Metal-Ceramic Alloys in Dentistry: A Review

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Abstract

Purpose: The purpose of this article is to review basic information about the alloys used for fabricating metal-ceramic restorations in dentistry. Their compositions, properties, advantages, and disadvantages are presented and compared. In addition to reviewing traditional noble-metal and base-metal metal-ceramic alloys, titanium and gold composite alloys are also discussed.
Materials and Methods: A broad search of the published literature was performed using Medline to identify pertinent current articles on metal-ceramic alloys as well as articles providing a historical background about the development of these alloys. Textbooks, the internet, and manufacturers' literature were also used to supplement this information.
Results: The review discusses traditional as well as more recently-developed alloys and technologies used in dentistry for fabricating metal-ceramic restorations. Clear advantages and disadvantages for these alloy types are provided and discussed as well as the role that compositional variations have on the alloys' performance. This information should enable clinicians and technicians to easily identify the important physical properties of each type and their primary clinical indications.
Conclusions: A number of alloys and metals are available for metal-ceramic use in dentistry. Each has its advantages and disadvantages, primarily based on its specific composition. Continuing research and development are resulting in the production of new technologies and products, giving clinicians even more choices in designing and fabricating metal-ceramic restorations.

Porcelain and ceramic materials have been used for fabricating esthetic dental restorations since the early 1800s. The first published reports describing the successful use of porcelain fused to alloys appeared in the mid-1950s.[1,2] Since that time, research and improvements in materials and techniques have dramatically increased the use of metal-ceramic restorations. In large part, increasing use of these restorations was the result of their proven history of clinical performance, acceptable esthetics, and satisfactory physical properties. Good clinical performance has been attested to by longitudinal studies that reported that up to 88.7% of metal-ceramic crowns and 80.2% of metal-ceramic fixed partial dentures (FPDs) were still in function after 10 years.[3]

Requirements of metal-ceramic alloys

For any cast restoration to be successful, it must be made of an alloy that meets certain minimum requirements for strength, stability, castability, corrosion/tarnish resistance, burnishability, polishability, and biocompatibility. Metal-ceramic alloys have additional requirements that are not usually essential for alloys used for full cast-metal restorations. Although considerable function may be borne by the ceramic portion of a metal-ceramic restoration, the success of the entire prosthesis depends largely on the physical properties of the metal substructure.[4] Therefore, additional requirements of these alloys include higher melting temperature, thermal compatibility with ceramics, oxide formation, and sag resistance.

Noble-metal metal-ceramic alloys

Gold–platinum–palladium (Au–Pt–Pd) alloys

The Au–Pt–Pd alloys were the first to be used successfully for metal-ceramic restorations; however, their use decreased after more economical alloys were developed with significantly

Table 1 Compositional ranges (wt%) of noble-metal metal-ceramic alloys

Type	Au	Pt	Pd	Ag	Cu	Sn	Ga	In	Other
Au–Pt–Pd	75–88	≤8	≤11	≤5	–	2–5	–	<1	Fe, Re
Au–Pd	44–55	–	35–45	–	–	8–12	≤5	8–12	Ru, Re
Au–Pd–Ag	39–77	–	25–35	12–22	–	3–7	–	1.5	Fe, Ru, Re
Pd–Ag	–	–	50–60	28–40	–	4–8	–	1–5	Ru
Pd–Cu	≤2	≤1	70–80	–	9–15	0–8	3–9	0–8	Ru
Pd–Ga	0–2	–	74–85	1–7	–	—	6–10	6	Ru

Table 2 Properties of noble-metal metal-ceramic alloys

Type	Ultimate tensile strength (MPa)	0.2% yield strength (MPa)	Elastic modulus (GPa)	Elongation (%)	Diamond pyramid hardness (kg/mm^2)	Casting temperature (°C)
Au–Pt–Pd	480–500	400–420	81–96	3–10	175–180	1150
Au–Pd	700–730	550–575	100–117	8–16	210–230	1320–1330
Au–Pd–Ag	650–680	475–525	100–113	8–18	210–230	1320–1350
Pd–Ag	550–730	400–525	95–117	10–14	185–235	1310–1350
Pd–Cu	690–1300	550–1100	94–97	8–15	350–400	1170–1190

