional melt quenching routes and the sol–gel technique.

Melt-Quenching technique:

In melt quenching technique, glass is prepared by taking required stoichiometric amounts of different constituent oxides or carbonates of high purity (99.9%). These constituents are first mixed together by ball-mill in an acetone medium. The powder obtained after ball milling is melted at high temperatures in a high resistance furnace depending upon the composition chosen. The melt is then poured into molds to produce rods/cylinders or any other desired shape of interest. The melt can also be quenched in air using copper plates to obtain frits. The quenched glass is then annealed at 500◦C to remove the internal stresses from the glasses (7). Figure (5) is a schematic representation of melt-quenching processing.

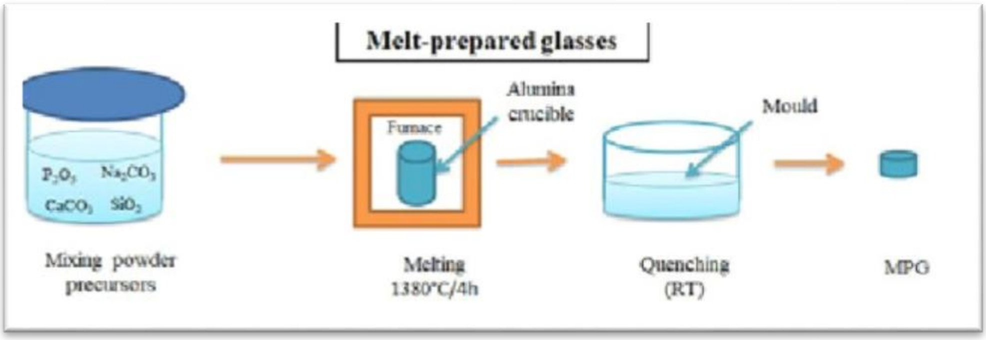

Figure (5) Schematic representation for melt-quenching method

Sol-Gel technique:

A sol–gel process has been used to prepare porous scaffolds of bioactive glasses. The process involves hydrolysis, polymerization, gelation, drying, and a dehydration process. Sol (or solution) evolves towards the formation of a gel-like diphasic system (with the aid of surfactant) containing both a liquid phase and solid phase. Its morphology can range from discrete particles to continuous polymer networks. Nano pores present in the glass prepared from a sol–gel method yield a high surface area. Consequently, this leads to degradation and a faster conversion of these glasses to HA than scaffolds of melt-derived glass with the same composition (7).

In addition, the sol-gel method provides high purity glasses with more homogeneity. Moreover, a lower processing temperature is required. However, these sol–gel-derived scaffolds have low strength (2–3 MPa) and consequently they are suitable for substituting defects in low-load sites only (7).

Preparation of Bioactive glass fibers:

Bioactive glass is first prepared by one of the previously mentioned methods (melt-quenching or sol-gel) then fibers are prepared by drawing or electrospinning as shown in figure (6) (10).

