Ceramo-metal alloys are “metal substructures that support a porcelain veneer” for crowns and bridges. About 85% of all crowns and bridges are still based on PFM approaches. While all-ceramic crowns (and bridges) are very popular, their real value will not be realized until the problem of brittle fracture is solved. Currently, there is very exciting research in other industries to produce woven or textured ceramic microstructures that effectively make the materials “damage tolerant.” As this technology is adopted by dentistry, there will most likely be a major shift away from PFMs toward all-ceramic materials. Most likely this will take another 5-15 years to occur, but it is imminent.
It's helpful, for a second, to consider the fabrication steps for a PFM restoration. As shown above, the actual restoration consists of the cast metal substructure AND a series of porcelain layers that are processed on top of it. Once the metal substructure has been cast, then it is sandblasted to remove the scale (or chemical debris) caused by the high-temperature reaction of the metal alloy with the investment material during casting. Normally phosphate-bonded (PBI) or silicate-bonded investments (SBI) are used for these alloys because gypsum-bonded investment (GBI) decomposes before it reaches the necessary casting temperature.

Porcelain veneering utilizes powdered ceramic. Porcelain (SiO₂-Al₂O₃-K₂O and other oxides) is ground by manufacturers. The powder is used by slurring it with water and painting the thick suspension onto the metal to create a thin film using a fine brush. The water is slowly lost leaving particles held together by weak van der Waals forces. The packing fraction of the particles is about 65% so the powdered film has 35% porosity. Heating to high enough temperatures ultimately causes the particles to partially melt (vitrification) and this allows flow and filling of the spaces between the particles to create a continuous porcelain layer. During vitrification the film shrinks 35%. This is a tremendous change in dimensions that can produce excessive distortion so it is only practical to work with thin films. Building up a porcelain veneer often takes 3-5 porcelain applications and firing cycles.

The first layer of porcelain that is applied contains reflective oxides particles (TiO₂ or SnO) to hide the metal color and reflect light back out of the porcelain. It is called the “opaque layer” or “opaque porcelain.” Next “body shades” of porcelain are added that produce colors to mimic gingival, facial, or incisal shades of dentin and enamel.

It is extremely important that the opaque layer be well-attached to the metal substructure. You will learn more about this process layer. Basically opaque porcelain takes advantage of both micro-mechanical and chemical bonding. The metal surface is rough from the sandblasting step. This permits micro-mechanical interlocking of the opaque porcelain to the metal surface. The metal alloy includes at least 0.5 to 1.0% of elements (Sn, In, Fe) that migrate to surfaces, oxidize, and create a ceramic film that can alloy with the opaque porcelain. The thin metal oxide surface lets the opaque porcelain easily flow onto it and mix (alloy) with it at high temperatures. This mixed oxide layer is the basis of chemical bonding.
The figure above represent the processing conditions involved with casting a single unit gold crown (on the left) in contrast to the processing for a PFM crown (on the right). Each portion of the figure is a plot of fabrication temperature versus time. The light blue monitors the temperature of the investment mold for the casting. The light green shows the casting alloy temperature. Light yellow shows the temperature for porcelain vitrification processes.

Start by examining the first figure which is on the left. [CLICK] For a single unit gold crown, investment material (containing the wax pattern) (light blue line) is heated in a burnout furnace at low temperature for 1-2 hours to eliminate the wax and then heated further to just below the metal alloy melting temperature to create a slightly cold mold. The alloy (dotted line) [CLICK] is heated in a crucible quickly to about 100°C which is just above the Tm for the alloy and cast into the slightly colder mold. The investment initially absorbs some heat, causing rapid solidification. Then, the entire investment and casting are quenched to room temperature.