Adapted from Powers and Sakaguchi.[7]

better mechanical properties and sag resistance. If the alloy contains more palladium than platinum, it is referred to as a gold–palladium–platinum alloy. Alloys in which palladium has been eliminated are referred to as gold–platinum alloys.[5] Because of their low sag resistance, the use of these alloys should be limited to crowns and three-unit FPDs.[6] The composition and properties of noble-metal metal-ceramic alloys are shown in Tables 1 and 2.

Gold–palladium–silver (Au–Pd–Ag) alloys

The Au–Pd–Ag alloys were developed in an attempt to overcome the major disadvantages of the Au–Pt–Pd alloys: high cost, low hardness, and poor sag resistance.[5] The Au–Pd–Ag alloys can be further subdivided in two smaller groups: high silver and low silver. The principle disadvantage of these alloys is the potential for their silver content to discolor porcelain.[6,8]

Gold–palladium (Au–Pd) alloys

The Au–Pd alloys were developed to address the two main problems associated with silver-containing alloys: porcelain discoloration and a high coefficient of thermal expansion.[5] The first alloy of this type was introduced in 1977.[6,8] These alloys exhibit a "white gold" color and have been commercially successful.[6,8] Their only significant disadvantage is having a degree of thermal expansion incompatible with some high-expansion porcelains.[5,6,8] In an effort to address this problem, a number of Au–Pd alloys have recently been developed that contain less (<5%) silver.[9] Due to these alloys' low silver content, porcelain does not discolor, castability is improved, and the coefficient of thermal expansion is increased.[8]

Palladium–silver (Pd–Ag) alloys

In 1974 the first "gold-free" noble-metal metal-ceramic alloys, the Pd–Ag alloys, were introduced. They were specifically developed to offer an economical alternative to more expensive gold-based alloys.[5] Typically, Pd–Ag alloys contain approximately 60% palladium, with the balance being silver and small amounts of indium and tin.[5] Actually, two types of Pd–Ag alloys are marketed. One contains approximately 60% (55–60%) palladium and 28–30% silver; indium, tin, and other trace elements make up the balance.[5] The other type has slightly less palladium (50–55%), more silver (35–40%), tin, and other trace elements, but little or no indium.[5] The elastic modulus for Pd–Ag alloys is the most favorable of all of the noble-metal metal-ceramic alloys. In fact, only base-metal alloys have a higher elastic modulus.[8] As a result of their high elastic modulus, Pd–Ag alloys have excellent sag resistance. The porcelain bond strength is also acceptable.[6,8] Some Pd–Ag alloys form internal rather than external oxides. Interestingly, some of the alloys form nodules on the external surface of the metal that may provide more mechanical than chemical retention for the porcelain.[9,10] This nodule formation has not produced a significant enough number of porcelain bonding failures to determine if it is a problem.[6]

Unfortunately, some Pd–Ag alloys produce more porcelain discoloration than Au–Pd–Ag alloys.[6,8,11] The exact mechanism by which silver ions are transported from the alloy to the porcelain is not known and has been the subject of research and speculation. Payan et al[12] investigated changes in physical and chemical properties of a Pd–Ag alloy during metal–porcelain bonding. Using microprobes, they were unable to detect silver diffusion across the porcelain–metal interface. Tuccillo[13] suggested that silver may be responsible for staining when it evaporates as a positively charged ion during porcelain firing. Potentially adding support for this theory is the fact that Ringle et al[14] observed discoloration of porcelain specimens fired in the presence of, but not in contact with, a Pd–Ag alloy. Mackert et al[9] reported Pd–Ag nodule formation on the surface of a palladium–silver–tin–indium alloy and suggested that the nodules provide an oxide-free surface that might contribute to the evaporation of silver ions. Moya et al[15] demonstrated that silver can quickly diffuse from the surface to the interior of porcelain during normal firing sequences.

