

# Dental Materials and Their Selection

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Third Edition

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# High-Temperature Investments

The main use of high-temperature **investments** is for casting dental alloys that need to be heated to casting temperatures in excess of about 1,200°C to 1,300°C (2,192°F to 2,372°F).<sup>\*</sup> Alloys that fit this description include many high-gold and palladium-based alloys used for the fabrication of porcelain-veneered fixed partial dentures and those dental alloys based on nickel, cobalt, or titanium. These investments are also used for creating **fixtures** that hold sections of prostheses in proper apposition while joining them together during soldering, brazing, or welding operations.

These investments are not gypsum based, as are those used for the casting of alloys that have casting temperatures less than approximately 1,200°C (2,192°F), but instead have a variety of basic formulations that are better suited to withstand exposure to high temperatures. The predominate compositions, used for the casting of high-temperature alloys and for creating veneering dies, are based on the use of a phosphate binder. Silicate-bound systems are also used (Kondic, 1960), but because of their difficult handling, their use tends to be restricted to the casting of cobalt-chromium alloys at temperatures above 1,425°C (2,600°F).

Either entirely new systems or modifications of the aforementioned ones have been needed for the casting of titanium-based alloys. These alloys require special investments because they are cast from higher temperatures than the others and are also highly reactive. They can easily degrade the more conventional molds at elevated temperatures and, as a result, produce poor surface finishes. Further, they can be contaminated by degradation of the investment components, such as silica and carbon, and by oxygen and nitrogen present in

the atmosphere. These contaminations serve to harden and embrittle the surface of titanium castings. Because of the developments of investments for the casting of titanium alloys for dental applications, a separate section is devoted to this subject.

## Phosphate-Bonded Investments

### Applications

#### Casting of alloys

Phosphate-bonded investments have been used for many years in dentistry to make **molds** into which high-melting-temperature dental alloys were cast. There are two types of casting investments. Type I traditionally has been employed for the casting of inlays, crowns, and other restorations, especially for alloys based on gold, platinum, palladium, cobalt-chromium, and nickel-chromium, to which porcelain is fused in the construction of esthetic fixed restorations. Type II is used for the casting of removable partial dentures. These applications are still in use, but the number of alloy applications has grown. Some variations are used for cast titanium alloys, discussed later in this chapter.

For the burnout process of the conventional Type I investment for inlays and crowns, it is recommended that the mold be set in a furnace at room temperature, 1 hour after trituration, heated to 800°C (1,471°F)

<sup>\*</sup>Casting temperature is approximately 65°C to 150°C (150°F to 300°F) above the top of the melting range for most dental alloys.

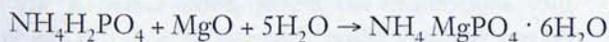
over 1 to 2 hours (depending on the size of the mold) and held at 800°C for 30 minutes before casting. Recently, newer investments that allow insertion of the set investment directly into a furnace at the burnout temperature (800°C) have been developed. These investments are inserted 30 minutes after the powder has been mixed with the liquid.

### Soldering and porcelain veneering

Another traditional use of phosphate-bonded investments is to make “soldering” fixtures that hold prosthetic components in alignment while they are being joined with solders, brazing alloys, or welding alloys. Since around 1980 modifications have been used to make **refractory** dies for the fabrication of custom veneer facings from dental porcelains.

### Composition

These investments are available as two-component systems that react to form a solid when mixed together (Takahashi et al, 1990). One component consists of a powder, and the other is an aqueous solution stabilized with **colloidal** silica. The powder has a variety of ingredients. There are particles of refractory materials such as quartz, cristobalite, or a mixture of the two, in a mass fraction of about 80%, to control **thermal expansion** and thermal stresses related to thermal phase transformations of cristobalite, and, along with glasses and other metal oxides, to provide bulk and help control the surface finish of a casting. There is also powdered ammonium dihydrogen phosphate,  $\text{NH}_4\text{H}_2\text{PO}_4$  (provided in excess), which, in reaction with water in the presence of **calcined** magnesium oxide (MgO) powder (another ingredient), provides for the binding of the particles at ambient temperatures. The liquid provides the water needed for the room-temperature setting reaction. The setting reaction of the  $\text{NH}_4\text{H}_2\text{PO}_4$  with calcined magnesium oxide in the presence of water is:



After a mixed **slurry** sets to form a mold, it is fired to burn out consumable patterns (mostly waxes, but some polymers are used also).

