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Alloys for Metal-Ceramic Restorations

Abstract: The requirements of a metal-ceramic dental restoration consisting of a rigid substrate, which supports an aesthetic veneer, are assessed. The contemporary, cast, bonding alloys that have good track records as substrates are categorized and their properties are compared. Several alternatives to cast metals are considered.

Clinical Relevance: Despite developments in all-ceramic restoration technology, the metal-ceramic dental restoration still has a significant place in the dentist's armamentarium.

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Whilst there is little doubt that aesthetic dental restorations can be created by skilled technicians using a range of dental porcelains, some of the most realistic can only be created in materials like the feldspathic porcelains, which have such inferior mechanical properties that they suffer from premature failure when in service. For over 50 years these problems have been overcome by bonding these aesthetic porcelain veneers to strong and rigid metallic substrates and, although in 2005 the clinician and technician have available to them an increasingly large group of *all-ceramic* restorations, many of these require expensive, dedicated equipment and specialized techniques to produce what are, effectively, very strong ceramic cores to which are bonded the more aesthetic but weaker porcelain veneers. As yet, many of these new systems await the evidence of long-term clinical use, something at which the metal-ceramic restorations have a head start.[1]

The requirements of the two components of a metal-ceramic restoration for use in the mouth are quite different, and it is worthwhile considering these. But first, consider the general requirements of materials that are destined to become dental restorations or appliances.

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General requirements

- They should not harm the patient or those members of the dental team who have to handle them;
- They should not dissolve or disintegrate in the patient's mouth;
- They should be rigid so as to resist deformation or bending and strong so as to resist breaking – no matter how they are loaded; and
- They should resist wear.

Requirements of the metal substrate

Assuming that a material complies with the above general requirements, a substrate is required which is rigid in thin section so that it allows for a minimum of invasive tooth preparation and does not flex under stress. Flexing will give rise to the growth and propagation of cracks in the bonded porcelain veneer.

One of the effects of bringing metals together to form alloys is that the rigidity of the alloy exceeds that of either component. The alloy thus produced must be biocompatible and resistant to those conditions in the mouth that might lead to corrosion. It should also be capable of forming a strong and durable bond with the porcelain. During the firing of the ceramic veneer, oxides of the constituent metals form on the surface of the substrate and these diffuse into the porcelain. Whilst this creates a chemical contribution to the bond that forms, ions from the metal should not change the colour of the porcelain.

Requirements of the veneering porcelain

The porcelain is retained on the metallic substrate by a combination of physical, chemical and mechanical bonds. During the firing process, the aesthetic porcelain must wet the substrate (this contributes a physical component); it should flow into any surface asperities (on cooling this gives a mechanical component) and at this stage it may dissolve metallic oxides (these can contribute to chemical bonding).[2] When it cools, the porcelain should be under a small compressive stress owing to the differences in the coefficients of thermal expansion of the metal and the porcelain. This provides an added contribution to the bond between the two materials.

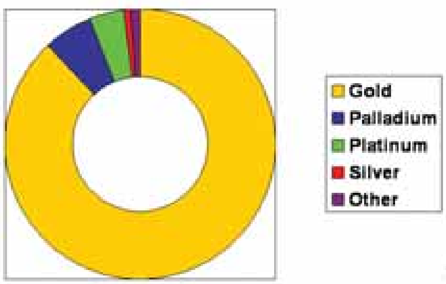

Figure 1. Typical composition of a modern, high-gold metal-ceramic alloy.

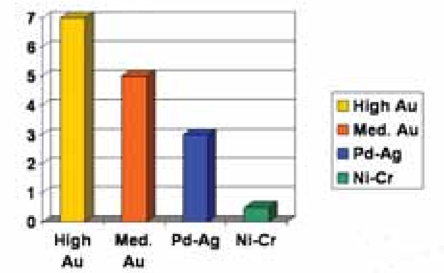

Figure 2. The cost per gram in £ sterling of the four types of metal-ceramic bonding alloys available in 2005.