High-palladium alloys

Several types of high-palladium alloys were introduced in the 1980s.[6] These alloys were primarily developed for economic reasons, to address biocompatibility concerns of nickel-based casting alloys, and to minimize the possibility of porcelain discoloration seen with Pd–Ag alloys.[16] The high-palladium alloys have more palladium (>70 wt%) than the Pd–Ag alloys.[16] Although popular in the 1990s, price volatility of palladium in the early 2000s led to the use of other alloys.[6] The most popular types have been Pd–Cu, Pd–Co, and Pd–Ga.[16]

Palladium–copper (Pd–Cu) alloys

Although copper has been reported to be the reason for porcelain discoloration and bonding problems when present in gold-based metal-ceramic alloys, the same problems are not seen with high-palladium copper-containing alloys.[8] The addition of copper and indium has been reported to decrease the solid solubility of gallium in palladium, causing the eutectic reaction to occur at lower weight percentages of gallium.[16] It is suggested that this provides excellent hardening and strengthening, as the eutectic constituent is formed in greater amounts.[16] This can, however, lead to a problem during prosthesis fabrication when using first-generation Pd–Cu alloys because their high yield strengths and hardnesses make them difficult to finish and polish.[16] Another problem with some Pd–Cu alloys is low sag resistance due to the alloys' poor creep resistance at high stress levels and temperatures close to porcelain's glass transition temperature.[17]

Reports suggest that copper is essential for adequate porcelain bonding of high-palladium alloys.[18,19] However, Vrijhoef and van der Zel[20] reported that oxides of gallium and indium, rather than copper, were predominant in a Pd–Cu alloy. Suoninen and Herø[21] studied another Pd–Cu alloy and found only a 15-μm-thick gallium oxide layer in a subsurface region dispersed within the alloy and around its grain boundaries. However, Hautaniemi et al[22] investigated another Pd–Cu alloy and reported that $CuGa_2O_4$ predominantly formed on the surface layer, along with some internal oxidation occurring to a depth of 10 μm.

Palladium–cobalt (Pd–Co) alloys

The Pd–Co alloys have had only limited use. Their main advantage is a relatively high coefficient of thermal expansion that is useful with certain porcelain systems.[8] Recently, some manufacturers have added 1% to 2% of a noble metal such as gold and/or platinum in an attempt to improve the Pd–Co alloy's grain structure.[5] The chief disadvantage of Pd–Co alloys is their tendency to form a dark oxide layer,[16] which can compromise porcelain esthetics.[23] In addition, it has been reported that Pd–Co alloys have lower porcelain bond strengths than do Pd–Cu alloys.[24]

Palladium–Gallium (Pd–Ga) Alloys

Although evidence is equivocal,[19,25] the Pd–Ga alloys produce oxide layers reported to have less capability for ceramic bonding than the Pd–Cu alloys. One specific type of Pd–Ga alloy, the palladium–gallium–silver (Pd–Ga–Ag) alloy, is a noble-metal metal-ceramic alloy recently introduced into the market. This alloy was formulated to have a slightly lighter-colored oxide layer than the Pd–Cu alloys and is thermally compatible with some of the lower-expansion porcelains.[6] The Pd–Ga–Ag alloys tend to consist of 80% to 85% Pd, 6.3% to 10% Ga, and 1.2% to 5% Ag; the balance is Sn, Zn, and In.[6] Compared to other high-palladium alloys, the Pd–Ga–Ag alloys tend to be softer, and although other physical properties appear to be adequate, more clinical data are necessary to confirm that the alloys perform successfully.[6]

