Castable Metal Alloys in Dentistry

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Objectives

Upon completion of this educational activity the learner will be able to:

- Understand how metal castings are made.
- Describe the lost wax technique.
- Describe the difference between a crystal and a grain.
- Describe a face-centered structure.
- List four noble metals.
- Describe the role of ruthenium, iridium, and rhenium when added to alloys.

Course Description

Castable Metal Alloys in Dentistry is a course that gives you everything you really need to know (and just about everything you ever wanted to ask) about wrought and castable metal dental alloys. What is the difference between type I, II, and III gold? What is palladium, and how does it affect the alloy? How about all the other trace metals in an alloy? How does porcelain stick to a metallic substructure? Why choose one type of metal for a removable partial denture framework as opposed to another? What's the difference between grains and crystals? Why is gold soft? What is "strain hardening" and "cold working"? Who is allergic to which metals? We make it simple and interesting.

Martin S. Spiller, DMD

Martin Spiller graduated in 1978 from Tufts School of Dental Medicine. He is licensed in the state of Massachusetts and has been practicing general dentistry in Townsend, MA since 1984. Upon graduation from dental school, Dr. Spiller spent four years as an U.S. Army officer. During this time, he attended a dental general practice residency in which he received training in numerous dental specialties including oral surgery, endodontics, pedodontics, and orofacial surgical techniques and facial trauma. In 2000, he began work on a general dentistry website (www.doctorspiller.com). The intention at first was to educate the general public about dental procedures and the concepts behind them. Eventually, the website became popular with professional dental students. The content of the web pages began to reflect this readership. Dr. Spiller was asked to write this course based on academic study, hard won experience in the practice of dentistry, and his proven ability to write clear and concise content.
Introduction

Metal castings are made by fabricating a hollow mold, pouring a molten metal into it allowing the metal to solidify, and separating the now, solid metal casting from the mold. Ultimately, all metallic objects originate from castings. In dentistry, metal castings are used to:

- Restore teeth
- Replace teeth
- As frameworks for removable partial dentures

Today, metal castings are also used as metal frameworks to support porcelain crowns or fixed partial dentures in order to produce strong yet very esthetic restorations.

This course in dental alloys is for persons interested in gaining a basic working knowledge of dental alloys. The course discusses the history of restorations and the lost wax technique, chemistry as it relates to dental restorations and various metals and substances used when creating restorations.

The History and Description of the Lost Wax Technique in Dentistry

The lost wax technique was probably invented in ancient China or Egypt. The technique requires carving a wax replica of an item which is then duplicated in gold. The wax is placed (invested) in plaster or clay and burned out which leaves an image (hole) where the wax used to be. The image is filled with molten gold through a small hole. This technique works quite nicely for fairly large castings, but gravity alone is not sufficient to draw gold into the very fine detail necessary to fabricate a tiny filling for a tooth.

Prior to 1855, dentistry consisted mostly of extracting decayed and abscessed teeth and replacing them with some sort of removable denture. Silver amalgam, made from shaved silver coins mixed with mercury, was invented in France in 1819 but was an unreliable filling material due to the haphazard way it was formulated. While itinerant entrepreneurs traveled the countryside plugging amalgam into decayed teeth, most reputable dentists refused to use it.

Gold leaf was first used to fill teeth in 1483 by Giovanni d'Arcoli, but the technique was tedious and expensive. Only the most wealthy and determined patients could afford and withstand having their decayed teeth repaired this way.

The cohesive gold foil technique was perfected and codified in 1855. It was much less tedious and less expensive than using gold leaf and made restoration of decayed teeth a real option for many more consumers. The gold foil technique is laborious and an expensive process involving hammering tiny pieces of pure (cohesive) gold foil into a
prepared cavity preparation. Only affluent people could afford this sort of dentistry, but it was reliable. Gold foil became the industry standard for repairing damaged teeth.

In 1895, G.V. Black standardized a reliable and safe formula for dental amalgam. This made it possible for the average person to save a decaying tooth rather than having to extract it. Unfortunately, not all dentists offered mercury fillings; many dentists remained wedded to the gold foil technique.

In 1907, William H. Taggart invented a centrifugal casting machine for use with the lost wax technique. When centrifugal force replaced gravity as the method to fill the casted image inside an investment, it became possible to cast small, highly detailed objects.

Taggart patented the technique, but subsequently lost the patent when it was discovered that Dr. Philbrook of Denison, Iowa had published a paper on the subject twenty-five years earlier. Taggart's procedure involved carving a wax pattern directly inside of a patient's mouth. Today, a dentist takes an impression and sends it to a dental laboratory. The lost wax technique is explained below.

**Lost Wax Technique**

The dentist drills out the tooth decay and refines the shape of the preparation making sure there are no undercuts which might interfere with an unrestricted path of withdrawal. Next, the dentist takes an impression of the prepared tooth. This impression is sent to the lab for fabrication of the restoration. The images presented below show how a gold crown is fabricated in the laboratory.

After pouring the impression with a fine plaster called dental stone, the die (the plaster model of the prepared tooth) is covered with wax and carved into the appropriate tooth shape. (Images by Bothell Dental Lab)
A sprue (a small wax rod) is attached to the wax replica. In the image below, the sprue is the green extension from the crown down toward the casting ring cap at the bottom. The bulb in the sprue serves as a reservoir for the gold to help equalize the pressure of the liquid gold, so it flows evenly into each wax pattern.

The casting ring cap is fitted over the casting ring. The casting ring serves as a container to hold the plaster which is then flowed around the wax patterns.

Once the investment has set, the casting ring cap is removed leaving the sprues sticking up out of the now, hard investment. The cylinder, with its invested wax, is placed in a very hot oven. When the wax burns away, the plaster in the ring contains a space in the shape of the original wax filling (a hollow three-dimensional image of the filling with attached sprue).