### Properties

Important properties of phosphate-bonded investments are given in Table 19-1. High-temperature mold

strength is achieved by the formation of complex silicophosphates from the reaction of some of the silica with the excess dihydrogen phosphate. Liquid that is supplied with the investment may be used either full strength or diluted with water to provide some degree of control over the setting and thermal expansions (Fig 19-1).

Although the basic binding reaction is the same for all of the phosphate-bonded investments, there are some important differences in properties due to composition. Those used for the casting of high-temperature alloys and for making dies used in the fabrication of porcelain veneers contain quartz and cristobalite to achieve expansion, which compensates for the shrinkage (contraction) of the cast alloy during cooling from elevated temperatures. Soldering investments, however, do not require especially fine powders and are designed without high-expansion fillers. The latter is to keep parts that are to be joined from shifting while they and the surrounding investment are heated to the joining temperature. Graphite is found in some investments to render them more permeable after burnout and/or to provide a reducing atmosphere.

### Advantages and disadvantages

There are several advantages associated with phosphate-bonded investments. They have both high **green strength** and **fired strength**. This makes them easy to handle without breaking before they are placed in a furnace for the wax burnout process and strong enough afterward to withstand the impact and pressure of centrifugally cast molten alloy. They can also provide setting and thermal expansions high enough to compensate for the thermal contraction of cast-metal prostheses or porcelain veneers during cooling. Finally, they have the ability to withstand the burnout process with temperatures that reach 900°C (1,650°F), and they can withstand temperatures up to 1,000°C (1,831°F) for short periods of time (useful for fabricating porcelain veneers or performing metal-joining operations).

These investments are at a disadvantage when used with higher-melting alloys, those with casting temperatures higher than about 1,375°C (2,500°F). These temperatures, coupled with high mold temperatures, result in mold breakdown and rougher surfaces on castings. The high strength of these investments, although an advantage during casting, can make divesting (removal of the casting from the investment) a difficult and tedious task without the use of a simple tool, such as a press, to force the investment out of the metal casting

**Table 19-1** Properties of phosphate-bonded investments used for high-temperature operations with dental materials (except titanium alloys)**Casting investments**

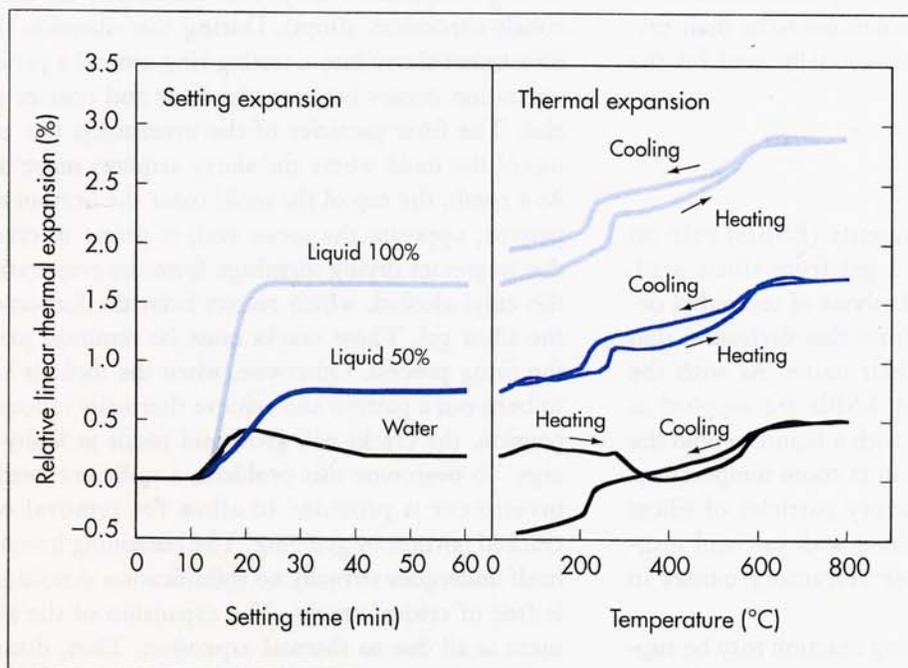
Compressive strength	2.5 MPa minimum, Type I (for inlays, crowns, etc)* 3 MPa minimum, Type II (for removable appliances)*
Setting expansion (linear)	Within 15% of manufacturer's stated value* With use of full-strength liquid about 0.4% can be attained with some investments; when a hygroscopic technique is used, about another 0.6% to 0.8% can be realized†
Thermal expansion	Within 15% of manufacturer's stated value* About 0.8% can be attained with a 50:50 mixture of liquid and water; about 1% to 1.2% can be attained with the use of undiluted liquid†
Modulus of rupture	0.1 to 0.5 MPa (14.4 to 72.5 psi); green, about 0.8 MPa (116 psi), as fired†