Palladium–silver–gold (Pd–Ag–Au) alloys

Although the Pd–Ag–Au alloys were marketed at approximately the same time as the Pd–Cu and Pd–Co alloys, it was not until after the shortcomings of Pd–Cu and Pd–Co alloys became apparent that market attention turned back to them.[5] Pd–Ag–Au alloys have been reported to have greater high-temperature strength and a lighter surface oxide layer than other high-palladium alloys.[5]

Base-metal metal-ceramic alloys

Two main categories of base-metal metal-ceramic alloy systems exist: nickel based and cobalt based (Tables 3 and 4). Alloys in both systems contain chromium as their second largest constituent and depend upon it for corrosion resistance.[5] Base-metal alloys have excellent physical properties. For example, they exhibit the highest modulus of any alloy type used for cast restorations.[26] Although the nickel- and cobalt-based alloys have dominated the market for many years, research continues with other base-metal metal-ceramic alloys, especially titanium[7] (Fig 1).

Table 3 Compositional ranges (wt%) of base-metal metal-ceramic alloys

Type	Ni	Cr	Co	Ti	Mo	Al	V	Fe	Be	Ga	Mn	Nb	W	B	Ru
Ni–Cr	62–77	11–22	–	–	4–14	0–4	–	0–1	0–2	0–2	0–1	–	–	–	–
Co–Cr	–	25–34	53–68	–	0–4	0–2	–	0–1	–	0–3	–	0–3	0–5	0–1	0–6

Table 4 Properties of base-metal metal-ceramic alloys

Type	Ultimate tensile strength (MPa)	0.2% yield strength (MPa)	Elastic modulus (GPa)	Elongation (%)	Diamond pyramid hardness (kg/mm^2)	Casting temperature (°C)
Ni–Cr	400–1000	255–730	150–210	8–20	210–380	1300–1450
Co–Cr	520–820	460–640	145–220	6–15	330–465	1350–1450

Adapted from Powers and Sakaguchi.[7]

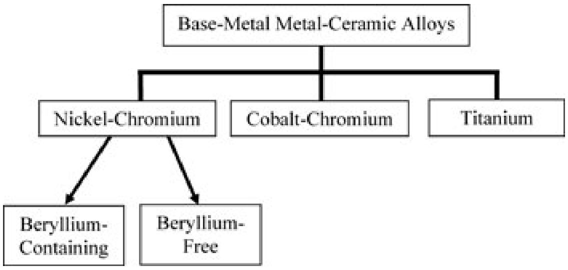

Figure 1 Compositional classification of base-metal metal-ceramic alloys (adapted from Naylor[5] and O'Brien[27]).

For metal-ceramic use, base-metal alloys have been reported to have better castability than noble-metal alloys,[24] but they tend to form thicker, darker oxide layers that may present esthetic problems.[26] Historically, the base-metal alloys were divided into four groups: nickel–chromium–beryllium, nickel–chromium, nickel–high-chromium, and cobalt–chromium.[26] The nickel–chromium–beryllium alloys were used frequently in the past, because beryllium facilitated casting[24] and enhanced porcelain bonding.[28] However, because of health concerns associated with beryllium, this type of nickel-chromium alloy is not recommended.

Nickel–chromium (Ni–Cr) alloys

Not surprisingly, the major constituents of Ni–Cr alloys are nickel and chromium; however, they also contain a wide array of minor alloying metals.[5] All Ni–Cr alloys are closely related in their composition and physical properties, but may differ in corrosion resistance.[26] Aluminum and titanium are added in small amounts to form strengthening precipitates of Ni_3Al or Ti_3Al; iron, tungsten, and vanadium are added for solid-solution hardening.[29] Of all of the elements added for hardening, molybdenum and tungsten are the most effective.[29] Molybdenum has the added benefit of influencing the coefficient of thermal expansion.[30] When used for partial denture frameworks, Ni–Cr alloys may be formulated with trace amounts (~0.1 wt%) of carbon to enhance yield strength and hardness.[26] Ni–Cr alloys for cast restorations, however, are generally carbon-free.[26]

