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

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

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

I. Introduction

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

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

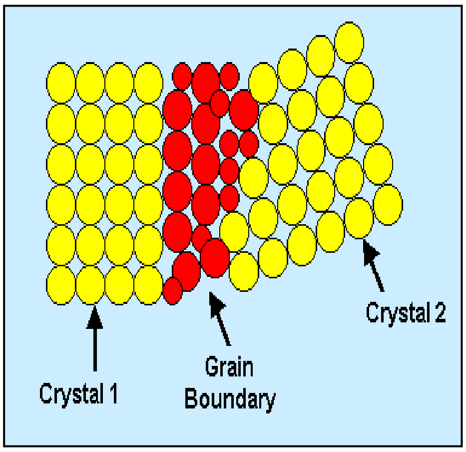
Microstructure of metals:

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

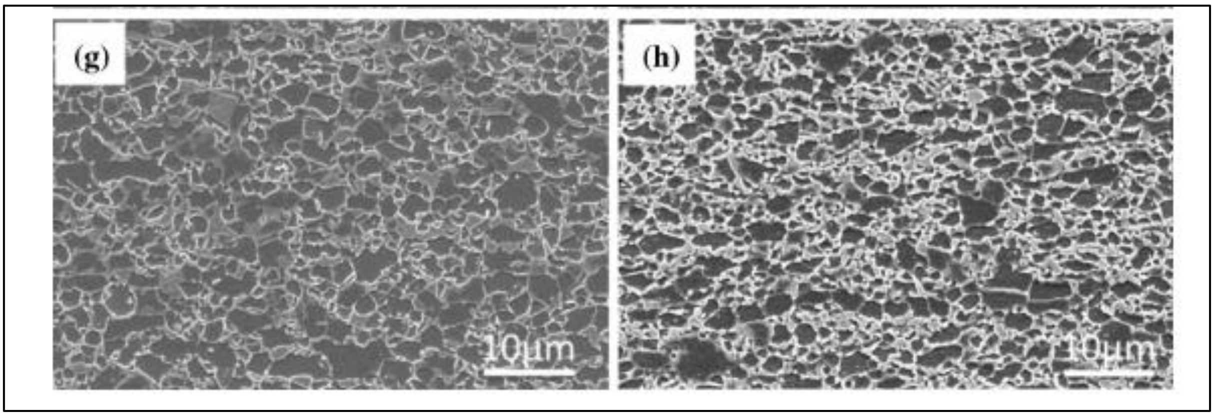
Different factors in microstructure can influence the physical properties of the final alloy as; grain size, grain boundaries and its distribution, dispersed particles and dislocations. All these can affect strength, toughness, ductility, hardness, corrosion resistance, or wear resistance of the alloy.

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

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

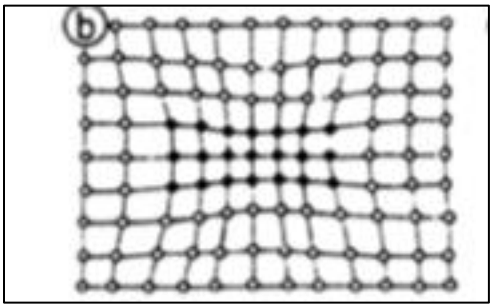


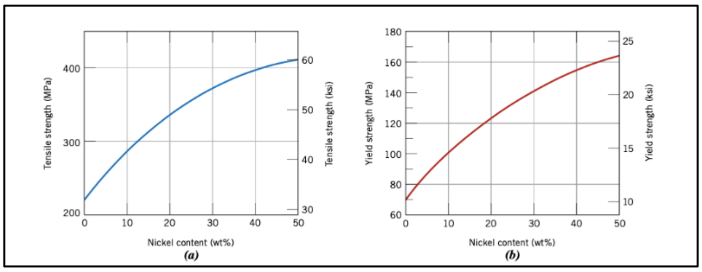
Scanning electron microstructure of (g) vanadium free steel and (h) vanadium containing steel (0.06 wt%)



(2)

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





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

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

II. Classification of alloys:

II.1. According to number of metallic elements

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

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

II.2. According to miscibility

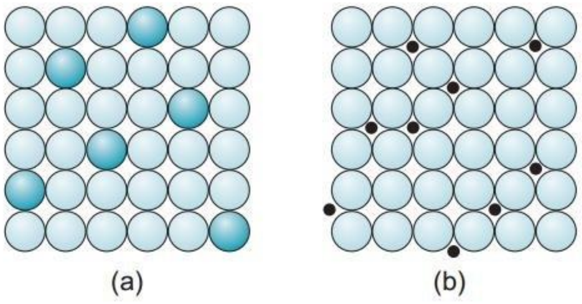
Alloys are classified according to the number of distinct solid phases. A phase is defined as a structurally homogeneous part of the system that is separated from other parts by a definite physical boundary. Each phase will have its own distinct structure and will affect the final properties of the alloy.