Now examine the figure to the right. PFM restorations involve both the fabrication of a metal substructure and then subsequent addition of porcelain to create a veneer on the substructure. The metal alloy much have a Tm that is at least 100-200°C higher than the porcelain forming temperature (vitrification temperature range). [CLICK] Burnout of the wax from the investment and metal casting parallels the processes for a full gold crown just shown on the left, but arrive at a higher temperature. [CLICK] After producing the metal substructure, the casting is de-vested, the sprue is removed, the casting is cleaned, and it is sandblasted. Now it is ready for porcelain addition. Opaque porcelain is added manually as a thin layer. The prosthesis is then carefully balanced on a ceramic support pin and [CLICK] fired in a porcelain furnace to vitrify the porcelain into a real layer. [CLICK]

[CLICK] Each firing cycle is slow to minimize potential thermal stresses between the metal and porcelain. Metal conducts heat quickly away but porcelain is an insulator and cools slowly. In the right-hand diagram, the slow heating cycle is represented schematically as a long ramp up to the vitrification peak temperature and then slowly back down again to room temperature. A firing cycle can take 4-5 hours. Generally several layers of porcelain will be fired. Production of a PFM crown often requires a couple of days.
HISTORICAL BACKGROUND

A. Historical Review of Porcelain Use in Dentistry:
- 1806 - Fonzi prepared porcelain teeth with baked in Pt posts
- 1817 - Plantous introduces porcelain teeth to the US
- 1844 - SS White begins large scale production of porcelain in US
- 1854 - Loomis patents the totally porcelain denture
- 1884 - Logan makes porcelain crown with baked Pt metal post
- 1889 - Land develops the all porcelain jacket crown
- 1957 - First P/M restorations
- 1959 - Weinstein patents the P/M process for dentistry

B. Historical Review of Casting Alloys in Dentistry:
- 1870 - Cast restorations produced from gold coins
- 1907 - Taggart introduces a inlay casting technique
- 1940 - Bronze alloys replace casting gold alloys during the war
- 1968 - US allows price of gold to fluctuate on the open market
- 1970 - Large scale introduction of gold-substitute alloys

Look at the top of the first page of your handout. A brief historical review of key points in the dental history of porcelain and of metal use is listed. Let’s take a look at each of these to understand why PFM prostheses came into dentistry relatively late in the game.

Dentists were already trying to utilize porcelain as early as the 1806 but were frustrated by the extreme fragility of ceramic objects. It seemed that tiny stresses easily caused fracture. At the time, the real problem was the presence of large numbers of defects in the ceramic structures. Thus began the long search for an effective method to support or strength ceramic for dental use. It was not until 1959 that Weinstein developed a method to use metal substructures to provide support and produce the first PFM crowns.

[CLICK] While metal alloys were being cast routinely in the late 1970s, most dentistry at the time involved amalgam or vulcanite dentures. The first reliable dental casting equipment was invented by Taggart at the turn of the 20th century. Early casting alloys were low melting, high-gold alloys.

The principal challenge for combining a porcelain veneer onto a rigid metal substructure was to solve the problem of significantly different coefficients of thermal expansion (α, or LCTE). [CLICK] Porcelain has a low value, typically in the range of 11 ppm/°C, while gold casting alloy is 16-18 ppm/°C. Tooth structure is 9-11 ppm/°C. While porcelain and metal values may seem relatively close together, the difference is exacerbated by the large range of heating and cooling that is involved in fabrication process. It turns out that only 0.1 ppm/°C differences can be tolerated over large temperature ranges or else the stress that is created will easily de-bond the two materials. The solution to the problem was the production of special porcelains and alloys with “well-matched” coefficients of thermal expansion. Ceramo-metal alloys typically have values of 14.4 ppm/°C while the porcelains are 14.3 ppm/°C for most systems.
MAJOR PFM ALLOY REQUIREMENTS

1. **Physical Properties:**
   a. High fusing temperature to prevent distortion in porcelain bake
   b. Matched LCTE of porcelain and metal

2. **Chemical Properties:**
   a. Chemical bonding between porcelain and oxide layer on metal
   b. Chemical corrosion resistance (no tarnish)
   c. Electrochemical corrosion resistance
   d. No porcelain discoloration reactions

3. **Mechanical Properties:**
   a. High E (= stiffness) (e.g., E = 90 to 220 GPa) (Space for ceramic esthetics, but metal thickness for rigidity)
   b. High Hardness (H = 125-465 kg/mm²) (Need metal to be capable of being ground and polished)

4. **Biological Properties:**
   a. Non-toxic
   b. Non-irritating

Technically the category of metal alloys are designated ceramo-metal alloys. However, there are quite a number of synonymous slang terms that have evolved. Since the metal and ceramic need to be bonded, the restorations are often called “porcelain-fused-to-metal” or PFM alloys.