**Refractory die stones**

Compressive strength	13 MPa minimum
Setting expansion (linear)	Within 30% of manufacturer's stated value*
Thermal expansion	Within 15% of manufacturer's stated value* Manufacturers state that their materials are designed to be compatible with their porcelain at temperatures in the vicinity of the glass-transition temperature. Values of about $12$ to $13 \times 10^{-6}/^{\circ}\text{C}$ would be expected.

\*According to ISO #9694 (December 19, 1996).

†Approximate values attainable with some of the commercial brands.

**Fig 19-1** Example of setting expansion and thermal expansion of phosphate-bonded investments. (Courtesy of Shofu Co.)

**Table 19-2** Properties of ethyl silicate–bonded investments used for high-temperature operations with dental materials

Casting investments	
Compressive strength	1.5 MPa, minimum*
Setting expansion (linear)	There is no requirement for setting expansion Setting contractions of 0% to 0.4% have been reported This value will depend on the method of measurement One manufacturer reports virtually no (0% to 0.05%) contraction†
Thermal expansion (linear)	Within 1.5% of manufacturer's stated value* About 1.5% to 1.8% can be attained between room temperature and 1,000°C to 1,177°C (1,800°F to 2,150°F)†

\*According to ISO #11246 (June 13, 1996).

†Approximate values attainable with some of the commercial brands.

these investments is low, and refractory models are best handled by reinforcing them with a resin dip. A fine-grained **surface coat** is sometimes applied to the reinforced model and to the pattern on the model in order to achieve a superior surface finish on the cast appliance.

### Advantages and disadvantages

Ethyl silicate–bonded investments offer the ability to cast high-temperature cobalt-chromium and nickel-chromium alloys, and attain good surface finishes, low distortion, and high thermal expansion (good fit). They are less dense (more permeable) than the phosphate-bonded investments, and thin sections with fine detail can be reproduced. Their low fired strength makes divestiture easier than with phosphate-bonded investments.

Their disadvantages lie primarily in the added processing attention (resin-model reinforced dies, pattern coats) and the extra precaution needed in handling the low-strength fired molds. The low strength and high thermal expansion require a more precise burnout process and firing schedule to avoid cracking and, hence, destruction of a mold.

## Other Systems

### Applications

Newer investments have been aimed at the casting of titanium and titanium-based alloys, although the possibility of applications for the casting of other alloys or for refractory pattern coats becomes apparent from some of the properties shown in the following section.

Efforts in Japan, Europe, and the United States to cast dental appliances from titanium or titanium-based alloys have shown that the conventional phosphate-bonded investments and ethyl silicate–based investments are deficient for that purpose. This is because molten titanium is highly reactive with oxygen and is capable of reducing some of the oxides commonly found in those investments. Titanium can also dissolve residual oxygen, nitrogen, and carbon from the investment; these elements can harden and embrittle titanium in the solid state. As a result, either modifications of existing refractory formulations and binders or new refractory formulations and binder systems are required.