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

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

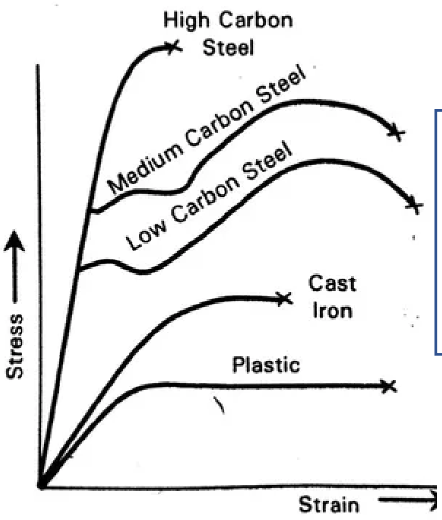
Several features of the solute and solvent atoms determine the degree of dissolution and which type of solid solution will occur. **These are expressed as four *Hume–Rothery rules* (3):**

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



a) Substitutional solid solution

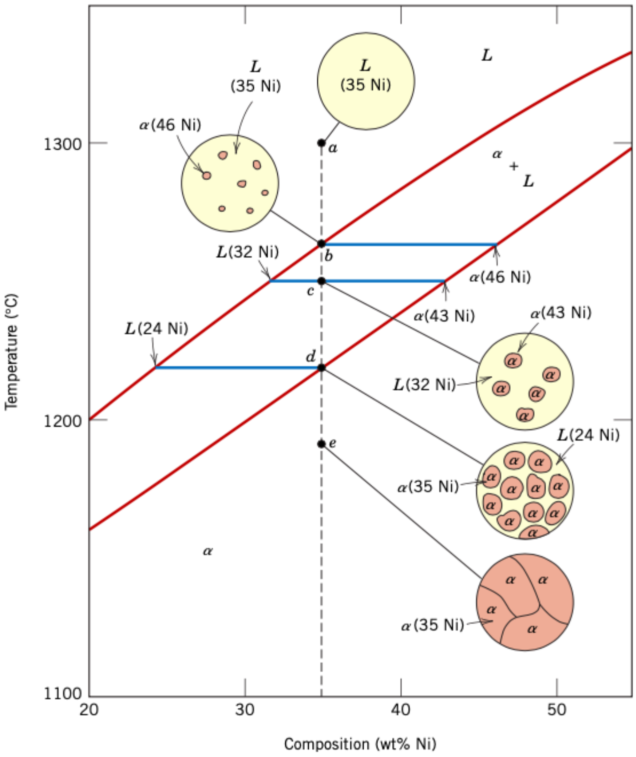
b) Interstitial solid solution



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

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

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

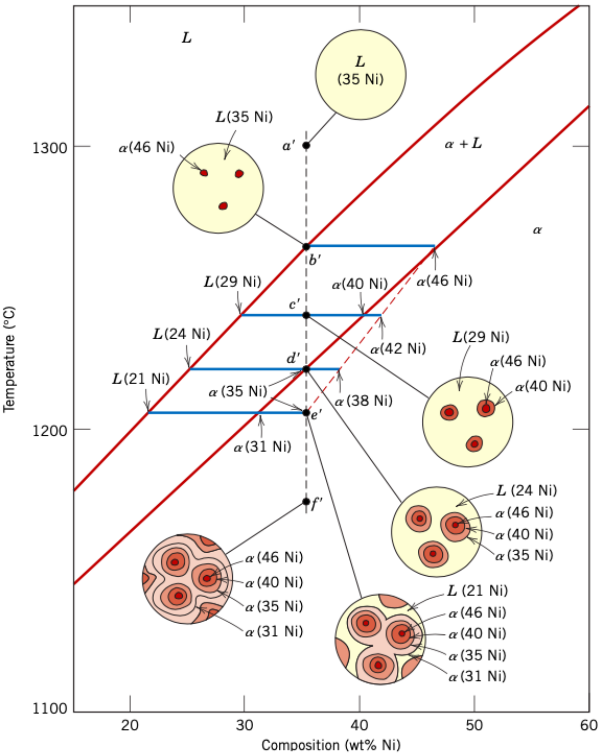


The development of microstructure during the equilibrium solidification of a 35 wt% Ni–65 wt% Cu al-

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

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

- In rapid cooling, new layers are formed on top of the pre-existing grains. No diffusion occurs between different layers. As diffusion in the solid-state is very slow. Thus, having different composition at this temperature when compared with the equilibrium cooling.
- As a result, the formation of layered grains and the invalidity of the tie-line method to determine the composition of the solid phase.
- Solidus line is shifted to the right when compared to equilibrium solidification due to higher Ni contents depositions at first.While, the outer part of the grains will be richer in the low-melting component forming cored structure and solidification will be completed at lower temperature.



