It is now time to consider the important characteristics of gold casting systems. This and other information can now be referenced directly from the DENTAL MATERIALS home page [CLICK] as well as the electronic syllabus.
To produce an enduring gold restoration for dentistry, requires the production of strong gold alloys and establishment of suitable fabrication procedures.

Gold has been used in jewelry and early efforts at dentistry for several thousand years – primarily as gold foil. The procedure for building up anything of much thickness or detail is relatively slow. Pure gold is also very soft.

Gold casting alloys have been used readily in dentistry since the mid-1800s but the alloys were inconsistent in composition and the procedures were crude at best. At the turn of the century in 1900, the lost-wax process took center stage with the invention of the centrifugal casting machine and the availability of electricity for electric motors and furnaces.

[CLICK] The lost-wax process is simply the construction of a wax pattern to make a mold so that molten alloy can be cast into an accurate mold space. 
[http://www.ada.org/public/topics/history/timeline_20cent.asp] You can go to the website on the bottom of this page to investigate it further.

During the first half of the 20th century, alloy compositions evolved and casting processes became more sophisticated. Cast gold restorations became the primary choice for situations in which a large amount of lost tooth structure was being replaced.
INDIRECT RESTORATIONS
Review of Errors

ERRORS:

- Impressions: 0.1 to 0.2%
- Models/Casts: -----%
- Waxing: -----%
- Investing: +1.5 to 1.7%
- Casting: -1.5 to 1.7%
- Finishing/Polishing: -----%
- Cementing: -----%

Calculation of ideal permissible error:

\[ \frac{2 \times 25 \, \mu m}{10,000 \, \mu m} = 0.5\% \]

All of the steps involved (impressions, models/casts, waxing, investing, casting, finishing/polishing, and cementing) potentially involve errors that can become compounded as we have considered before. [CLICK] Because casting includes significant dimensional changes during cooling from the casting temperature to room temperature, it is paramount that the investing process produce the proper oversize mold space to cancel out the shrinkage effects. Under the proper conditions, this will occur.

The overall error is directly related to the amount that can be accommodated in the final step of cementation. If one were to assume that 50 \( \mu m \) of cement film thickness (25 \( \mu m \) per side) were ideal for a 1 cm (10,000 \( \mu m \)) wide cast crown, [CLICK] then the overall error that could be accepted would be 0.5\%. Cementation fills in the error spaces between the oversize of the casting and the walls of the cavity preparation.

For crowns, errors tend to be in the direction of producing an oversize crown. This is easily accommodated by the dental cement. However, for an inlay this may lead to some difficulties in seating the restoration.
GENERAL REQUIREMENTS

0. Fabrication requirements vs final properties:

1. Physical Properties:
   a. Reasonably low MP (flow)
   b. Moderately high density (castability) →

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (gms/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>12.45</td>
</tr>
<tr>
<td>Gold</td>
<td>18.88</td>
</tr>
<tr>
<td>Palladium</td>
<td>12.02</td>
</tr>
<tr>
<td>Silver</td>
<td>10.50</td>
</tr>
<tr>
<td>Copper</td>
<td>8.96</td>
</tr>
<tr>
<td>Cobalt</td>
<td>8.90</td>
</tr>
<tr>
<td>Nickel</td>
<td>8.90</td>
</tr>
<tr>
<td>Iron</td>
<td>7.87</td>
</tr>
<tr>
<td>Chromium</td>
<td>7.17</td>
</tr>
<tr>
<td>Iron</td>
<td>7.87</td>
</tr>
</tbody>
</table>

   c. Low coefficient of thermal expansion (α) →

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient ppm/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tooth</td>
<td>9-11</td>
</tr>
<tr>
<td>PFM alloys</td>
<td>14</td>
</tr>
<tr>
<td>Gold alloys</td>
<td>18</td>
</tr>
<tr>
<td>Amalgam</td>
<td>25</td>
</tr>
<tr>
<td>Composite</td>
<td>35-45</td>
</tr>
</tbody>
</table>

2. Chemical Properties:
   a. Chemical corrosion (tarnish) resistance
   b. Electrochemical corrosion resistance
   c. Solubility (solderability)

Since gold casting alloys are fabricated in a dental laboratory (indirect procedure) rather than in-the-mouth, there are requirements involving ease-of-fabrication, as well as requirements for final intraoral properties. Categories of physical, chemical, mechanical, and biological properties will now be reviewed.