### Composition

A variety of investment formulations for the casting of titanium have been developed over the past several years (Table 19-3) (Togaya, 1993; Miyazaki and Tamaki, 1993). These investments might be classified as phosphate-bonded, ethyl silicate–bonded, and “cemented” according to the source of the binder. Many kinds of refractories such as silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), magnesia ( $\text{MgO}$ ), and zirconia ( $\text{ZrO}_2$ ) have been used.

### Properties

Standards do not exist, nor are they in development, for investments for the casting of titanium and titanium alloys in dentistry. It is reasonable to expect that those mechanical properties being contemplated for the conventional phosphate and ethyl silicate–based binders would apply here as well.

**Table 19-3** Titanium investments available in Japan and Germany

Mold-casting temperature (°C)	Binder	Refractory	Burnout temperature (°C)	Country
RT*	MgO, phosphate	Al <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub>	900	Japan
RT*		Al <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub>	1,100	Japan
800		Al <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub>	1,150–1,200	Japan
RT*		Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub>	900–1,000	Japan
200		Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub>	1,100	Both
500		Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub>	950	Both
100		ZrSiO <sub>4</sub> , SiO <sub>2</sub>	1,100	Japan
RT*		Al <sub>2</sub> O <sub>3</sub> , LiAlSi <sub>2</sub> O <sub>6</sub>	1,050	Japan
600–700	Ethyl silicate	MgO, Al <sub>2</sub> O <sub>3</sub>	900	Japan
600–700		MgO, SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>	900	Japan
100		MgO, Zr <sup>†</sup>	850	Japan
100	Aluminous cement	MgO, Zr <sup>†</sup>	850	Japan
600–700		MgO, Al <sub>2</sub> O <sub>3</sub>	900	Japan

\*RT = room temperature.

<sup>†</sup>Addition for attaining expansion by volume change through oxidation.

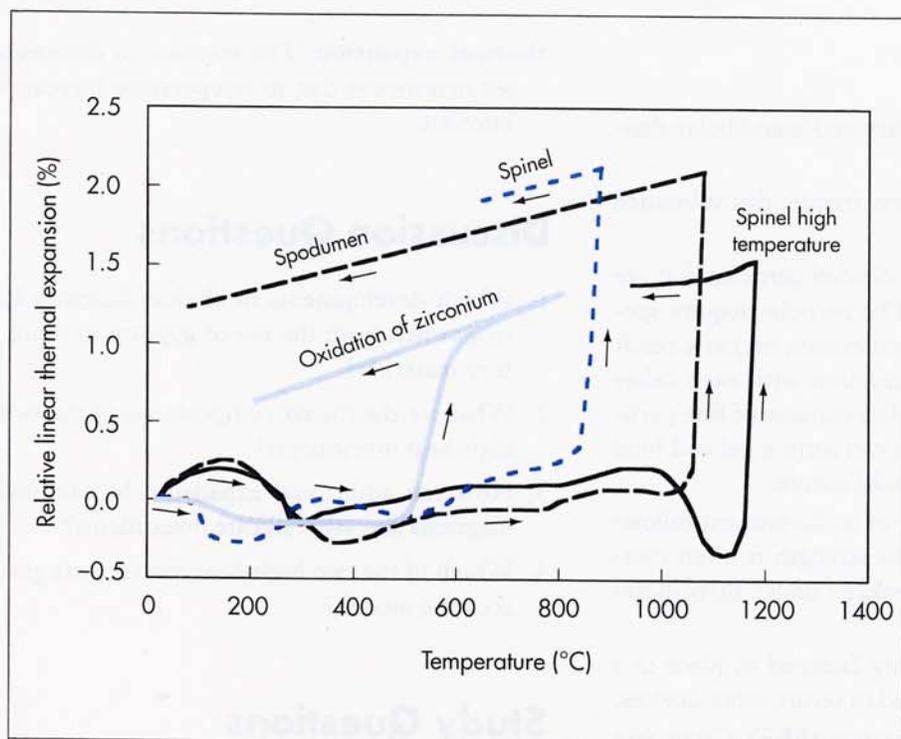
New refractory compositions and binders have been investigated for the casting of titanium prostheses. The objectives have been to reduce breakdown of the investment and the contamination of titanium. One approach to reducing the reaction with investment is to employ molds that have been expanded by the burnout process and then cooled back to near ambient temperatures prior to the casting process. This reduces the time that the alloy is in contact with the mold at elevated temperatures, and the overall reactivity is reduced. However, lowering of the mold temperature requires that either nonreversible expanders, such as metals that expand by oxidation at the elevated temperatures, be used or that the temperature of the mold be kept just above the temperature where a reversal of expansion due to crystalline phase changes takes place.