The image is filled with molten gold using a centrifugal casting machine. By immersing the hot plaster with the gold inside in water, the plaster shatters away leaving behind the casting which includes the gold filling and the attached sprue. After removing the sprue, the gold casting is polished up and cemented into the original cavity preparation in the tooth.
This technique works equally well for fillings in teeth as well as full gold crowns. When a casting does not replace the cusp of a tooth, it is called an inlay.

When a casting replaces one or more cusps on a tooth, it is called an onlay.

Taggart’s Centrifugal Casting Machine

Taggart’s centrifugal casting machine made it possible to apply enough gravity to force the molten gold into the tiny invested image of a filling. The picture above shows a modern version of Taggart’s invention. The white piece, with the hole in it, is a small crucible used to melt the gold alloy with a gas and forced-air torch. The burned out image (originally invested in a metal cylinder called a casting ring) is placed behind the hole in the crucible. The orange stand contains a spring which has been wound several times in preparation for the casting operation. Once the image is in place and the alloy
has been melted, the technician allows the locking pin, which sticks up on the left side of the base, to drop. This releases the armature, and when the technician lets the armature loose, the armature, along with the crucible and its attached casting ring, spins at considerable speed. The crucible apparatus swings out so that it is facing the counterweights on the opposite side of the armature. Centrifugal force forces the melted alloy through the hole in the crucible. Molten metal proceeds to fill the image in the casting ring behind it.

Unfortunately, Taggart's technique did not produce the accuracy many dentists demanded for small restorations. Most dentists still resisted cast-metal restorations in favor of gold foil or the newly improved silver amalgam, both of which always produced the tightest restorations possible. In 1910, wealthy people wanted high class dentistry and were willing to pay for the privilege of not having to suffer while the dentist hammered gold into the cavity preparation. Thus, gold cast restorations began to compete successfully with gold foil despite the fact that castings did not fit the preparation perfectly.

Since gold was the metal used to make crowns worn by kings, the mentality during the early 1900s was that gold fillings brought a royal distinction to the patient. Thus the term "gold crown" was something like an advertising slogan. The term "crown" was used to denote any gold restoration applied to a single tooth, including gold foil restorations, inlays, and onlays. Today, the term "crown" is reserved for any full coverage restoration, whether gold or porcelain. The terms inlay, onlay, and filling are used to denote restorations that cover only a part of a tooth's clinical crown.

In 1929, Coleman and Weinstein invented cristobalite investments to replace plaster of Paris. Cristobalite eliminated most of the shrinkage and distortion problems that had plagued the production of gold castings. (Cristobalite is one of three crystalline configurations of silica. It has unique thermal expansion qualities which makes it especially suitable as an investment material for metal casting.) Even cristobalite investments did not produce perfect castings. It was not until the 1940's that cristobalite investment materials compensated for all of the distortions encountered in the original lost wax technique.

**Solids, Liquids and the Chemistry of Metals**

Although it is not readily apparent from everyday experience, metals are very much like water. Metals can exist in solid, liquid, and gaseous forms. Water freezes at 32°F. Below that temperature, water exists as a crystalline solid. Above that temperature, water exists as an amorphous liquid. In a crystal, the molecules take on a uniform orientation and configuration relative to each other.
What’s the Difference Between Atoms and Molecules?

A molecule is the smallest physical unit of an element or compound. Compounds are chemical combinations of different elements. A molecule of water is composed of two atoms of hydrogen combined with one atom of oxygen. The smallest component in water that can still be called water is the molecule H2O which is composed of three atoms. Gold forms cubic crystalline units containing 14 atoms and still retains its identity as gold as a single atom. A molecule of gold is composed of a single gold atom.

Water forms hexagonal structures. These are familiar to everyone in the form of snowflakes. When ice melts, it turns back into loosely ordered, amorphous water molecules. (Amorphous means lacking a definite form or shape.) The transition between water and ice occurs at a specific temperature. All water molecules and the potential bonds between them are identical; the transition from ice to water happens under uniform conditions. Temperature does not change instantaneously throughout an ice mass. Near melting temperature, some water will be found in the form of ice, and some in the form of liquid water. Slush is in a multiphasic state, in this case ice and water. The solid ice particles are called grains. As the temperature drops, these grains grow larger as more and more water molecules adhere to the growing crystals of ice. Each grain is composed of a single, fairly continuous crystalline structure.

The analogy between metals and water is fairly exact. All metals have definite melting temperatures above which they exist as amorphous liquids and below which they exist as crystalline solids. Like ice, when cooled slowly from its liquid state, a metal will form crystals. Grains form and grow separately during the liquid phase until the entire matrix freezes. The grains freeze in random orientations. The size of the grains will depend on the length of time they were allowed to grow before the metal cooled “freezing” them into place. Thus, the microscopic structure of a solid metal will display a jumble of grains of various sizes randomly oriented throughout its metallic mass.

Like aqueous solutions, liquid metals may be mixed together. Some metals are soluble in each other, while others are partially soluble at lower temperatures and insoluble at higher temperatures. Some metals in the molten state will chemically react with others to form new chemical compounds. When two or more molten metals are mixed together and cooled to a solid crystalline state, the result is called an alloy.
Solid alloys form mixed crystalline structures with complex microscopic internal structures composed of grains from various phases. The melting temperature of each phase differs from that of the others depending on its chemical composition. Each type of grain in the crystal body may have a different shape, depending on its chemical composition, as well as a different size and orientation.

**What’s the Difference Between a Crystal and a Grain?**

Metal atoms have large numbers of electrons in their valence shells. These become delocalized and form a "sea" of electrons surrounding a giant lattice of positive ions. Metallic bonds are something like covalent bonds except that large numbers of electrons are shared by massive numbers of atoms. This trading back and forth of electrons is what holds metallic crystals together, sort of like a massive, communal, covalent group hug. ☺ Each metal forms a specific type of crystalline structure based upon the internal atomic properties for that metal.