Gold alloys need to have a relatively low melting temperature so that simple heating equipment can be used for casting. The process is one of creating a mold of ceramic composition and then casting the alloy into the space.

Dental restorations (inlays, onlays, crowns, bridges, partials) usually include fine surface details. It is important to force the molten alloy into the mold firmly against the mold walls with sufficient force (or pressure) that the alloy adapts well to all the intricacies and fills up the mold space. [CLICK] An alloy of high density is easier to cast in low-cost centrifugal casting machines. Gold has high density (approximately 18 gms/cm³) and works well. Most of the other alloying elements that we use are not as helpful.

Once cast, the restoration shrinks while cooling as dictated by its coefficient of thermal expansion/contraction (LCTE or α). [CLICK] Gold has a moderate to low LCTE (18 ppm/°C) but when cooled over about 900°C it still produces a significant contraction. See the table above for comparisons to other materials.

Obviously, a primary requirement is excellent intraoral corrosion resistance (both chemical and electrochemical). Since high gold containing alloys are immune systems (rather than passive or active) they are a good starting point. Even under conditions that encourage electrochemical corrosion (local galvanic corrosion, crevice corrosion, stress corrosion), the corrosion rates for gold alloys are very low. These details will be reviewed shortly.
To insure that no elastic or plastic deformation will take place in service, it is key that the alloy have a high modulus and high hardness. At the same time, some elongation is desirable for finishing and polishing. Once mechanical shaping procedures are completed in the lab it is preferable to heat harden (disorder-order or other procedures) the alloy before final cementation.

The mechanical properties [CLICK] can be easily summarized in terms of stress-strain diagram for the alloy. [CLICK] Consider the white curve first. The straight portion of the curve indicates the proportional behavior of strain in response to stress that is characteristic of totally elastic deformation. The slope or steepness of this line indicated the stiffness (modulus or resistance to straining) of the material. Clinically, it is important to have a material with a high modulus. At some point (e.g., the white dot), plastic deformation occurs in combination with continuing elastic deformation. This point (elastic limit, proportional limit, yield strength, or hardness) show be as high as possible. Once plastic deformation starts to occur their will be a point at which fracture follows. It is important that plastic deformation not occur clinically. If it does, then it is preferable to have as much chance to deform before fracture. Thus the ultimate strength should be as high as possible.

If the white curve is assumed to represent the as-cast condition of the alloy, [CLICK] then the yellow line might represent the new mechanical properties for a heat-treated prosthesis. Some alloys are hardenable by heat treatment after all the fabrication steps are completed. As will be discussed later, the prosthesis is heated to 200-300°C for 30-60 minutes to allow the atoms to organize themselves into a low energy

Finally, it is critical that the elements in the alloy not be released by corrosion or wear procedures at levels that could be considered toxic to a patient. All metal elements and ions could be toxic at sufficient levels but are generally not a problem for dentistry. However, some low gold systems are more prone to corrosion and may be suspect.
A quick review of corrosion is provided above. Corrosion either occurs as chemical corrosion or electrochemical corrosion. Chemical corrosion is a direct bimolecular reaction. Electrochemical corrosion is an indirect reaction involving at least a pair of half-cells with oxidation at one half-cell and reduction at the other.

[CLICK] The principal requirements for electrochemical corrosion are the presence of an identifiable anode, cathode, circuit, and electrolyte. [CLICK] Despite the fact that alloys may be relatively resistant (immune) to chemical and electrochemical corrosion, electrochemical cells may make them susceptible to slow corrosion events. While electrochemical corrosion may involve as many as a dozen mechanisms, [CLICK] the four major ones are galvanic, local galvanic, crevice, and stress corrosion.

[CLICK] In galvanic corrosion situations, the gold alloys are the cathodes (e.g., an amalgam touching a cast gold restoration) and are not threatened. Under most circumstances, gold alloys are fabricated with only one microstructural phase present. However, to take advantage of precipitation hardening for more extreme mechanical situations (e.g., some bridges and partial dentures), a second phase is often precipitated. But this second phase now permits local galvanic corrosion to occur. One phase acts as a local anode while the other is the local cathode. This leads to pitting over the long term.

Plaque encourages corrosion as well (crevice corrosion) and causes pitting. Quite often the facial surfaces of casting, especially near gingival margins, begin to looks dull over 15 to 20 years due to the effects of pitting. Plaque suppresses the local pH and pO₂ in comparison to other uncovered portions of the restoration surface. Since the local electrolytes are different, the surface under the plaque behaves as an anode by comparison and undergoes corrosion.