To avoid contamination of titanium by oxygen through the reduction of refractory oxides of the investment, refractory materials that are less easily reduced by titanium should be used. The **Gibbs free energy of formation (FEF)** per mole of oxygen (Chase et al, 1985) for titanium oxide (TiO) at 1,727°C is -716 kJ/mol of oxygen, and that for titanium dioxide (TiO<sub>2</sub>)

at 1,727°C (3,138°F) is -580 kJ/mol of oxygen. The corresponding FEFs of SiO<sub>2</sub> in the forms of cristobalite and quartz are -550 and -549 kJ, respectively. From this, it is clear that titanium may be expected to be oxidized by SiO<sub>2</sub>, which is reduced.

Some modifications of phosphate-bonded investments have been explored for the purpose of rendering them more compatible with molten titanium metals. One investment consisting of a phosphate binder, magnesia, and quartz was developed under the hypothesis that quartz would not be as reactive as silica (Takahashi, 1993). On the basis of FEFs, there is little advantage in the use of one form of SiO<sub>2</sub> over another, and any advantages of one form over another would have to lie elsewhere (perhaps their decomposition kinetics are sufficiently different). This investment was recommended for use as a room-temperature mold, ostensibly to reduce reaction with titanium. However, contamination of castings by reaction with the investment was still encountered, as would be expected from the previous discussion on FEFs.

To make use of the setting expansion of a phosphate binder, alumina (FEF = -687 kJ/mol of oxygen at 1,727°C) and magnesia (FEF = -640 kJ/mol of oxygen



**Fig 19-2** Example of thermal expansion of titanium investments. (Courtesy of Y. Tamaki and T. Miyazaki.)

at 1,727°C), both of which have good heat resistance, can be used as refractories; however, the thermal expansions of these oxides is low. If either of their powders is mixed with colloidal silica to raise the expansion, some contamination from the silica again becomes a problem.

To achieve expansion without the use of reactive powders, a phosphate investment that contains *both* magnesia and alumina as refractories was developed. This investment can attain large expansion by the spinel reaction of alumina and magnesia ( $\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgO} - \text{Al}_2\text{O}_3$ ) when it is burned out at 1,150°C to 1,200°C. The spinel is, of course, also highly refractory. The spinel-forming temperature can also be reduced by mixing with magnesia acetate. Another approach to obtaining the needed expansion is through the use of spodumen ( $\text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ ) (Okuda et al, 1991). Spodumen expands irreversibly upon heating through the temperature range of 900°C to 1100°C. Figure 19-2 shows the thermal expansion curves of these titanium instruments.

Reaction of ethyl silicate-bonded investments with liquid titanium has been reported to be somewhat less than that of phosphate-bonded investments; this is most likely due to the use of highly refractory oxides in the powder (see Table 19-3). Regardless, these investments require a more complex procedure for their use.