Given enough time and ideal conditions, a metallic crystal lattice can grow to be very large with a perfect internal crystalline structure. A single crystal of any metal could theoretically grow to be infinite in size. Almost every metal exists in a polycrystalline state composed of a jumble of crystals at odd angles and of varying sizes. When this happens, each individual crystal in the body is called a grain.

Each grain is usually not a perfect crystal. In nature, crystal growth does not proceed in a regular fashion. Instead, growth is random with some positions in the lattice left vacant and other atoms positioned in irregular places within the lattice. Grains are fairly regular crystalline structures with many imperfections which distort the crystal lattice.
The physical properties of any alloy depend on the nature of its internal microscopic crystalline structure. Its structure can be affected by factors such as cooling time as well as subsequent heating and cooling cycles.

The phases in a cooling metal solution separate out tiny grains which are distributed throughout the alloy. The growth of the grains depends on cooling time. Alloys that have the least permanent deformation during service also have finer grain structures. Small grain size is advantageous in dental alloys. The longer it takes for an alloy to cool, the more time the grains have to grow and the larger they will become. Smaller grain size is achieved by rapid cooling of the molten metal.

Inclusions of tiny amounts of iridium, rhenium, or ruthenium are used as "grain refiners". These metals solidify very early in the cooling process and act as nuclei around which other metal grains can form.

**Why Gold is Soft; How Grain Structure Affects Hardness and Strength**

Pure gold is fairly soft and malleable. It is not a suitable material for large restorations or denture frameworks, because its malleability leads to wear and deformation while in service in the mouth. However, adding small amounts of soluble metals into a solution of molten gold creates a much harder alloy. Pure cast gold is only one-fifth as strong and one-sixth as hard as a typical gold-based casting alloy. In order to understand why this is so, it is necessary to delve into the structure of crystals and grains.

Gold forms a face-centered cubic crystal. Not all metals form this shape in crystalline form. Some form hexagonal plate-like shapes or long needle structures. But face-centered structures are common in metallurgy. It is a crystalline shape shared by gold, palladium, platinum, nickel, and silver. The diagram below shows what a face-centered cubic form looks like if you could see all its atoms. It is a bit confusing, so the diagram on the right is provided to make a face-centered cubic crystal easier to conceptualize.
A single crystalline unit like the face-centered cubic crystal is quite strong and difficult to break apart. However, the bonds between its atoms are able to stretch. A force applied to the top left side of a single face-centered cubic crystal may temporarily distort its form, but the crystal “bounces back” into its original shape once the force ceases. Non-permanent distortion of this sort is called elastic deformation.

When metals cool, their naturally occurring crystalline structures stack together to form larger and larger crystals. The shape of any crystal depends on the natural shape of the native crystalline structure. A face-centered cubic crystal will extend in all directions forming a larger and larger cube until it “bumps into” another crystal growing in a different orientation. Silica (silicone oxide), has a tetrahedral (pyramid shaped) molecular structure and forms six-sided crystals with six-sided pyramids on top. In general, each grain of any substance will maintain a fairly coherent crystalline structure. The difference between one grain and its neighbor is mostly in the orientation and size of each crystal.

When enough shear (side to side) force is placed on a perfect crystal, the individual molecules in the structure begin to slip past each other causing a permanent deformation. This form of slippage involves offsetting the molecular units one or more places along the natural planes that make up the crystalline lattice. Owing to the strength of the atomic bonds that keep the crystalline structure in its pristine state, much force must be applied to make a pure crystal of any material deform permanently.

Most crystals do not form perfectly. Frequently there are vacancies in the atomic lattice which may be configured in a number of ways. Sometimes vacancies are arranged as point defects remaining as single-point imperfections in an otherwise perfect crystalline lattice. More frequently, vacancies alter the arrangement of other parts of the lattice. This type of defect, known as an edge dislocation, weakens the crystalline structure.
Edge dislocations are especially frequent in face-centered cubic crystalline elements such as gold. This is a major reason that gold is such a plastic (soft) metal.

The hour glass structure caused by a missing line of atoms in the lattice causes bending of the interatomic bonds between neighboring atoms in the lattice. This bending causes an elastic deformation which wants to relieve itself allowing the bent, interatomic bonds to become straight again. However, since the defect is firmly embedded within the lattice, the structure cannot “fix itself” unless energy is added to the system. Edge dislocations can be relieved by placing shear stresses on the crystalline lattice. Shear is graphically demonstrated in the image of the red-faced cubic crystal on the previous page. Because of the presence of an edge dislocation, the amount of shear force necessary to cause a permanent plane slippage is much less than it would be in a perfect crystal lattice. Depending on the metal involved, it can take a little as 50% of the force needed to permanently distort an imperfect crystalline structure as it would to distort a perfect crystal of the same metal.

When shear force is applied as in the diagram above, (Phillips Science of Dental Materials) the horizontal plane containing the vacancy becomes the slip plane. If a sufficiently large shear stress is applied across the top and bottom faces of the metal crystal as shown, the bonds in the row of atoms adjacent to the dislocation are broken. New bonds are forged with the next row resulting in movement of the dislocation by one interatomic distance. If the force continues, this process happens again and again until the dislocation reaches the boundary of the crystal.
Strengthening Soft Metal Structures

It is apparent from the above discussion that there is little to hinder the movement of edge dislocations in pure metal grains. Edge dislocations are the dominant reason for plasticity in pure metals. In order to strengthen a metal body, a mechanism must be found to impede the progression of edge dislocations. There are three major ways to do this.

Cold Working

Cold working, or strain hardening is defined as mechanical deformation below the recrystallization temperature. Sheer stress is applied to the metal body. This process causes permanent deformation by working edge dislocations to the boundaries of a grain. It relieves stress in the lattice and allows the reformation of a more perfect and harder crystalline structure.