Lastly, during function mechanical stresses are not distributed equally throughout a restoration. High stresses occur at the points of occlusal contact and near margins (where the stresses are transferred). Those regions that experience the highest stress behave as anodes and are more prone to electrochemical corrosion (stress corrosion).
CLASSIFICATION OF ALLOYS

1. Full Gold Crown and Bridge Alloys (based on precious metals)

   a. ADA Classification System (see phase diagrams)
      (1) Type I \( \geq 83\% \text{ Au} \) (Non-heat hardenable) -- inlay
      (2) Type II \( \geq 78\% \text{ Au} \) (Non-heat hardenable) -- inlay, onlay, ...
      (3) Type III \( \geq 78\% \text{ Au} \) (Heat hardenable) -- onlay, crown
      (4) Type IV \( \geq 75\% \text{ Au} \) (Heat hardenable) -- crown, bridge

   b. Effects of Alloys Components:
      (1) Gold \( (\text{Au}) \) \( \rightarrow \) Corrosion resistance
      (2) Copper \( (\text{Cu}) \) \( \rightarrow \) Hardness
      (3) Silver \( (\text{Ag}) \) \( \rightarrow \) Counteract orange color of copper
      (4) Palladium \( (\text{Pd}) \) \( \rightarrow \) Increase MP and hardness
      (5) Platinum \( (\text{Pt}) \) \( \rightarrow \) Increase MP
      (6) Zinc \( (\text{Zn}) \) \( \rightarrow \) Prevent oxidation during melting \( (\text{O}_2 \text{ getter}) \)

Look at the second page of your handout. Gold alloys traditionally have been classified into 4 types by the American Dental Association on the basis of their application. Type I have been typically used for inlays. Since they require less mechanical strength, they can be made of a higher-gold alloy and are not capable of being hardened. Type II alloys are used for larger inlays and/or onlays. Type III alloys are generally in the range of 78% gold in the compositions, are hardenable by disorder-order reactions, and are used for large onlays and crowns. Type IV alloys are hardenable and contain two phases as well. While they can be used for crowns, they are most often used for bridges. The hardenability will be more obvious when we review Au-Cu phase diagrams shortly.

There are several reasons for putting various elements in (low temperature) gold casting alloys.

[CLICK] Gold produces corrosion resistance (or immunity). [CLICK] Copper produces solution hardening but also makes the color appear more orange-like. [CLICK] Silver is added to counteract the orange effect of copper. [CLICK] Pt and Pd elevate the melting point slightly [CLICK] but increase the hardness as well. [CLICK] Zinc is added as a sacrificial element to produce a ZnO film during the manufacturing process while the alloy is in molten form.
TERMINOLOGY

1. Precious Metal = containing metals of high economic value such as gold, platinum, palladium, silver, (rhodium), (iridium), (ruthenium), and (osmium).

2. Noble Metal = a precious metal that is resistant to tarnish. This excludes “silver” by definition.

3. Low Gold Alloys = Alloys containing <75% gold (less than 50 a/o gold) which means that gold atoms represent less than every other atom.

4. Gold-substitute Alloys = precious metal alloys not containing gold.

5. Base-Metal Alloys = alloys not containing precious metals to impart their corrosion resistance.

Several terms are used frequently when describing the elements or compositions for casting alloys. Make sure that these are well-understood.

[CLICK] Precious metals (or elements) refer to those that are of high economic value (i.e., are most expensive). All of these except silver are also noble metals. [CLICK] Nobility has the same meaning as corrosion and electrochemical corrosion resistance. Since silver is prone to tarnish, it is not included under this definition.

[CLICK] Low gold alloys are ones that include less than every other atom as gold (<50 atomic percent). At these lowered Au contents, the material is much more corrosion prone but certainly less expensive. Low gold alloys may contain as little as 8-10% Au while still retaining some gold appearance overall.

[CLICK] Gold-substitute alloys eliminate gold from the composition but attempt to select other precious metal combinations that will still retain corrosion resistance. The most popular of these is Ag-Pd and will be discussed later.

[CLICK] Finally, corrosion-prone alloys (base metals) can be used if there is a tendency to generate a protective oxide film on their surfaces which prevents continuing corrosion. They do not contain precious metals in the alloy that could impart corrosion resistance.