- Cored structure affects the mechanical properties negatively by decreasing tanish and corrosion resistance and increasing the brittleness that leads to premature failure. This can be eliminated by homogenization.
- **Homogenization heat treatment** is done at temperature below the solidus point for the particular alloy composition. During this process, atomic diffusion occurs, producing compositionally homogeneous grains.

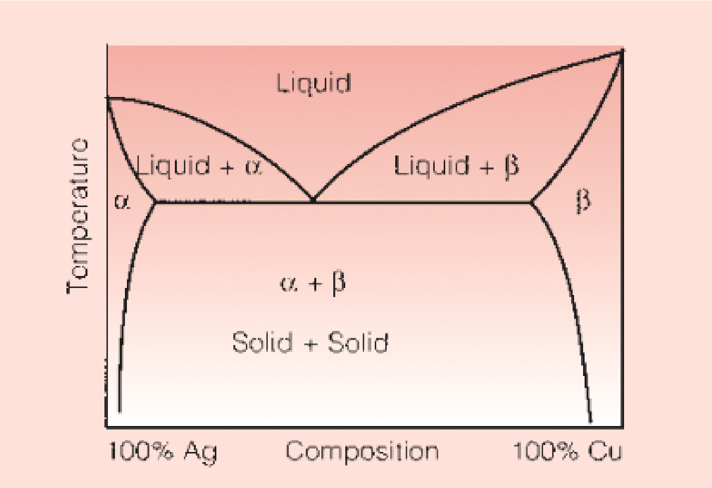
Eutectic alloy (3,5)

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

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

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

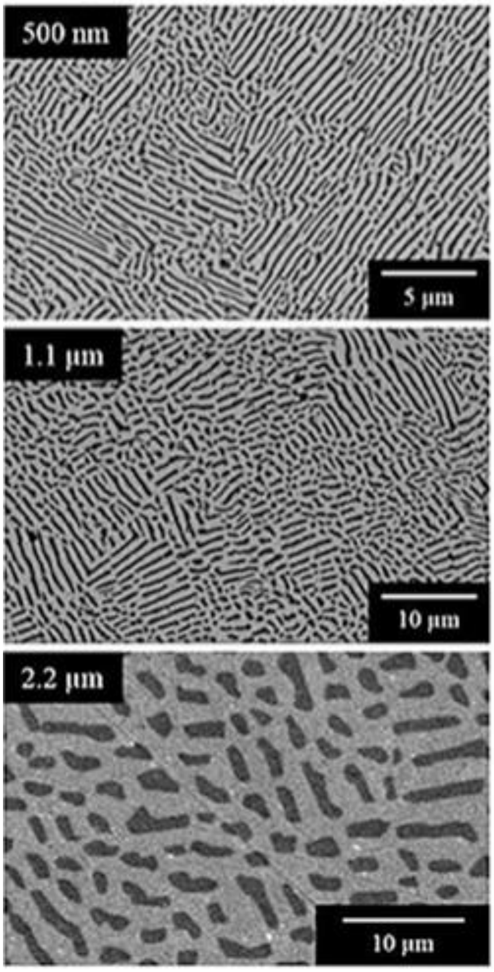
An important feature of the phase diagram of the Ag–Cu system is the depression of the temperature of the liquidus at a composition of **72Ag : 28Cu** wt%. At a temperature of 780°C, this composition called the **eutectic composition**, and the temperature at the intersection of the three phases is the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



Equilibrium phase diagram for the Ag–Cu system

Development of microstructure in eutectic alloys at equilibrium cooling.