Shear Force

Shear force can be applied to a metal in several ways. Bending is one way to apply shear. For example, when a soft metal wire is bent repeatedly, the edge dislocations in the area of the bend are worked out of the crystalline lattice causing it to become harder and more brittle. As bending continues, numerous micro-cracks develop within the grains causing them to break into many smaller grains. As the number of micro-cracks multiply, the grains rub against each other causing friction and heat, and eventually the wire breaks.

Burnishing

Another method of applying strain is burnishing. This is done by rubbing the metal surface with a hard object. This distorts the surface and hardens it at the same time. The most common industrial process used to harden metals in this way is called forging. Burnishing is accomplished using hydraulic presses, pounding the metal with hammers, or running it through rollers to flatten or further shape it. Burnishing causes the grains to deform in the shape of the finished object.

Wrought wire is made this way. It is composed of grains that look like bundles of spaghetti running along the length of the wire. Wrought wire is cold-forged, but many industrial processes heat the wire while it is being forged to soften it during prolonged operations. After forming a more perfect, harder metallic structure, forging leads to the addition of vast numbers of additional dislocations throughout the increasingly brittle wire. The new dislocations appear in the form of micro-cracks throughout the grain structure and cause large grains to break into smaller grains which further strengthen the metal.
Grain boundaries block the movement of dislocations. One of the keys to strengthening metal objects is to force formation of smaller grains throughout the body as it cools below its melting temperature. The most common method to force the formation of small grains is to cool the metal quickly after casting. In dental labs this is done by quenching the hot invested casting with cold water. This method shatters the investment away from the casting and also "freezes" the casting before the crystals have time to grow.

Another method to use to achieve small grain size is to add small quantities of grain refiners such as ruthenium, iridium, and rhenium to the alloy. These metals have high melting temperatures and crystallize before other phases of the metal. Vast numbers of these tiny crystals force the formation of very small crystal grains in other phases that form around them.

Mixing two or more molten metals together forms an alloy. An alloy of two soft metals creates a much harder structure than either of them alone. Silver and tin, two soft metals, when alloyed, will form pewter. For centuries, pewter was the basis of high class, unbreakable tableware among wealthy people.

Whenever two or more molten metals are mixed together and allowed to cool, the resulting grain structure becomes very complex. Each metal solidifies into grains with inherently different shapes and sizes. This process is complicated when metals chemically combine to form a third phase. The close approximation of grains precipitated from different phases makes edge dislocation slippage within any grain difficult. This hardens the alloy.

Finally, each grain of any phase will include atoms from each of the other phases. Grains contaminated with foreign atoms are called solid solutions. Foreign molecules within an otherwise pure grain cause localized distortions in the crystal lattice. The presence of the foreign molecule within the lattice acts as a sort of lock and key preventing the movement of slip planes and further hardening the alloy.

Prior to the introduction of Porcelain Fused to Metal (PFM) restorations, gold-based alloys were virtually the only castable alloys used in dentistry. There were four types:

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<tr>
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<tr>
<td>IV</td>
<td>Extra-Hard</td>
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Type I was hard enough to stand up to biting forces but soft enough to burnish against the margins of a cavity preparation. It was used mostly for one-surface inlays.
Type II was less burnishable but hard enough to stand up in small, multiple surface inlays that did not include buccal or lingual surfaces.

Type IV was used for partial denture frameworks but was not used in fixed prosthetics.

The most commonly used type of gold for all-metal crowns and bridges was Type III. It is still used when a patient requests an all-gold restoration such as an all-gold crown, inlay, or onlay. A typical type III gold alloy includes the following metals:

- Gold 75%
- Silver 10%
- Copper 10%
- Palladium 3%
- Zinc 2%

The purpose of each component is as follows:

Gold is a "noble metal". It resists tarnish and corrosion and will participate in very few chemical reactions. It is non toxic and hypoallergenic. It is also highly ductile and malleable and has a relatively low melting point. Gold's long standing use and incorruptibility made it a natural first choice for use in dentistry. It forms the bulk of the composition of a dental alloy.

The other noble metals are:

- Palladium
- Silver
- Tantalum
- Platinum
- Iridium
- Osmium
- Ruthenium
- Rhodium

The classification of noble metals is an ancient one and rather loosely defined since silver certainly tarnishes and copper is sometimes included in the list.

Silver lowers the melting temperature and modifies the red color produced by the combination of gold and copper. Silver increases ductility and malleability.

Copper is a principal hardener. It is necessary to use in heat treatment and is usually added in concentrations of greater than 10%.
Palladium raises the melting temperature, increases hardness and whitens gold even in very small concentrations. Palladium prevents tarnish and corrosion and acts to absorb hydrogen gas which may be released during casting.

Zinc acts as an oxygen scavenger and prevents the formation of porosity in the finished alloy. Zinc also increases fluidity and reduces surface tension in the molten state improving the casting characteristics of the alloy.

**Porcelain Alloys**

Until the mid-20th century, gold and amalgam were the only materials available for the restoration and replacement of posterior teeth. Porcelain jacket crowns were available for front teeth, but they did not fit well and were prone to fracture easily. In 1962, Dr. Abraham Weinstein patented the first gold-based alloy upon which porcelain could be baked. The metal substructure reinforced the porcelain and gave it the durability and the strength to resist fracturing. For the first time, it was possible to replace missing teeth with natural looking, tooth colored, fixed bridgework. Due to the accuracy of the lost wax technique, these appliances could fit tooth preparations exactly.

Porcelain will not chemically bond with gold alone. Trace elements need to be in the alloy composition to form an oxide layer on the surface which then bonds the porcelain to gold.