Alloys that are used for full cast alloy crowns and bridges must be modified to create PFM restorations. These will be discussed at a future date. The primary requirement for these other alloys is that they melt at a higher temperature to withstand the high temperatures associated with the porcelain application procedures.
Gold is not used as a pure material for restorations because it is too soft. It is always alloyed with copper to generate sufficient mechanical strength (hardness). Events related to alloying levels and effects are well-described by phase diagrams. The phase diagram above is a binary (Cu-Au) phase diagram (2 components). The diagram which follows is a ternary phase diagram (3 components). These two diagrams are used to summarize the temperature versus composition events which occur in gold based systems.

In the binary phase diagram above, we are assuming that Au and Cu alone can be used to describe the overall behavior of a more complicated alloy (Au-Cu-Ag-Pt-Pd-Zn) since these are the two dominant alloying elements. Pure Cu and Au are represented by the vertical lines at the extreme edges of the diagram. Temperature is reported from 0°C (just below room temperature) to about 1100°C. The horizontal axis at the bottom of the diagram reports the range of possible Cu and Au alloying mixtures in atomic percentage. [CLICK] The weight percentages for these are shown at the top of the diagram. [CLICK] It is important to recognize that 50 atomic percent Au-Cu is equivalent to 75 percent Au-Cu. As one drops below a level of every other atom being gold, then the tendency toward corrosion dramatically increases. Therefore, the lower level for high-gold alloys is 50 atomic percent (75 weight percent) Au. [CLICK]

[CLICK] The curved lines connecting the melting points of Cu (1060°C) and Au (1050°C) define the region above (liquid) and below (solid). The region in between them encompasses the liquid plus solid transitional areas. Note that the lowest melting range for a Cu-Au (or Au-Cu) composition is about 50 to 60 atomic percent (75 to 82 weight percent). [CLICK] This is also the same general range that is chosen for gold alloy compositions for use in dentistry.

Once a molten alloy hardens in the mold space of the investment, the atoms are only randomly situated within the crystals. [CLICK] However, if the mass is cooled slowly enough, then there is a strong tendency around 400°C for the atoms to arrange themselves in a pattern so that every other atom is Au. This is called disorder-order hardening. [CLICK] If cooling occurs quickly then there is no time for this to happen. Most alloys are quenched to prevent this from occurring initially so that the alloy is in the soft condition for manipulation such as sprue removal and finishing or polishing. After manipulation and before cementation the alloy can be heat treated at 200-300°C for 30-60 minutes to allow the transformation to occur.
Instead of using simply a Cu-Au phase diagram to represent the overall alloy, we could have selected a Cu-Au-Ag diagram instead. However, ternary phase diagrams are much more complicated since they are 3-dimensional solids. Therefore, we will examine a constant temperature (room temperature) cut through the solid to point out a couple of other features of gold alloys. On the diagram above, the corners of the isothermal cut represent the pure elements and the atomic percents of components in the mixture are measured along the sides of the triangle. [CLICK] Only the details for the Au-rich corner are shown.

[CLICK] A line is drawn from pure Ag to pure Cu that separates a region in which the alloy only forms a single phase (single type of crystal, $\alpha$) from a much bigger region in which two phases (two crystal types, $\alpha + \beta$) occur. A 2-phase alloy is stronger because of the effect of the second phase but it is also more corrosion prone because of the opportunity to create local anodes and cathodes. Longer span bridges are usually made from 2-phase alloys, choosing strength over corrosion resistance.

Marked on the diagram above are two circular zones that include most gold alloy compositions. [CLICK] The one at the top includes all the ADA Type I, II, and III systems (which are all single phase solids). [CLICK] The zone below includes 2-phase alloys that are ADA Type IV systems.
An extensive list of commercial examples of casting alloy compositions is presented in the handout. Most gold alloy compositions are not patentable or their patents expired many years ago. Therefore, companies are free to duplicate each others compositions freely. The list shows a large number of very similar or equivalent products. In most cases, your laboratory prescription will simply state the ADA Type that is required (e.g., Type I, II, III, or IV) for the procedure. Most contemporary laboratories cast everything from either Type III or IV. In the absence of any special instructions, they will normally choose Type III. You may indicate a particular product that you prefer, but they may also substitute an equivalent one that has the same composition.

Examine the examples presented in the slide above. [CLICK] Looking at Modulay you will quickly discover that this is a Type II gold alloy. It has 78% noble metal content (77% Au and 1% Pt). The total precious metal content (Au, Pt, Pd, and Ag) is 92%. The remaining 8% is the non-precious content and is almost entirely Cu. Generally about 0.3-0.5% Zn will be included.