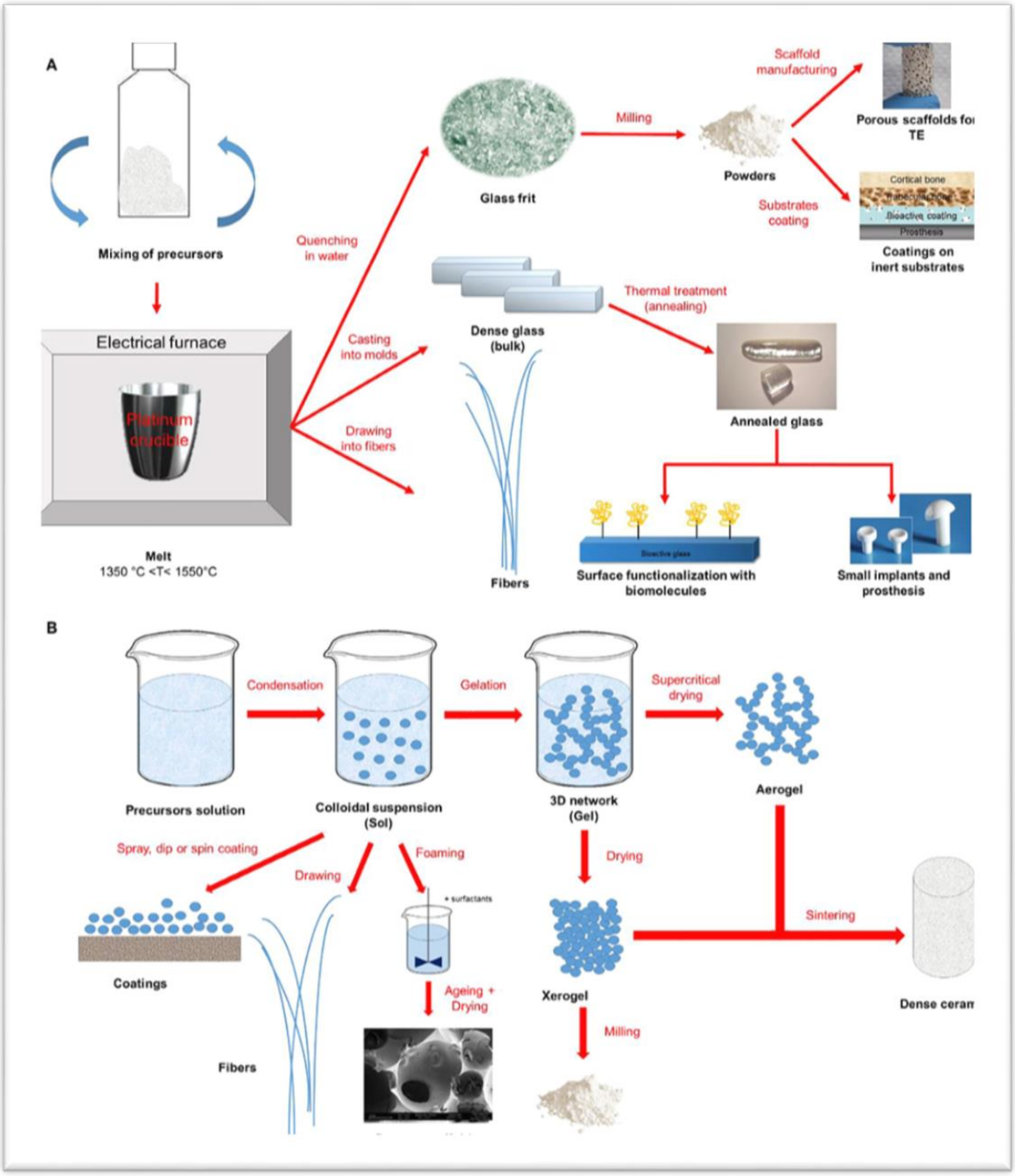

Figure (6) Preparation of bioactive glass fillers and fibers

Surface modifications of bioactive fillers:

The major issue during preparation of a composite material is to ensure proper bonding between the matrix and the fillers, and to ensure proper dispersion of the inorganic fillers within the matrix. Therefore, surface modifications for the bioactive fillers are done (11).

Chemical treatments:

The surface modification of nanoparticles by chemical treatments (such as the absorption of silane coupling agents) is a useful method to improve the dispersion stability of nanoparticles in various liquid media and to improve the compatibility between the particle and polymer surfaces, consequently the properties of composite materials (11). Figure (7) demonstrates silanization of HA fillers.

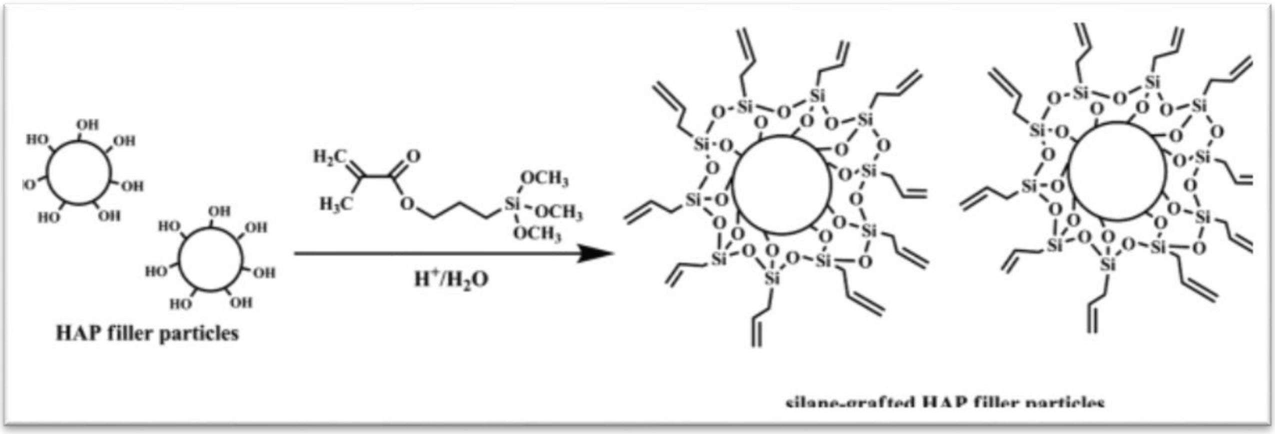

Figure (7) Silanization of HA fillers particles

Grafting of synthetic polymers:

Another approach to modify the surfaces of inorganic and organic materials is based on grafting synthetic polymers to the substrate surface, which enhances the chemical functionality and alters the surface topology of the native inorganic and organic materials. Such polymer-grafted inorganic nanoparticles are considered to be organic–inorganic nanocomposite particles (11).