Three oxide-forming elements are:

- Iron
- Indium
- Tin

Porcelain is made of metal oxides. It will bind with oxides on the surface of gold frameworks.
The necessity of metal oxide formation on the surface of the underlying casting means that ions from the metal casting will mix with the porcelain. This mixing affects the color, reflective properties, and translucency of the finished tooth. The porcelain must be formulated to overcome these effects.

Porcelain melts at high temperatures (between 850°C and 1350°C). It is applied as wet powder over the metal framework and then baked or fired in order to fuse the powder particles together. The metal substructure upon which the porcelain is applied must resist sagging and deformation while being held at this high temperature, or the casting will not fit well in the patient's mouth.

Metal is opaque and generally has a gold or gray color. Porcelain must be translucent, or it fails the tests of esthetics. There must be a mechanism to "opaque" the underlying metal framework, or the finished appliance will have a gray cast.

The thermal expansion of the metal must be nearly identical to that of the porcelain; otherwise, the porcelain will simply shatter off of the framework as it cools. If the metal shrinks less than the porcelain during cooling, the porcelain will "craze" (develop little cracks throughout its structure). If the metal shrinks much more than the porcelain during cooling, the porcelain will "shiver" (the opposite of crazing, sort of like "puckering") but will break the porcelain off the framework.

Ideally, porcelain should be under slight compression in the final restoration. This is accomplished by selecting an alloy/porcelain combination in which the alloy contracts slightly more than the porcelain during cooling. Compression of the porcelain reduces the likelihood that cracks will develop throughout the tooth during service.

All porcelains used to veneer metallic substructures contain Lucite crystals. These crystals serve two functions in the porcelain.

- They act to limit the development of cracks in the porcelain veneer.
- They serve to increase the index of thermal expansion of the porcelain.

By carefully adjusting the proportion of Lucite crystals in the glass, it can be made to "fit" the metallic substructure during the sintering and fusing phases of manufacture.

**How Porcelain is Applied to a Metal Coping**

In the image below, a cast metal coping is placed back on the die after the buccal gingival margin is removed. This is done in order to allow a butt porcelain margin so that no metal will show in the final crown. (Bothell Dental Lab)
Next, a thin layer of opaque porcelain powder (frit) is layered over the metal in order to mask the underlying darkness. Otherwise, the finished crown will always show a gray caste.

After the opaque layer is fused onto the metal coping, the first layer of overlying porcelain is applied with a wet paintbrush. Different shades of frit are applied over various parts of the crown in order to make the finished tooth look more natural.
The coping along with its "green" porcelain is removed from the die and placed in a vacuum kiln and fired at about 1700 degrees F.

The green porcelain shrinks during its firing, so a second layer of porcelain frit is layered over the first bake.

When the technician has finished rebuilding the correct contours, he replaces the crown in the vacuum kiln for its second and final firing.
Composition of Porcelain Alloys

(Alloys That Are Formulated to Act as Substructures for Porcelain Fused to Metal (PFM) Restorations)

PFM alloys are classified according to the proportion and types of noble metals they contain. High-noble alloys have a minimum of 60% noble metals (any combination of gold, palladium, and silver) and a minimum of 40% by weight of gold. They usually contain a small amount of tin, indium, or iron which provides for oxide layer formation. These metals provide a chemical bond for the porcelain. High-noble alloys have low rigidity and poor sag resistance. They may be yellow or white in color. There are three general types of high-noble alloys.

- **Gold-Platinum Alloys**
  
  Gold-platinum alloys were developed as a yellow alternative to otherwise white palladium alloys. Gold-platinum alloys are used for full-cast as well as metal-ceramic restorations. Because they are more prone to sagging, they should be limited to short span bridges. A typical formula is gold 85%, platinum 12%, zinc 1%, and silver to adjust the expansion properties (in some brands).

- **Gold-Palladium Alloys**
  
  Gold-palladium alloys can be used for full-cast or metal-ceramic restorations. Palladium has a high melting temperature. Small amounts of it will impart a white or gray color to the finished alloy. The palladium content reduces the casting’s tendency to sag during porcelain firing. These alloys usually contain indium, tin, or gallium to promote an oxide layer. A typical formula is gold 52%, palladium 38%, indium 8.5%, and silver to adjust the expansion properties (in some brands).
• **Gold-Copper-Silver-Palladium Alloys**

Gold-copper-silver-palladium alloys have a low melting temperature and are not used for metal-ceramic applications. They contain silver, which can cause a green appearance in the porcelain, and copper, which tends to cause sagging during porcelain processing. A typical composition is gold 72%, copper 10%, silver 14%, and palladium 3%.

Noble alloys (gold, palladium, or silver) contain at least 25% by weight noble metal. Any combination of these metals totaling at least 25% places the alloy in the noble alloy category. They are the most diverse group of alloys. They have relatively high strength, durability, hardness, and ductility. They may be yellow or white in color. Palladium imparts a white color, even in small amounts. Palladium also imparts a high melting temperature.

Gold-copper-silver-palladium alloys are also included the high-noble alloy category. The difference here is that the proportion of gold and palladium is a great deal less than its high-noble cousin. More copper and silver are in the mix in its place. These alloys have a fairly low melting temperature and are more prone to sagging during application of porcelain. They are used mostly for full-cast restorations rather than PFM applications. A typical formula is: gold 45%, copper 15%, silver 25%, and palladium 5%.

Palladium-based alloys offer a less expensive alternative to high-noble alloys since they can cost between one half and one quarter as much as the high gold alternative.

Palladium-copper-gallium alloys are very rigid and make excellent full-cast or PFM restorations. They do contain copper and sometimes are prone to sagging during porcelain firing. Gallium is added to reduce the melting temperature of the alloy. A typical formula is palladium 79%, copper 7%, and gallium 6%.