Overall, there are 5 major requirements for a good PFM alloy are: (1) high melting temperature, (2) properly matched LCTE, (3) good bonding (both micro-mechanical and chemical), (4) good corrosion resistance, and (5) high modulus. These are underlined above in the list of physical, chemical, mechanical, and biological properties. The reasons for each are explained as follows.

1. [CLICK] A high melting temperature allows the alloy to resist sagging during the multiple firing processes for porcelain applications. Remember that the stress-strain curve for a solid changes as you elevate the temperature. Effectively the stress-strain curve tips over toward the right and begins to include more and more plastic deformation. At high temperature, the hot metal substructure is not very strong but must resist sagging during the porcelain firing. The greater the difference in Tm between the alloy and porcelain, the greater the relative sag resistance.

2. [CLICK] A matched LCTE is necessary to avoid interfacial stress during processing (i.e., heating and cooling) that could de-bond the porcelain from the alloy.

3. [CLICK] Good bonding is necessary to insure the PFM prosthesis retains its integrity and effectively transfers stresses from porcelain to metal. The metal substructure must be stiff to keep the porcelain from flexing. The PFM bond should transfer the stress. The alloy (before porcelain application) is normally sand-blasted to provide some surface roughness for micromechanical bonding. However, chemical bonding is required as well. To get porcelain to bond to metal, the alloy is doped with special elements (Sn, In, or Fe) that preferentially migrate to the alloy surfaces, oxidize, and cling tightly to the alloy. This oxidized surface then becomes alloyed with the porcelain oxides connecting the two materials. Only about 0.5 to 1.0% of oxidizing elements are required but as much as 10% can be added in certain cases. [CLICK]

4. [CLICK] Good alloy corrosion resistance is crucial or otherwise crevice corrosion would undermine the porcelain. Either gold-based or passivating alloys are used. These will be discussed in more detail shortly. [CLICK]

5. [CLICK] High modulus (i.e., stiffness, slope of the elastic region of the stress-strain curve) is necessary to prevent deformation of the porcelain that would create cracks and rapidly lead to fracture. Stiffness of the substructure depends a combination of both metal modulus and metal thickness. If no metal at all were included in the design of the prosthesis, the resulting all-ceramic restoration would need to be much thicker to resist strains. This will be considered at a later time when all-ceramic restorations are discussed. [CLICK]
CLASSIFICATION OF ALLOYS

1. Full Gold Crown and Bridge Alloys (REVIEW of precious alloys)
   a. ADA Classification System (see phase diagrams)
      (1) Type I  ≥ 83% Au+ (Non-heat hardenable) -- inlay
      (2) Type II ≥ 78% Au+ (Non-heat hardenable) -- inlay, onlay, ...
      (3) Type III ≥ 78% Au+ (Heat hardenable) -- onlay, crown
      (4) Type IV ≥ 75% Au+ (Heat hardenable) -- crown, bridge

   b. Effects of Alloys Components:
      (1) Gold (Au) → corrosion resistance
      (2) Copper (Cu) → increased hardness
      (3) Silver (Ag) → counteracts orange color of copper
      (4) Palladium (Pd) → increased MP and hardness
      (5) Platinum (Pt) → increased MP
      (6) Zinc (Zn) → oxygen scavenger

On the second page of your handout, you will notice that much of included information is a review from discussions of “gold casting alloys.” For a moment reconsider the reason for putting various elements in (low temperature) gold casting alloys. Gold produces corrosion resistance (or immunity). Copper produces solution hardening but also alters the color to appear more orange-like. Silver is added to counteract the orange effect of copper. Pt and Pd elevate the melting point slightly but simultaneously increase the hardness. Zinc is added as a sacrificial element (or scavenger) to produce a ZnO film over the melt during the manufacturing process and protect the rest of the alloy from unwanted oxidation.
CLASSIFICATION OF ALLOYS

2. Other Crown and Bridge Casting Alloys:

a. ADA Classification System (see phase diagrams)
   (1) High-gold alloys (IMMUNE)
       (a) Au-Pt-Pd
       (b) Au-Pd-Ag
   (2) Low-gold alloys (SEMI-IMMUNE)
   (3) Gold-substitute alloys (PASSIVE)
       (a) Ag-Pd (85% of all PFM alloys)
       (b) Pd-X
   (4) Base-metal alloys (PASSIVE)
       (a) Ni-Cr (with or without Be)
       (b) Co-Cr
       (c) Fe-Cr
   (5) Titanium alloys (PASSIVE)
   (6) Other alloys – Al Bronzes, Brasses (ACTIVE)

Au–Pt–Pd → Au-Pd-Ag → Pd-Ag → Pd-X → Ni-Cr ...