A more recent development is an investment using magnesia bonded by an aluminous cement ( $\text{CaO} - \text{Al}_2\text{O}_3$ ), which contains a mass fraction of 5% zirconium powder (Togaya et al, 1985). The aluminous cement serves as a binder for the magnesia refractory, and it sets by mixing with water. Oxidation of the zirconium powder to zirconia during the burnout process provides irreversible expansion to compensate for shrinkage of the casting during cooling from the solidification temperature. The zirconia formed is highly stable; it has an FEF of  $-728$  kJ/mol of oxygen, and it should not contaminate the titanium. Titanium castings from this investment were reported to have smooth surfaces free of contamination from mold reaction.

## Glossary

- articulate** To join the maxillary and mandibular dentition or a replica of it.
- calcined** Rendered a powdery, friable, dry substance by the application of heat.
- colloidal** The state of finely divided particles that are in suspension in a liquid. The particles acquire special properties (electrical, gelatinous, etc) as a result of their fine size and interaction with each other and the liquid. Colloidal silica consists of fine particles of hydrated silicas that can form a gel and bind larger particles of noncolloidal nature.
- fired strength** The strength of an investment following a burnout process. This strength is often measured by resistance to breakage under three-point loading or bending.
- fixture** A device that is firmly fastened in place in a mechanical sense, often used to secure other devices.
- Gibbs free energy of formation (FEF)** Gibbs free energy is the thermodynamic function  $\Delta G = \Delta H - T\Delta S$ , where H is enthalpy, T is absolute temperature, and S is entropy. Also called *free energy*. Free energy of formation (FEF) is the free energy change for formation of a particular compound.
- green strength** The prefired strength of an investment, acquired through some chemical reaction at or near room temperature. (See *fired strength*.)
- hydrolysis** Decomposition of a compound by water, or the interaction of positive and negative ions of a salt with hydroxyl and hydrogen ions to form an acid and a base.
- hygroscopic** Pertaining to the absorption of water.
- investment** A heat-resistant material used to form a mold around a wax pattern.
- mold** A cavity into which molten metal is cast.
- refractory** A heat-resistant material.
- ring** A thin-walled structure used to contain an investment slurry before it sets; also provides support for set or fired investments that have poor strength.
- setting expansion** The volumetric or linear increase in physical dimensions of an investment, caused by the chemical reactions that occur during hardening to a rigid structure.
- slurry** A thin mixture of liquid and powder.
- surface coat** The first coating that is applied to a wax pattern or the surface of the mold that comes into direct contact with a cast metal.

**thermal expansion** The increase in dimension of a set investment due to temperature increase during burnout.

## Discussion Questions

1. Which developments in clinical dentistry have led to a switch from the use of gypsum to more refractory materials?
2. What are the matrix compositions of the two major high-heat investments?
3. How can additional expansion be obtained with magnesia and ethyl silicate investments?
4. Which of the two high-heat investments gives more accurate models?

## Study Questions

(See Appendix E for answers.)

1. Given a multicomponent system that includes ethyl silicate as a reacting component, how can the reaction time for hydrolysis be altered?
2. Cooling hydrated ethyl silicate to 4.4°C (40°F) extends its shelf life. (a) Would the shelf life be extended by refrigeration to lower temperatures? (b) To what extent may the liquid be cooled without encountering adverse effects?
3. Why is denatured ethyl alcohol used rather than 95% ethyl alcohol as a component of an ethyl silicate system?
4. List advantages and disadvantages of phosphate-bonded investments.
5. List advantages and disadvantages of ethyl silicate-bonded investments.
6. For the casting of nonprecious fixed partial denture alloys, which technique would be recommended with a phosphate-bonded investment?
7. What is the investment of choice for casting (a) ceramic gold alloy; (b) cobalt-chromium partial denture alloy; (c) nickel-based fixed partial denture alloy?
8. List the six approaches to altering the fit of a casting.

9. What might be an advantage of a mixed colloidal silica-ethyl silicate system?
10. A carbon-filled and a noncarbon-filled phosphate investment are available to you for casting ceramic alloys. Would you use a gold alloy or a non-precious alloy for casting? Why?

## Recommended Reading

- Chase MW, et al (eds) (1985). JANAF Thermochemical Tables, vol 14, suppl #1. National Bureau of Standards, American Chemical Society, and American Institute of Physics.
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