Palladium-silver and silver-palladium alloys are used in varying mixes depending on the relative content of palladium and silver. These alloys were popular in the early 1970's as a noble alternative to the base-metal alloys. High palladium alloys are popular for PFM frameworks. High silver alloys are more susceptible to corrosion, and the silver may lead to greening of the porcelain unless precautions are taken. These alloys have high resistance to sagging during porcelain firing and are very rigid. They are good for long spans. They are also more castable (more fluid in the molten state), easier to solder, and easier to work with than the base-metal alloys. Typical recipes include: palladium 61%, silver 24% and tin (in some formulas). Another formula is silver 66%, palladium 23%, and gold. (In some formulas, a low percentage of gold was included to satisfy insurance requirements regarding the definition of nobility in the alloy.)
Base-metal alloys have been around since the 1970’s. They contain less than 25% noble metal, but in actuality, most contain no noble metal at all. They can be used for full-cast or PFM restorations as well as for partial denture frameworks. As a group, they are much harder, stronger and have twice the elasticity of the high-noble and noble-metal alloys. Castings can be made thinner and still retain the rigidity needed to support porcelain. They have excellent sag resistance and are great for long span porcelain bridges. They appear to be the ideal metal for cast-dental restorations and were heavily used for PFM frameworks due to their low cost and high strength characteristics.

Unfortunately, nickel and beryllium, two of the most commonly used constituents of base-metal alloys can cause allergic reactions when in intimate contact with the gingiva. Since many women and men have been sensitized to these metals by wearing inexpensive skin piercing jewelry, crowns and bridges made from these alloys have been known to cause gingival discoloration, swelling, and redness in susceptible individuals.

Note that the allergic reaction is limited to contact gingivitis and affects the gingiva alone. There are no known systemic reactions reported as a result of exposure to oral appliances made from base-metal alloys. Allergic reactions appear to be limited to fixed appliances (crowns and bridges). Nickel containing metals rarely cause allergic dermatitis when used for removable partial denture frameworks.

Very high intake of nickel and beryllium is known to be carcinogenic (cancer causing). Alloys containing these metals are ubiquitous in jewelry and in dental restorations in countries outside of the US, Canada, and Europe and are not associated with any form of cancer when used in contact with skin or mucosa. The sorts of exposures required for evidence of carcinogenicity to appear are uniquely associated with occupational exposures during the smelting and refining of nickel or beryllium. In dentistry, the only people known to be at risk of cancer from exposure to these metals are dental technicians who melt nickel and beryllium alloys and are exposed to the fumes.

Base-metal alloys also have other disadvantages for lab technicians and dentists. Base-metal alloys have a very high melting temperature which makes them more difficult to cast. They exhibit a high casting shrinkage (about 2.3%) which must be compensated for. Their hardness makes them difficult to burnish and polish. Their high melting temperature makes them difficult to solder. These alloys are more prone to corrosion under acidic conditions.

Today relatively few American, Canadian, or European dentists order fixed restorations (crowns and bridges) made from base-metal alloys. Companies that sell dental alloys still carry a line of these alloys specifically for making crowns and bridges, but they are mostly for sale outside the US, Canada, and Europe. Most American and European
doctors stick with palladium or gold-based alloys to avoid the possibility of legal problems if a patient turns out to be allergic to nickel or beryllium. Nickel containing alloys and compounds have not been associated with increased cancer risk by oral or dermal routes of exposure. Base-metal alloys are often used today in the manufacture of removable partial denture frameworks. There are two subcategories of base-metal alloys.

**Nickel-Chromium Alloys**

Nickel-chromium alloys contain least 60% nickel and may contain a small amount of carbon (about 0.1%) as a hardener. They contain either >20% chromium or <20% chromium with or without beryllium. These alloys are used for removable partial denture frameworks.

**Cobalt-Chromium Alloys**

Cobalt-chromium alloys are a nickel-free alternative to the nickel-chromium alloys. They have become the most commonly used type of base metal alloy for removable, partial-denture frameworks. They are used for PFM framework fabrication as well. The major problem with this formulation is that it is more difficult to work with than nickel-chromium alloys due to their high melting temperature requiring the use of specialized casting equipment. This alloy's high hardness and low ductility also make it difficult to finish and polish.

NOTE: Prior to the advent of base-metal alloys, the most common alloy used for removable, partial denture frameworks was type IV (extra hard) gold alloy. Gold alloys are rarely used in this capacity anymore, since chrome-cobalt frameworks are lighter, stronger, and much cheaper.

**Metals and Their Uses in Dental Alloys**

**Gold (Au)**

- Soft, malleable, and yellow colored with a low melting point.
- Looks great, but by itself lacks sufficient strength to stand up to the forces generated in the mouth.
- Gold is a noble metal and does not corrode or tarnish in the mouth. The softer alloys are "burnishable", meaning that the margins can be rubbed with a blunt instrument to seal them. Gold is also very kind to the opposing dentition and will not wear down opposing teeth.
- Gold’s native thermal expansion is too high to be used alone as a base upon which to build a porcelain superstructure. If porcelain were bonded directly to a gold understructure, it would "shiver" and break off
the substructure during cooling. This characteristic can be modified by alloying it with other metals.

- Finally, since gold is inert, it cannot chemically bond to porcelain.

Palladium (Pd)

- Palladium is hard, strong, white, and has a high melting point.
- It is not very ductile.
- Palladium is a noble metal. It resists corrosion and tarnish.
- Its native thermal expansion is very low and by itself, palladium cannot be used with porcelain. Porcelain would "craze" (the opposite of shivering) and break off the substructure during cooling.
- Even relatively small amounts of palladium will whiten gold dramatically. When added to a gold alloy, it will raise the melting range, raise the ductility, and improve strength and hardness.
- Small amounts of palladium dramatically improve the tarnish and corrosion resistance of gold-silver-copper crowns and bridge alloys. It is an essential component for preventing tarnish and corrosion in Au-Ag-Cu alloys with gold content below 68% by weight.
- Palladium and gold are completely soluble in one another both as liquids in the molten state and as solids in the finished alloy.
- Palladium and gold are found together in so many dental alloys because they complement each other. Unfortunately, the correct combination of gold and palladium sufficient to produce the correct coefficient of expansion will not necessarily produce an alloy that meets other necessary characteristics such as ductility, color, or stiffness that a lab or manufacturer may need to produce a lasting product. It is necessary to balance the formula with other metals.