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



Lamellar structure of the eutectic alloy

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

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

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

Intermetallic compounds

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

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

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

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

Stainless steel(5)

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

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

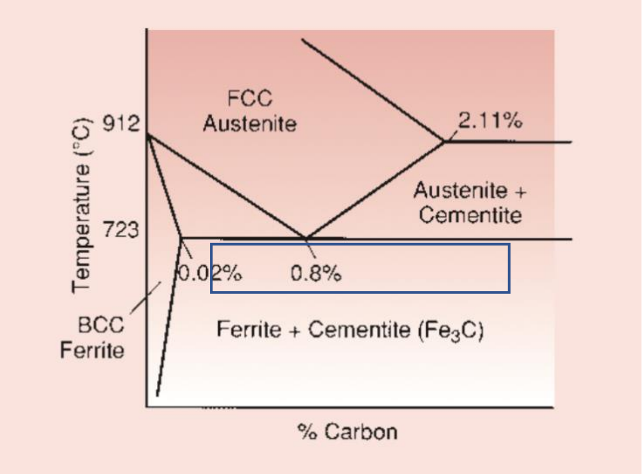
Carbon steels

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

Hypereutectoid and hypoeutectoid steels

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

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



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

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

Slow cooling

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

Rapid cooling (Quenching)

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

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

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

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

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

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

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

Clinical significance:

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

Stainless steel

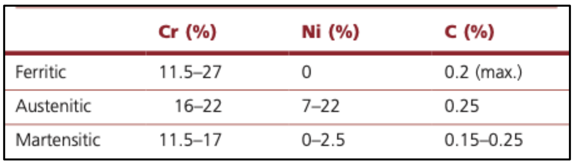
Although many other elements can be added to the basic carbon steels to improve the properties (e.g. molybdenum, silicon, cobalt, manganese), the two of greatest importance for dentistry are **chromium** and **nickel** for the production of stainless steel.

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

Austenitic stainless steel

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

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

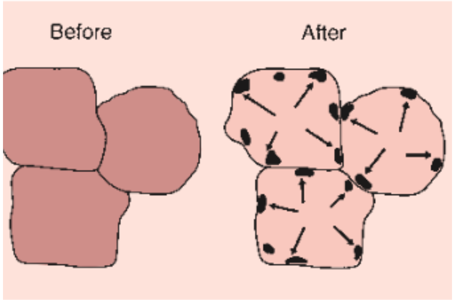


	Cr (%)	Ni (%)	C (%)
Ferritic	11.5–27	0	0.2 (max.)
Austenitic	16–22	7–22	0.25
Martensitic	11.5–17	0–2.5	0.15–0.25

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

Stabilized austenitic stainless steel

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



Weld decay due to overheating of the alloy

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

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

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

II.3. According to principal element

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

II.4. According to ADA Classification:

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

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

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

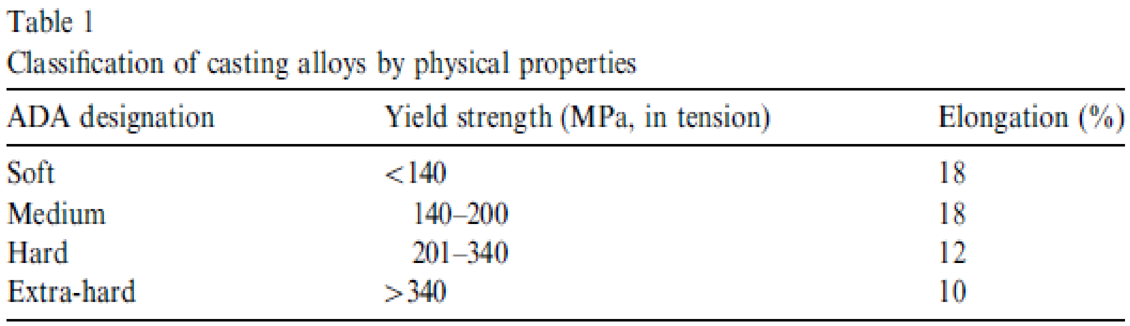


Table 1
Classification of casting alloys by physical properties

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

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

II.4.A. High-noble alloys

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

Gold-platinum (Au-Pt):