Because monomers usually have a low molecular weight by their nature, they can penetrate the aggregated nanoparticles and react with the activated sites on the nanoparticle surface. The interstitial volume inside the nanoparticle aggregates becomes partially filled with grafted macromolecular chains, and the aggregated nanoparticles become further separated. In addition, the surfaces of the nanoparticles become hydrophobic, which is important for the miscibility of the filler and matrix. Figure (8) shows the dispersion behavior of bare and polymer-grafted nanoparticles in a polymer matrix (11).

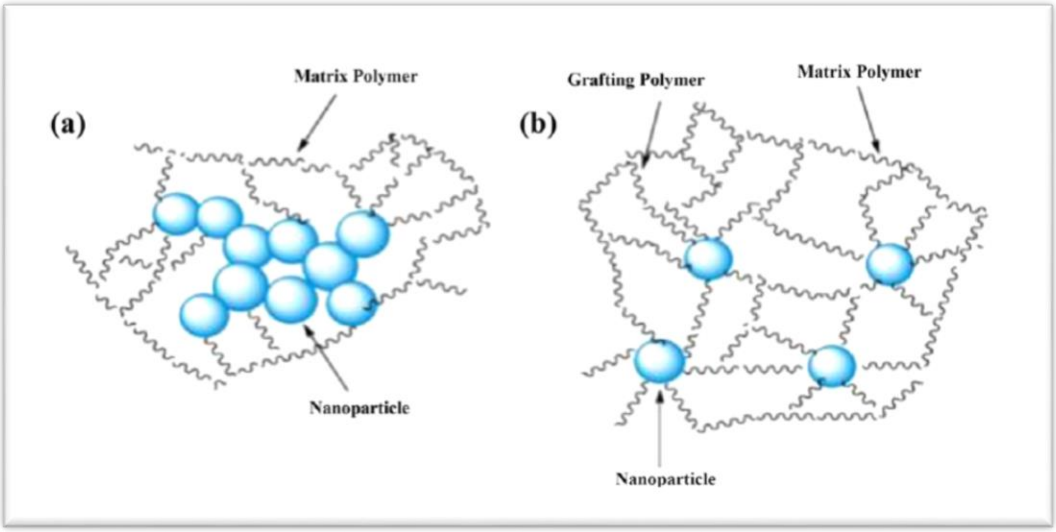

Figure (8) Schematics of: (a) agglomerated nanoparticles in the matrix polymer in the case without grafting polymer and (b) separation of particles due to the grafting polymer.

Adsorption of dispersants:

Other methods for surface modification of inorganic nanoparticles have been reported, including adsorption of polymeric dispersants and in situ surface modification. Surface modification by adsorption of polymeric dispersants is one of the simplest methods to improve the dispersion behavior of nanoparticles in aqueous systems. The hydrophilic nanoparticles can be dispersed in highly polar organic solvents by using anionic or cationic polymer dispersants. These dispersants generate steric repulsive forces among the polymer chains and increase the surface charge, which results in better dispersibility of the nanoparticles, shown in figure (9) (11).

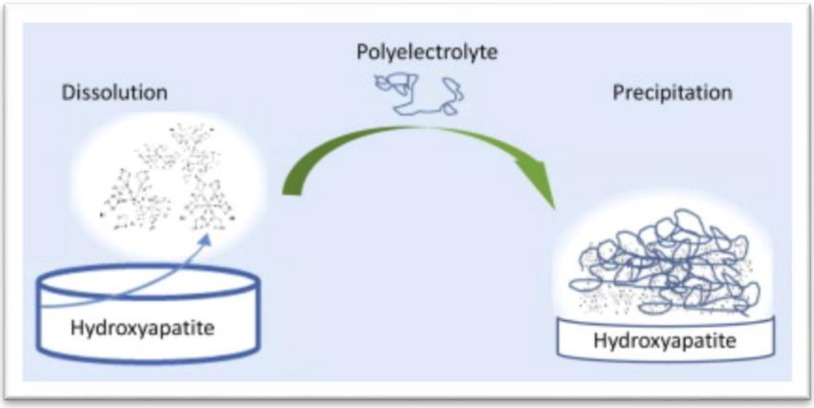

Figure (9) Adsorption of dispersants on HA fillers particles

Etching of fillers surfaces

Surface pores can be easily obtained through an etching process. The surface of glass-ceramic fillers can be chemically etched with hydrofluoric acid. Resin monomers will be forced into the porous fillers by high pressure or vacuum before polymerization, which will enable micromechanical interlocking in the cured composites. The idea of porous fillers is advantageous over using silane coupling agent due to the hydrolysis of silane coupling agents that can reduce the lifetime of dental composites (12).