Cobalt–chromium (Co–Cr) alloys

Cobalt is the main constituent of cobalt-based metal-ceramic alloys, with chromium added for strength and to provide corrosion resistance via passivation.[5] It has been suggested that Co–Cr alloys be further classified into two subgroups: those that contain ruthenium and those that are ruthenium-free;[5] however, the difference in physical properties between the two suggested types is unclear. Cobalt–chromium alloys are the most common base-metal alternative for patients known to be allergic to nickel.[26] With the exception of titanium alloys, the Co–Cr alloys have the highest melting ranges of the casting alloys. In part, this makes it difficult to manipulate these alloys in the laboratory.[26]

Titanium

The medical use of commercially pure titanium (CP Ti) and titanium alloys has increased significantly over the past 20 years. The successful use of titanium dental implants has generated considerable interest in other dental uses for pure titanium and titanium alloys, including all-metal and metal-ceramic prostheses, as well as partial denture frameworks.[31,32] Titanium is considered to be the most biocompatible metal for a dental prosthesis.

CP Ti undergoes a phase transformation at 885°C from a hexagonal close-packed structure (α-phase) to a body-centered crystalline structure (β-phase), which significantly changes its density and increases its cold workability. With alloying and appropriate heat treatment, four types of Ti alloys can be produced: α, near-α, α–β, and β.[31]

The most widely used titanium alloys for dental and other medical applications are the titanium–aluminum–vanadium (Ti–6Al–4V) alloys. Vanadium, which is isomorphous with the β phase and is a β-phase stabilizer, is added because it causes the transformation of the β-phase to the α-phase at lower temperatures. Aluminum is an α-phase stabilizer and causes the transformation of α-phase to β-phase to occur at higher temperatures.[31] Although Ti–6Al–4V alloys have greater strength than CP Ti, some authors recommend that they be used with caution, because slow release of aluminum and vanadium may cause biocompatibility problems.[31] The composition of Ti–6Al–4V alloys is shown in Table 5.

CP Ti and titanium alloys have high melting points (~1600°C), and casting is often done with special induction casting procedures under an argon atmosphere.[31] In addition to oxygen, nitrogen, and hydrogen, titanium has high reactivity with silica and requires magnesia-, alumina-, or calcium-based investments.[34] Typically, molten titanium is cast into either an 800°C or room-temperature mold to reduce its porosity and decrease the possibility of the metal reacting with mold components. The magnesia-based investments lack a sufficient

Table 5 Composition of Ti–6Al–4V alloys (wt%)

	Ti	Al	V	C	N	O	Fe	H
Ti–6Al–4V	89.15–90.40	5.5–6.75	3.5–4.5	0.08	0.05	0.20	0.25	0.0125

Source: RTI International Metals.[33]

coefficient of thermal expansion at higher temperatures, and research has been directed toward improving magnesia-based investments through the addition of zirconia.[34,35] One method used to overcome difficulties involved with casting titanium for metal-ceramic prostheses involves using a technique in which porcelain is added to a titanium coping prepared by a computer-assisted design.[36]

Research has also been done to evaluate the failure rates and overall post-placement performance of Procera titanium crowns. Milleding et al[37] reported a failure rate of 7.5% for 40 crowns after 2 years. As a result, the authors suggested that Procera titanium crowns may be a viable alternative to other metal-ceramic systems. Bergman et al[38] studied the clinical performance of 44 Procera titanium crowns followed for up to 78 months after cementation and also found a low failure rate: three crowns had porcelain fractures and two crown margins exhibited caries. Except for some noticeable porcelain surface and color changes, the authors concluded that the veneered titanium copings performed well. Another study by Bergman et al[39] compared Procera titanium crowns to conventional noble-metal metal-ceramic restorations using a split-mouth study design. Nineteen pairs of crowns were placed in 16 patients and evaluated after 2 years of clinical use. Results indicated little difference in marginal integrity, anatomic form, or bleeding index between the two metal-ceramic systems. Similar to the findings of Bergman et al,[38] the most noticeable change with the titanium restorations was the porcelain's surface quality and color. Differences, however, were not statistically significant.[39] Lövgren et al[40] reported a 5-year clinical study involving 333 Procera titanium restorations (242 single units, 91 FPD units) in 260 patients. They found that the cumulative success rate for single-unit restorations was 99.6% and 97.8% for FPDs. Porcelain fracture, which occurred in 6% of single units and 13% of the FPDs, was the most frequent problem. The majority of these fractures, however, were reported to be small and easily rectified by polishing. Based on the results of their study, the authors recommended the use of the Procera titanium system for metal-ceramic fixed prosthodontics.[40]