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

Composition

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

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

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

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

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

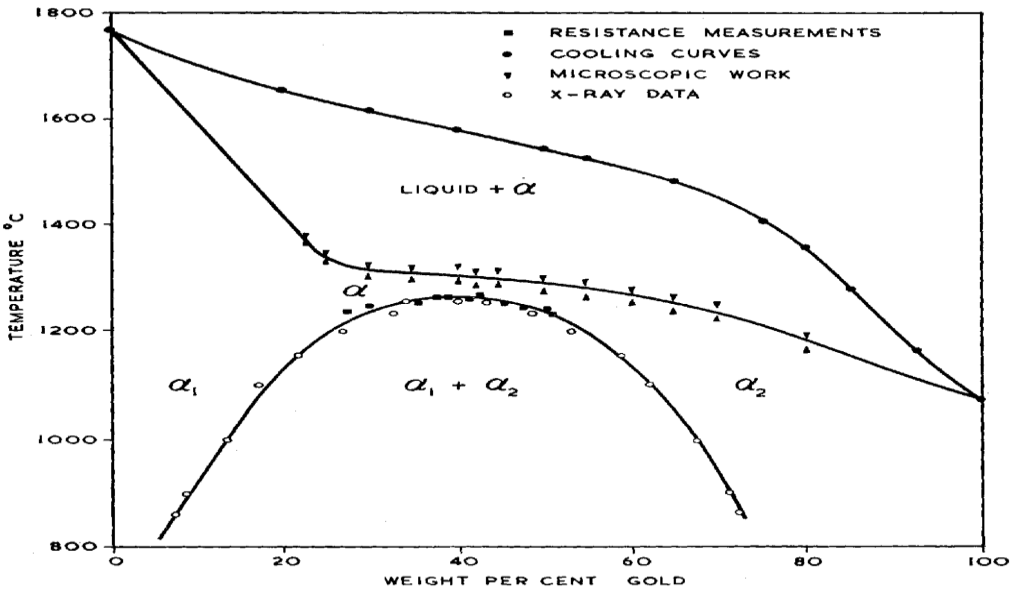


Figure 1: Phase diagram of the gold platinum system

Properties:

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

Microstructure:

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

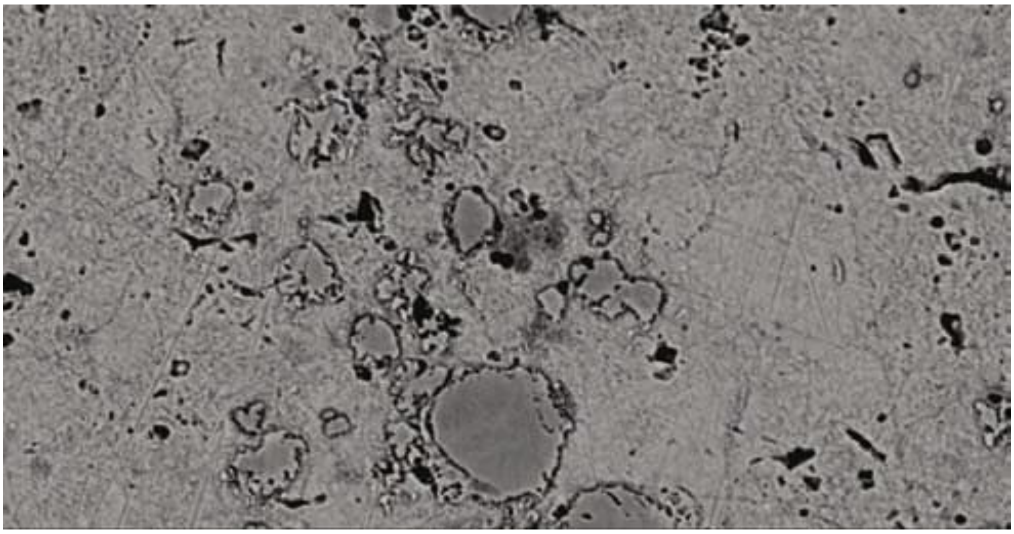


Figure 2: The SEM microstructure of Au-Pt alloy

Gold-palladium (Au-Pd)

Composition:

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

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

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

Properties:

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

Microstructure:

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

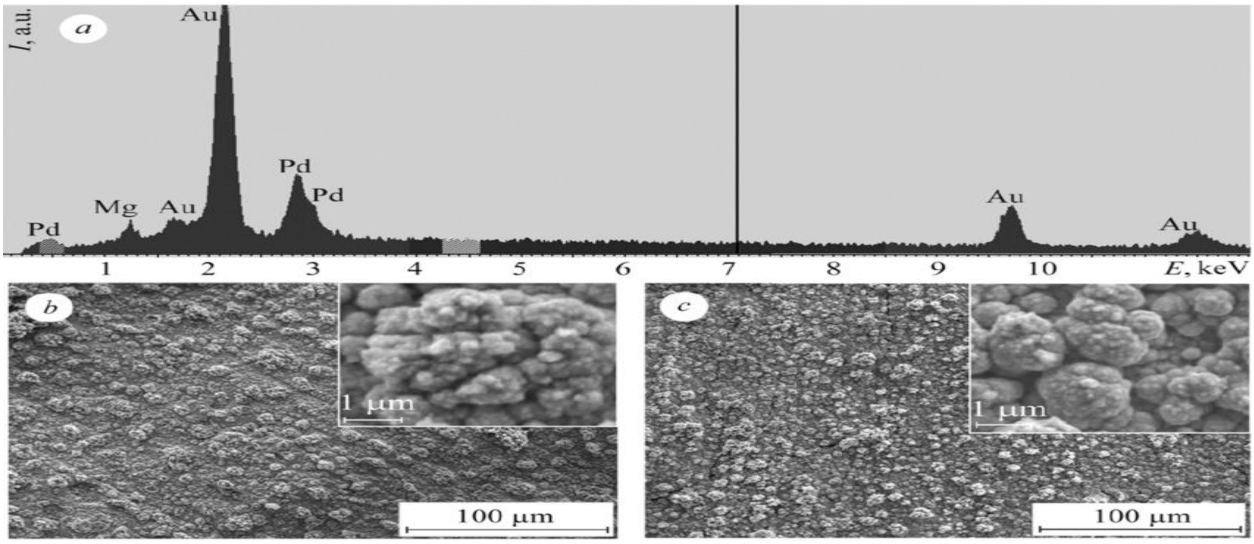


Figure 3: SEM of Au-Pd alloy

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

Composition and Properties:

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

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

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

Microstructure:

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

II.4.B. Noble alloys

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

Au-Cu-Ag

Composition:

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

Properties:

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

Pd-Cu-Ga

- **Composition and properties:**

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

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

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

Microstructure:

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

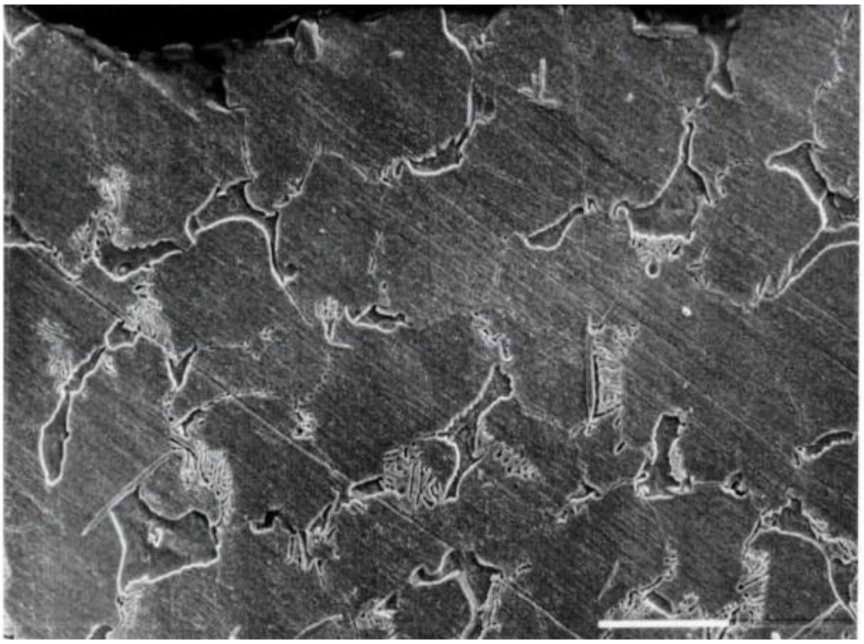


Figure 4: SEM of the microstructure of Pd-Cu-Ga alloys

Pd-Ag and Ag-Pd

Properties:

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

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

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

Microstructure:

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

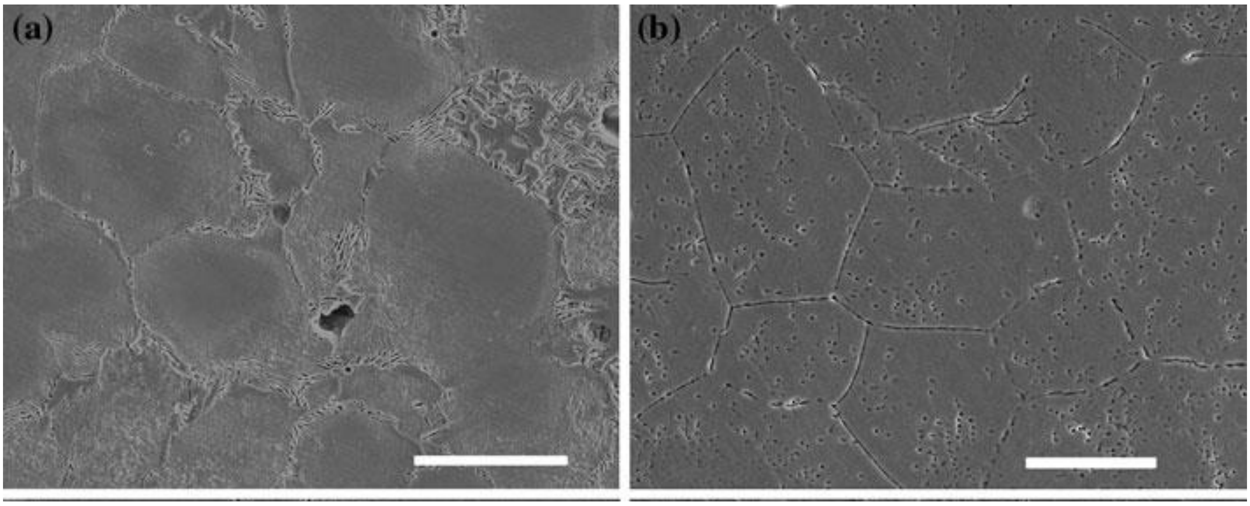


Figure 5: SEM images showing the microstructures of (a) as cast and (b) heat-treated Pd-Ag.