Platinum (Pt)

- Platinum is used as an alternative to palladium in order to maintain a yellow color in the final alloy. It raises the melting range, increases the hardness, strength and ductility, and lowers the thermal expansion of the alloy. It is less effective than palladium in producing these effects, but it is able to alter these characteristics with less impact on the golden color of the finished product.

Silver (Ag)

- In PFM alloys, silver is used principally to raise the thermal expansion of the alloy in order to balance the low thermal expansion of palladium.
Silver lowers the melting range of both gold and palladium and adds fluidity to the melt, improving its casting properties.

In gold-silver-copper alloys used for all-gold restorations, silver compensates for the reddish color imparted by the copper. It also acts along with copper to increase the strength and hardness of the alloy.

The major problem with silver in PFM formulations is that silver can impart a greenish tint to the finished porcelain. Discoloration is offset by the effect silver can have on the ductility, and because modern porcelains are now formulated to resist this greening effect.

Copper (Cu)

In crown and bridge alloys (all-gold), copper's major job is to harden and strengthen the alloy. Copper also imparts a reddish color, which may be an advantage, but this coloration can be offset by adding silver.

- In PFM alloys, silver is used mostly to increase the modulus of thermal expansion and is responsible for the dark oxide layer characteristic of palladium-copper-gallium alloys.
- Unfortunately like silver, copper can cause discoloration of the overlying porcelain; however this effect is seldom seen when there is a very high percentage of palladium in the mix. Copper is seldom used in high-noble PFM alloys (these alloys have lots of gold and little palladium).

Zinc (Zn)

- Zinc is used in crown and bridge alloys primarily as an oxygen scavenger. Zinc readily combines with oxygen that may have dissolved in alloys in molten state. Zinc prevents oxygen from forming gas porosity in the casting.
- In PFM formulations, zinc lowers the melting range, increases strength and hardness, and raises the thermal expansion.

Indium (In)

- In crown and bridge alloys such as gold-silver-copper, indium is added to improve the fluidity of the melt, thus improving castability.
• In PFM alloys, indium strengthens and hardens both gold and palladium and raises the thermal expansion of both. Indium also lowers the melting range of both gold and palladium.
• Indium contributes to the formation of the porcelain-bonding oxide layer.

Tin (Sn)

• Tin is added to an alloy to increase the strength and hardness of both palladium and gold. It also lowers the melting range and raises the thermal expansion.
• Like indium, tin also contributes to the formation of the porcelain-bonding oxide layer.

Gallium (Ga)

• Gallium is used almost exclusively in palladium-based PFM alloys. Gallium can be a potent strengthener, and it lowers the melting range of palladium.

Iron (Fe)

• Iron is used almost exclusively in gold-platinum based PFM alloys. It is used as a strengthener.
• Iron also contributes to the formation of the porcelain-bonding oxide layer.

Cobalt (Co)

• Cobalt is sometimes used as a substitute for copper in palladium-based PFM alloys. Mostly, cobalt is used along with nickel to formulate alloys for partial denture frameworks.

Ruthenium (Ru), Iridium (Ir) and Rhenium (Re)

These three elements are used in very small concentrations as grain refiners. Alloys have better characteristics if the grain structures are small (see the discussion of small grain size). The addition of small amounts of any of these three elements helps to produce small grain size when alloys cool. The theory behind this is as follows:

Ruthenium, iridium, and rhenium 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. As the grains of ruthenium, iridium, or rhenium form, they remain very small due to their low concentration throughout the solution. Since they crystallize first, these tiny grains form
the nucleus around which the other elements begin to form larger grains. The even
distribution of grain formation throughout the solution limits the size of the larger grains
as well.

**Updates as of 2017 in Castable Metal Alloys**

3-Dimensional Imaging is widely used in dentistry today, from orthodontic models to
being a game-changer in tissue and bone evaluation in implant treatment! Titled, In
June 2017, an online article titled, *Clinical Trial Finds 3-D Printed Dentures Are
Preferred To Conventional Cast Metal Dentures*, Corey Clarke reports on recent
research that had been collected “into the viability of 3D printed removable partial
dentures (RPD) in comparison to conventionally cast metal RPDs.”

Clarke continues:

“The research paper explains the purpose of the trial was to prove the viability of
3D printing as a viable production method in dentistry, clinical trials are needed to
evaluate this new technology in RPD fabrication before its use can be
recommended. The researchers explain the selective laser melting (SLM) AM
technique, which involves melting metal powder with lasers, is beneficial to
casting methods as it is less prone to error. 3D printing the RPD involves 3D
scanning the patient’s mold and designing the prosthesis with CAD software. The
design is then sent digitally to the 3D printer machine and with more reliance on
digital manufacturing, the team believes the process is more accurate and at
lower risk of human error. Elsewhere in the field of digital dentistry, U.S company
EnvisionTEC has announced its 3D printed dentures have been granted FDA
approval.”

He explains further:

“With an average age of 65.6 years, the researchers conducted the trial with 12
participants initially although 3 did not complete. Of the 9 that finished the trial, 5
preferred the 3D printed RPD, 3 had no preference and 1 preferred the
conventionally cast RPD. The team evaluated the patient’s results by conducting
a McGill Denture Satisfaction questionnaire. Using this instrument, they found
that ‘participants reported fewer complaints and more compliments when they
were using the laser-sintered RPDs than when using the cast RPDs.’”