Effect of surface modifications of bioactive fillers on properties:

Influence on dispersion of fillers in organic solvents/matrices:

The dispersion stability of ultrafine inorganic particles in organic solvents or polymer matrices is known to be remarkably improved after being silanized or when polymers have been grafted on their surfaces. The chemical surface modification of the fillers prevents aggregation of the particles and increase the affinity of the surface for the solvent or polymer matrix and consequently enhancing the cellular adsorption on its surface, as illustrated in figure (10) (13).

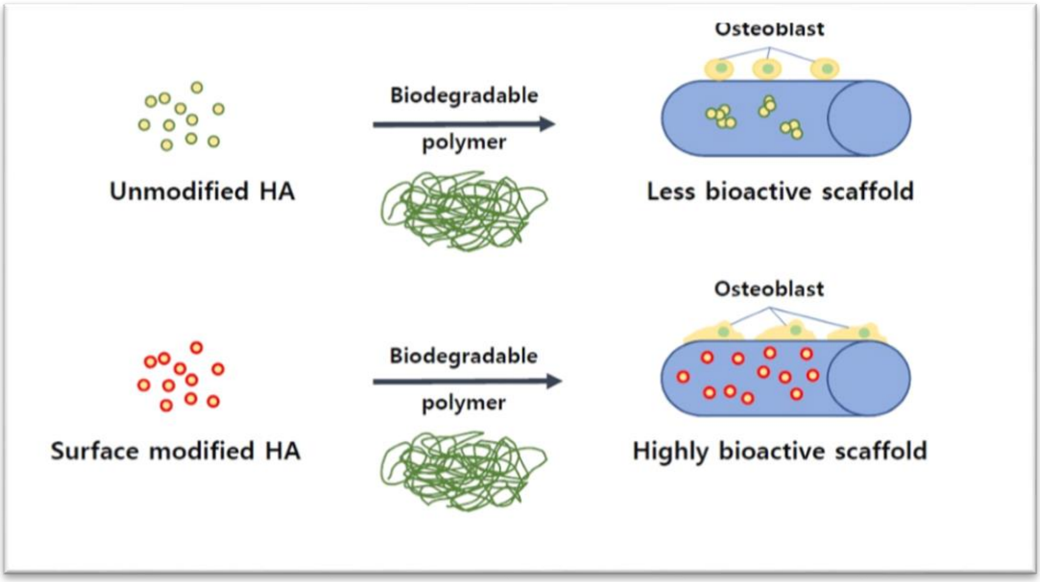

Figure (10) Schematic showing the effect of surface modification on Cellular adsorption of on HA fillers particles

Influence on mechanical properties:

The surface modified particles produced an increase in elastic modulus and impact strength of the resin matrix. The reverse effect was found for yield stress and tensile strength of the composites. These effects are explained by proper interfacial bonding between the fillers and the matrix which lead to proper stress transfer from the matrix to the fillers (13).

However, the interfacial bond in case of using fiber fillers should not be very strong that it prevents fiber pull-out mechanisms. Fiber pull out is considered as one of the main toughening mechanisms in fiber-reinforced composites (13).

Influence on degree of conversion:

The main limiting factor for reaching high degrees of conversion is an immense increase in viscosity in the composite during polymerization. High viscosity impairs mobility of free radicals and monomers, causing the polymerization reaction to stop well before all available reactants are consumed (4).

Studies have shown that silanized bioactive fillers in resin composite showed lower degree of conversion compared to unsilanized fillers. Also, for polymer grafting; it was shown than increasing the grafting ratio significantly decreases the degree of conversion due to increased viscosity (14).

Influence on ion release and bioactivity:

The bioactivity is essentially a dissolution/reprecipitation process. As the initial ACP particles are gradually dissolved, calcium and phosphate ions are solubilized and subsequently precipitated in the form of HA (4).

Since solubility is decreased by silanization, the bioactivity is substantially decreased. Some studies reported that bioactivity is not affected by graft polymerization unlike silanization (14). Also, bioactivity is better for fillers with porous structure that provide high surface area (for example; those fabricated by sol-gel method) with micromechanical interlocking interaction at the filler-matrix interface that can also increase mechanical properties (15).

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