Effects of Alloy Elements on Properties of High Noble and Noble Metal Alloys

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

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

II.4.C. Predominantly base-metal alloys

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

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

Nickel-chromium alloys

Composition and properties:

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

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

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

Microstructure:

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

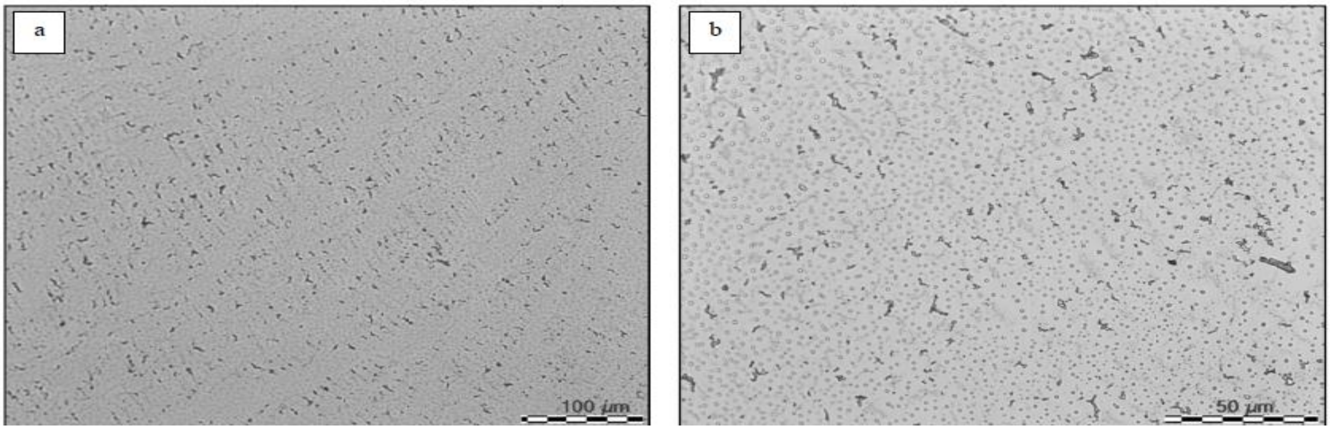


Figure 6: microstructure of Ni-Cr alloy

Co-Cr alloys

Composition:

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

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

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

Properties:

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

Microstructure:

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

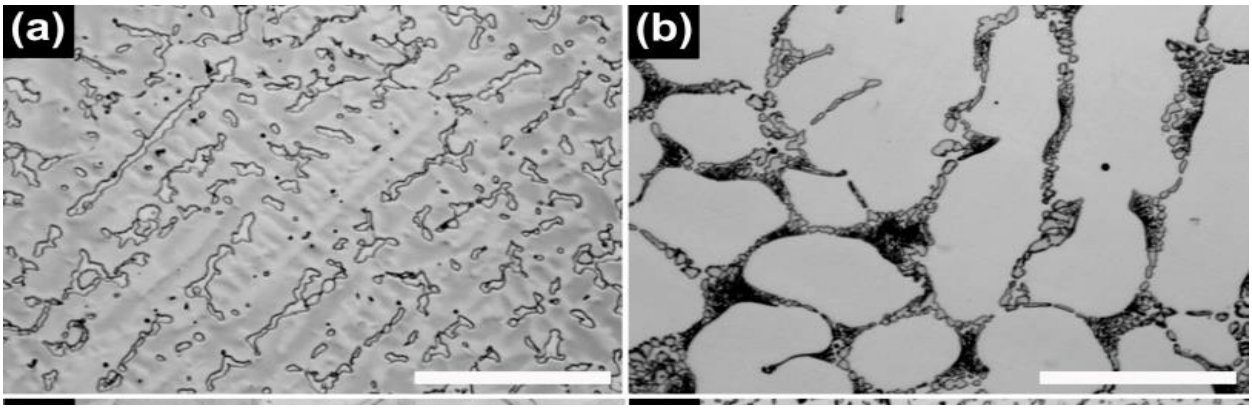


Figure 7: Optical microscopy images of the Co-Cr alloys tested. (**a**) CS; (**b**) ML