Now consider what changes are required to convert the design of a low-temperature casting alloy into a higher-temperature melting one. One still needs corrosion resistance so the options must be either immune or passive alloys. [CLICK]

Copper, zinc, and sometimes silver are removed. Copper is unstable at higher temperatures and too prone to oxidation. Zinc is much less effective as a scavenger for higher-temperature melting alloys but may still be present in small quantities. Silver is prone to oxidize but often remains in the composition because it is cheaper than Pt or Pd. This results in two principal high-gold ceramo-metal alloy categories [CLICK] [CLICK] (and the ADA classifies them as Type 1 and Type 2). The first is based mostly on Au with some Pt and Pd (Au-Pt-Pd). The second contains some silver (Au-Pd-Ag).

Low-gold alloys can be formulated by decreasing the Au concentration substantially. While these have a gold color, their corrosion resistance is much poorer. These are not legal for use in the US but are used in other countries.

[CLICK] To cheapen the price of these compositions (Au and Pt are expensive and are removed), Pd-Ag alloys are used. These are now called “gold-substitute alloys” because they do not contain gold but are relatively immune. They are conferred with corrosion resistance because Pd can form Pd-O as a protective passivating film but the alloys are also relatively corrosion resistant. This category represents almost 85% of all the alloys used for PFM restorations. You can state the name as Pd-Ag or Ag-Pd (silver-palladium). [CLICK] Elements other than silver will work as well to form similar alloys (Pd-X).

[CLICK] Further cost reductions are possible by shifting to base-metals (rapidly corroding) which produce passivating oxides. The three major categories are Ni-Cr, Co-Cr, and Fe-Cr (or stainless steel). They all produce passivating Cr₂O₃ oxide films on their surfaces. All three have high moduli but also are very high melting. Generally, laboratory technicians find these alloys difficult to process because of their hardness and prefer to use Pd-Ag instead.
CLASSIFICATION OF ALLOYS

2. Other Crown and Bridge Casting Alloys (cont):

b. Effects of Alloying Components in Gold Alloys:
   (1) Au, Ag, Pd, Pt → corrosion resistance
   (2) Pt → increased MP
   (3) Pd → increased MP and hardness
   (4) Ag → cheaper
   (5) Fe, In, Sn → oxide formers for gold alloys
   (6) Zn → oxygen scavenger

c. Effects of Alloying Components in Other Alloys:
   (1) Cr, Ti → oxide formers in other alloys
   (2) Ni, Co, Fe → increased modulus

The functions of the elements in ceramo-metal alloys are very similar to those for gold casting alloys. The precious elements (Au, Ag, Pd, Pt) contribute corrosion resistance. Pt and Pd have a strong influence on the final melting point. At gold is replaced with Ag the composition becomes lower cost. In gold casting alloys, Ag was used primarily to counteract the orange color induced by copper additions. It is not needed for that purpose in ceramo-metal alloys but is still useful as a substitute for Au. To insure that the cast ceramo-metal alloys will produce a consistent oxide on the surface for chemical bonding with porcelain, any of several special elements (Fe, In, Sn) may be present. Gold actually contains small quantities of Fe as contaminants, but this is not a dependable concentration of Fe so more is generally added. In and Sn are more commonly used and may represent up to 10% of the overall composition. Zn may still be present as an oxygen scavenger. However, it is much less efficient since it may be entirely consumed by the time the higher casting alloy temperatures are reached for these systems. Most of these alloys are casting in induction casting or other special machines that may use nitrogen or argon gas to suppress oxidation reactions.

In base-metal alloys, a passivating oxide film is responsible for corrosion protection. The film occurs because of 18-28% Cr additions that allow the formation of Cr₂O₃. With Ti or Ti-6Al-4V alloys, TiO₂ forms and provides passivation. The other elements in these compositions are also capable of forming oxides but are protected by the passivating oxides.