The bonding of porcelain to titanium has been an area of significant research.[41-53] Gilbert et al[41] investigated the porcelain bond strength to CP Ti using shear and three-point bend tests and found that key factors for improved bonding included control of high-temperature titanium oxidation and compensation for the titanium's lower coefficient of thermal expansion. Also, the study reported that a titanium particle-containing bonding agent significantly improved porcelain bonding to a milled titanium surface.[41] Oshida and Hashem[42] reported that the formation of surface TiN (i.e., nitridation) on CP Ti using an arc ion plating process controlled titanium oxide formation during simulated porcelain firing. Oshida et al[43] later reported that nitridation, as well as chromium-doped nitridation of both sandblasted and non-sandblasted CP Ti surfaces, resulted in a satisfactory porcelain-titanium bond strength. Yamada et al[51] studied the influence of a bonding agent on porcelain adherence to a Ti–Nb6–Al6 alloy and suggested that excessive formation of aluminum ions at the alloy surface was responsible for weaker porcelain bonding.

Other metal-ceramic alloys: Gold composite alloys

In contrast to metal-ceramic copings fabricated via the lost wax technique, technology became available in the mid-1990s based on a concept of a "gold composite alloy." One product, Captek (Precious Metals Inc., Longwood, FL), involves fabricating a metal substructure coping from alloy-impregnated waxes burnished onto a refractory die. The wax, after firing, is said to provide a porous matrix consisting of 88% Au, 4% Pt, 4% Pd, 3% Ag, and 1% Ir. Additional waxes of different composition are then added and fired to provide a 25-μm-thick surface layer of 97% gold. A proprietary bonding agent, which purportedly provides bonding between the gold and porcelain, is then applied. Although Captek technology has been available since 1995, there is surprisingly little peer-reviewed scientific literature (other than abstracts) reporting on the technology.[54-56] A manufacturer-supported graduate study was completed in 1995,[57] but data from this thesis have apparently not been reported in the scientific peer-reviewed literature.

A similar product is Sinterkor (Pentron Laboratory Technologies, LLC, Wallingford, CT). Sinterkor is comparable to Captek in that the metal-ceramic substructure is fabricated by sintering an alloy-impregnated wax directly on a refractory die. The manufacturer reports that the Sinterkor alloy consists of 95% Au and 5% Pt, and product information implies that a bonding agent is required for porcelain bonding to the substructure.[58] Again, with the exception of abstracts, little information regarding Sinterkor has been reported in the peer-reviewed dental literature. A third system for fabricating metal copings involves electroforming 99% gold on a special duplicate die (Gramm Technology Inc, Woodbridge VA).[59] Although these new techniques hold promise for metal-ceramic restorations, it is prudent to view them with caution until more information about their performance becomes available in the scientific literature.

Conclusion

Different types of time-tested metal-ceramic alloys and the roles of their constituents were reviewed in this article. More recent types of metal-ceramic alloys were also described, including ones used to produce high-gold sintered copings and electroformed copings. Although these newer methods and materials for metal-ceramic substructure fabrication are available, the scientific, peer-reviewed dental literature has not extensively reported on them. Accordingly, caution should be exercised with these products until objective information becomes available. Titanium alloys have been the subject of research for the past 15 years; however, much work remains to be done before this highly biocompatible alloy is routinely used as a metal-ceramic alloy.

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