[CLICK] Firmalay is representative of a Type II gold casting alloy with 78% noble metal and 11% Cu.

All high gold compositions will be relatively dense (15-17 gms/cm³) and thus easy to cast by centrifugal techniques.
The figure presents a schematic summary of the processing conditions involved with casting a single unit gold crown.

[CLICK] Investment material (containing the wax pattern) (see the dotted line) is heated in a burnout furnace to eliminate the wax. Then it is elevated to a temperature just below the melting temperature for the metal alloy to create a slightly cold mold. [CLICK] The alloy (dotted line) is heated in a crucible quickly to about 100°C above the Tm for the alloy and then cast into the mold. The investment absorbs some heat causing rapid solidification and then the entire investment and casting are quenched to room temperature.
CASTING PROBLEMS
for Gold Alloys

A. Distortion:

1. Margins: Probability highest in thinner portions of pattern.
   a. Wax Deformation: improper removal or handling of pattern.
   b. Premature Quenching: wait until button loses red color.
   c. Investment Expansion/Contraction:

There are three general categories of problems that may arise during fabrication processes for cast alloys.

The first is related to distortion of the overall shape of the prosthesis. [CLICK] This is most easily exemplified by considering the fabrication process for a crown, as shown above. Wax may inadvertently become deformed in the thinner portions of the wax pattern (e.g., margin) during removal from the die. During investing, the setting of the investment material produces localized expansion and contraction that may push on thinner portions of the wax pattern. Finally, during casting and quenching, it is critical that quenching not occur until the entire alloy is solidified. Generally this only takes 1-2 minutes. The alloy solidifies initially on the walls of the mold space and then transfers heat from the molten interior through the solid to the investment. As soon as everything is below the melting point, then quenching can proceed. This is easily identified as the loss of redness or glow of the sprue button when one looks into the end of the investment.
The second category of casting problems is associated with surface irregularities.

[CLICK] No casting will have a truly smooth surface. It is limited to the texture of the investment material itself. Investment is composed of filler particles bound together by a matrix of crystals. Whatever that surface texture is [CLICK] will be reflected onto the casting.

[CLICK] In addition there may be some unusual outcroppings of alloy. If the wax pattern was not carefully coated with a very thin film of de-bubbler (usually a soap solution), then small bubbles may occur where the investment does not wet the wax pattern particularly well. These bubbles will be preserved in the casting as small nodules along the surface. [CLICK] They can be easily removed but do create more work for the laboratory technician during finishing and polishing steps. Investment materials are predominantly water based. While the mixture should be homogeneous prior to setting, it is possible that water may segregate along the wax pattern surfaces. This will make the casting slightly larger and produce local ridges or veins. [CLICK] Again, this can easily be removed but is more work.

[CLICK] Finally, veins may appear due to gold alloy penetrating into cracked sections of the investment. [CLICK] During either heating to the point of casting or during initial casting, decomposition of the investment will generate cracks. If they occur before casting, the alloy will invade the crack and generate a fin.
CASTING PROBLEMS
for Gold Alloys

C. Incomplete Castings:

1. Internal Porosity: due to improper solidification.
   a. Improper Spruing: Diameter too small or too long.
   b. Low Temperature: Investment or metal too cold.
   c. Included Gases: Contaminated gold or oxidized old gold.
   d. Occluded Gases: Improper burnout of pattern.

2. Incomplete External Shape:
   a. Insufficient casting pressure.
   b. Excessive back pressure from investment.
   c. Suck back into sprue.

The third category of casting problems includes events leading to incomplete castings. This may lead to missing pieces of the pattern or internal voids. The latter can be easily remedied by simply filling in the voids or pores with gold solder, as long as the repair is not in a critical portion of the casting such as a margin, functional contact area, or proximal contact.

[CLICK] Internal porosity is often undetected. [CLICK] Unless a void or pore is at or near the surface it will not be discovered during the finishing and polishing process. There are a variety of causes as reviewed above.

[CLICK] Incomplete castings occur when there is inadequate pressure to force the molten alloy into the intricate portions of the pattern or gas within the mold space cannot be efficiently expelled into the void volume of the investment. [CLICK] Occasionally the material in the sprue hardens sooner than the rest of the pattern, [CLICK] sucking or drawing the molten alloy back toward it. Unfortunately, incomplete casting requires that the process of waxing, investing, and casting be redone.
Thank you.