At the bottom of the slide above, is a schematic picture of the metal, metal oxide (passivating film), opaque porcelain, and body porcelain layers that are part of a PFM restoration. The inset SEM images reveals that in addition to the chemical bonding (oxide mixing between the passivating oxide and opaque porcelain), that there is good micromechanical bonding between the metal substrate and the opaque porcelain. It is difficult to identify the passivating oxide film that exists over the metal and under the porcelain in the SEM view.
SPECIAL TERMINOLOGY

1. Color of Alloys:
   a. **White-Gold** = White color due to higher concentration of Pt or Pd.
   b. **Yellow-gold** = yellow color due to presence of copper and/or gold.

2. Synonyms for Ceramic-Metal Restorations:
   a. Porcelain Fused to Metal (PFM)
   b. Porcelain Bonded to Metal (PBM)
   c. Ceramo-Metal Restorations
   d. Porcelain-Metal Restorations (P/M)

The high-gold compositions still have a gold-like color, but they are appreciably whiter due to the Pt, Pd, or Ag additions. These are called white-golds and are more expensive than traditional yellow-gold compositions. White golds are often used in jewelry.

[CLICK] We have been employing the acronym PFM ("porcelain-fused-to-metal") but, as mentioned earlier, there are a number of other terms that mean the same thing. PBM is the acronym for "porcelain-bonded-to-metal." C/M is the short-hand for "ceramo-metal" restorations. P/M is short-hand for "porcelain-metal" restorations. They all denote the same thing and can be used interchangeably.
Above are examples of alloys that fall within the high-gold, gold-substitute, and base-metal alloy compositions. The most important thing to realize is that as the Tm increases, the alloys become better in sag resistance, are stiffer, and are harder. However, it is more difficult to cast and then finish them in dental laboratories. Hardness is an estimate of the elastic limit (e.g., onset of plastic deformation) and can be measured using indenters (e.g., Knoop hardness indenter produces a Knoop hardness number, KHN, which measures the hardness value in kg/mm²; Brinell hardness number, BHN). As the numbers go up, they represent increasing hardness (increasing elastic limits). The ones shown in the table are all well above those for low-temperature gold casting alloys.

Ni-Cr alloys are extremely hard and melt at very high temperatures. That is why they are routinely used as toaster wire (the metal elements within your toaster that heat up during its operation). Ni-Cr alloys for dentistry and for toaster wire are both 80Ni-20Cr. Corrosion resistance is imparted by formation of both Cr₂O₃ and NiO passivating oxides in the surface film.
Quickly look at some of the many commercial alloy compositions. There are numerous manufacturers and, for the most part, they routinely duplicate each other's compositions. There are almost no alloys that are any longer protected by US patents. Their 17-year protection has long since elapsed. Two examples are highlighted for closer consideration. [CLICK]

Will-Ceram (company name) W-1 (alloy name) contains 53.5% Pd and 37.5% Ag. [CLICK] To what category of alloys does it belong? Look at the components to figure this out. It is a Pd-Ag alloy. To what total does the compositional percentage add up? The total is only 91% -- because other elements such as In, Sn, etc. are generally not reported as details in these sort of lists.

[CLICK] Now look at the next alloy. Olympia is also PFM alloy (or ceramic alloy) that is white in color. To what category does it belong? It is a high-gold (Type 2) alloy. It contains 51.5% Au and 38.5% Pd. Most likely it also contains 10% In as the balance. Not all Au-Pd-Ag alloys must contain silver. The reason that it is not a Au-Pt-Pd alloy without Pt is that it contains a lot of Pd. Type 1 alloys have higher gold levels and less Pd.

Finally, all of these alloys tend to be less dense (10-14 g/cc or gms/cm³) than low-temperature gold casting alloys (16-18 gms/cm³) and are a little bit more difficult to cast. Therefore, they are processed in pressure/vacuum casting machines to push behind the molten alloy and pull ahead of the alloy to force it into the investment mold space.

Currently the price of Pd is rising and that of Au and Pt are decreasing. Therefore, there is some economic pressure for laboratories (and dentists) to use more of high-gold alloys. That has not happened yet. Differences in costs allow labs or dentists to actually make more profit. None of this profit is actually passed along to the patient.
The key to understanding these alloys is remembering the classification systems, their overall requirements, and the effects of different alloying elements on the processing and final properties. Thank you.