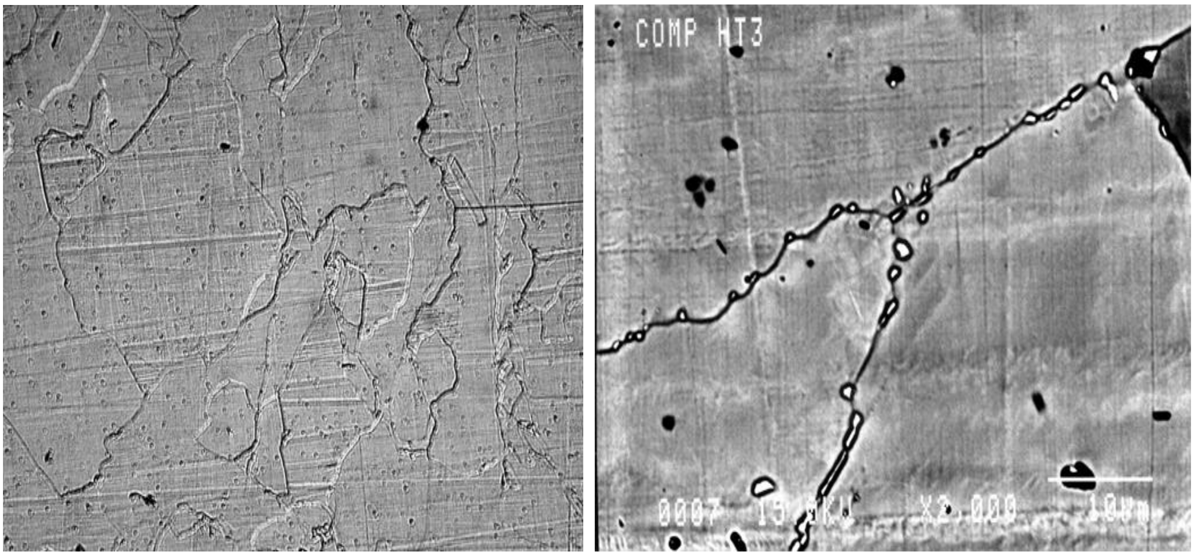


Figure 8: Optical micrograph and backscattered electron image showing sigma phase brittleness of cobalt-chromium alloy.

II.5. According to dental Application

A) Metallic restorations.

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

ii. All metal fixed prosthesis [19]

- **High noble and noble alloys**

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

- **Predominantly base metal alloys**

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

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

B) Metal ceramic restorations

i. Highly noble and noble metal ceramic alloys

ii. Base metal ceramic alloys

C) Removable partial dentures

i. Type IV gold alloys

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

D) Implants

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

E) Orthodontic brackets, wires & ligatures.

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

F) Instruments

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

G) Surgical plates and screws

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

Biodegradable alloys (28,29)

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

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

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

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

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

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

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

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

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

Alloy Microstructures

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

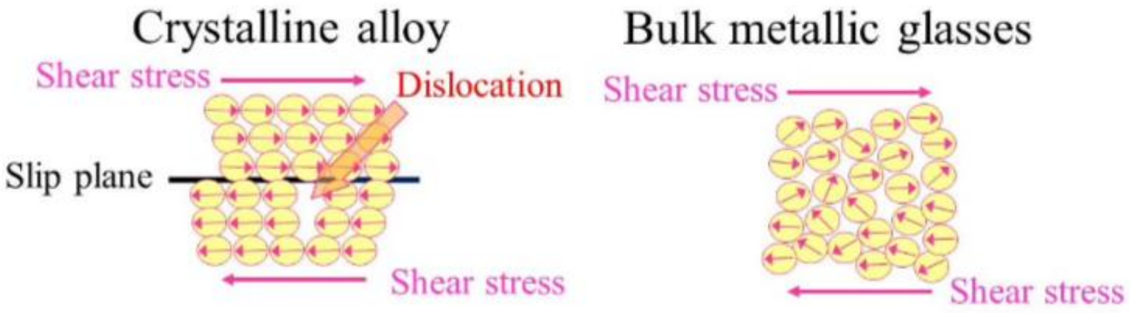
Some alloy elements have relatively high solid solubility in Mg, such as Y (12 wt.% limit), Sc (25.9 wt.% limit). It can exist in the form of solid solutions, thus achieving solid solution strengthening and improve corrosion resistance by reducing internal galvanic corrosion between the second phase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

Amorphous alloys[31]

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

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

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



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

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

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