Clarke states:

“additionally the research group noted, ‘participants were significantly more
satisfied with the laser-sintered prostheses than the cast prostheses in terms of
general satisfaction, ability to clean and speak, comfort, masticatory ability,
masticatory efficiency, and oral condition." Despite these results, the paper does point out some of the inhibiting factors of the technology, such as high initial costs for use of the machine and required time and expertise needed to learn the technology. Also noted that some patient’s will not be applicable for the technology due to current limitations in design software. The researchers did also understand there were limitations with their study in terms of small sample size and a relatively short sample period. However were able to conclude that, the use of laser sintering technology for the fabrication of RPDs may lead to higher short-term satisfaction for patients with partial edentulism than conventional methods.” (Clarke 2017)

Figure 3 shows the trend over time with 3D printed dentures shown in orange. Image via *The Journal of Prosthetic Dentistry.*

![Figure 3. Trend over time of both laser-sintered and cast prostheses for satisfaction items that were significantly different among the treatments (general satisfaction, ease of cleaning, ability to speak, comfort, stability, masticatory ability, masticatory efficiency, and oral condition). VAS, visual analog scale measurement in survey, 0 to 100 mm.](image-url)
Dr. Raghavan, Dr. Kumar, and Dr. Geethprasad, in their collective research displayed in an online article titled, **3-D printing – an innovation driving prosthodontics to future** explain:

“3-D Printing is a technology that can produce complex shapes according to computer design using patient’s anatomical data. Its initial use was as pre-surgical visualization models and tooling molds, but now 3D Printing has slowly evolved to create devices such as implants, scaffolds for tissue engineering, diagnostic models etc. Today 3-D printing finds a wide array of applications in prosthodontics. Recent developments like tissue engineering and whole tooth regeneration might find its way to day to day prosthodontic practice in near future. Early prototypes of 3D printed structures replicating the anatomy of the tooth and using composite inks of poly-ε-caprolactone and hydroxyapatite have already been tested in vitro and in vivo. The controlled formation of cell aggregates in vitro mimicking the epithelial mesenchymal interface that naturally occurs in the early stages of the tooth formation has been recognized as a fundamental step in whole-tooth regeneration. Thus, developing a tooth from its primitive stage may be possible in near future. Andreas Hermann of the University of Groningen in the Netherlands and his colleagues have developed an antimicrobial plastic, allowing them to 3D print teeth that also kill bacteria. They embedded antimicrobial quaternary ammonium salts inside existing dental resin polymers. The salts are positively charged and so disrupt the negatively charged bacterial membranes, causing them to burst and die. They found the material killed over 99 per cent of the bacteria, compared to less than 1 per cent for a control sample without the added salts. Further tests will have to be done before the material can be rolled out to patients.” (Raghavan et al. 2016)

**Conclusion**

In conclusion, prior to 1855, dentistry consisted mostly of extracting decayed and abscessed teeth and replacing them with some sort of removable denture. Practitioners used the lost wax technique which required carving a wax replica of an item (tooth) and then duplicating it in gold. In 1907, William H. Taggart invented a centrifugal casting machine for use with the lost wax technique. Today, metal castings are made and used to restore and replace teeth and as frameworks for removable partial dentures. They are also used as frameworks to support porcelain crowns or fixed partial dentures.

Until the mid-20th century, gold and amalgam were virtually the only materials available for the restoration and replacement of posterior teeth. Porcelain jacket crowns were available for front teeth. In 1962, Dr. Abraham Weinstein patented the first gold-based alloy upon which porcelain could be baked. The metal substructure reinforced the porcelain and gave it the durability and the strength to resist fracturing in the mouth.
Due to the accuracy of the lost wax technique, the appliances could fit the tooth preparations exactly.

PFM alloys are classified according to the proportion and types of noble metals they contain. High-noble alloys have a minimum of 60% noble metals (any combination of gold, palladium, and silver) with a minimum of 40% by weight of gold.

Base-metal alloys have been around since the 1970's. They contain less than 25% noble metal. They can be used for full cast, PFM restorations, and partial denture frameworks. Today few American, Canadian, or European dentists order fixed restorations (crowns and bridges) made from base-metal alloys because of the possibility of legal problems.

References


Spiller, Martin J., DMD, Faculty and advisory board member for Dental Learning A Course in Dental Alloys. Available: http://www.doctorspiller.com/dental alloys.htm? Course used with permission of author; references available upon request.


Course Test: Castable Metal Alloys Used in Dentistry

1. The lost wax technique is best characterized as a:
   a. Way to retrieve lost wax from a patient’s mouth.
   b. Way to create a wax replica of an item.
   c. Was first invented in France.
   d. None of the above.
2. The term “crown” describes any:
   a. Inlay restoration.
   b. Onlay restoration.
   c. Full-coverage restoration.
   d. All of the above.

3. Shear force causes:
   a. Deformation
   b. Edge dislocations
   c. Plane slippage
   d. All of the above.

4. Examples of noble metals are:
   a. Gold
   b. Palladium
   c. Copper
   d. A and B

5. Noble metals are resistant to:
   a. Bending
   b. Corrosion
   c. Oxidation
   d. None of the above.
   e. B and C
6. Three oxide-forming elements are:
   a. Iron, indium, tin
   b. Gold, palladium, platinum
   c. Copper, zinc, gold
   d. None of the above.

7. Porcelain will not chemically bond with gold.
   a. True
   b. False

8. All porcelains used to veneer metallic substructures contain Lucite crystals.
   a. True
   b. False

9. There are three general types of high-noble alloys. They are:
   a. Gold-platinum alloys.
   b. Gold-palladium alloys.
   c. Gold, copper, silver, and palladium alloys.
   d. All of the above.

10. Ruthenium (Ru), Iridium (Ir), and Rhenium (Re) are used as grain refiners.
    a. True
    b. False