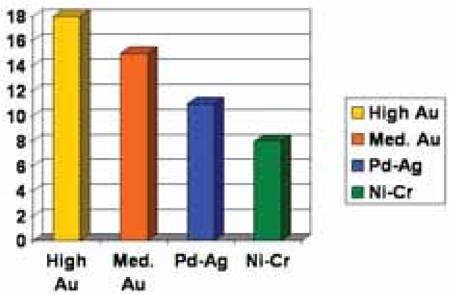

Figure 3. The density in g/cm^3 of the four types of metal-ceramic bonding alloys available in 2005.

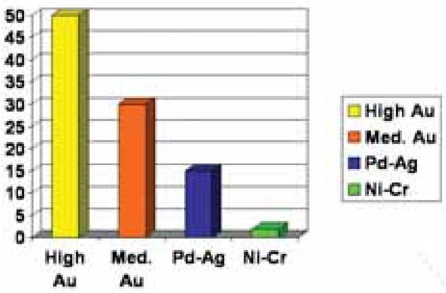

Figure 4. The cost in £ sterling of the amount of metal of each of the four types of metal-ceramic bonding alloys needed to produce a three-unit bridge.

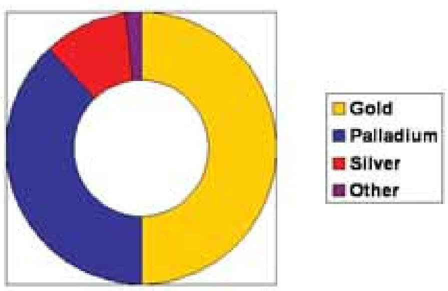

Figure 5. Typical composition of a medium-gold (gold-palladium) metal-ceramic alloy.

Realistic substrate alloys

In thermodynamic terms, when most metals are in either air or water the form of lowest energy is their oxidized state: hence the red oxides of rusting iron and steel. However, some metals, notably gold, platinum and palladium (the *noble* metals) do not suffer from this thermodynamic need and hence they do not oxidize, but remain bright and shiny indefinitely. Several *base* metals, such as chromium, titanium and aluminium, form oxides that have similar volumes to the metal being oxidized. Thus, once a thin oxide film has formed, no further oxidation takes place. This passive oxide layer allows light to be reflected from the metal surface and so such metals and many of their alloys therefore remain permanently shiny, developing neither the surface stain known as *tarnish,* nor disintegrating below the surface by the phenomenon described as *corrosion*.

Steels which contain a minimum of 12% chromium behave in this way and are known as *stainless* steels. They have been used in wrought form for many years by the manufacturers of the various types of dental hand instruments and spittoons. For use in the mouth, the steels tend to contain 18% of chromium and 8% of nickel, and they have been used as pre-formed temporary crowns, as wires for the construction of both fixed and removable orthodontic appliances and as partial denture clasps. Thin stainless steel sheets can also be swaged or hydraulically-pressed to make complete denture bases.

The other chromium-based alloys that have been successfully applied in dentistry are those that are cast, and these include the cobalt-chromium alloys with up to 35% of chromium (utilized for partial denture frameworks) and the nickel-chromium alloys with up to 20%, used for crown and bridge work.

Contemporary metal-ceramic alloys - cast

Gold-based

In 2005, there are two types of gold-rich alloys that are available for producing substrates suitable for veneering porcelain. The first is the one that has been around the longest. This contains little more than 10% of alloying additions, and these, as shown in Figure 1, are mainly platinum and palladium. Because of the high intrinsic cost of gold and platinum (Figure 2) and their high density (Figure 3), the cost of the amount of metal needed to construct a rigid, three-unit substrate to which porcelain can be successfully bonded without the bridge flexing and causing the metal-ceramic bond to fail, is the highest of all the alloys currently available (Figure 4).

In Figure 1 there are some elements listed as 'other'. These are added by the manufacturers of these alloys to assist in the creation of the chemical component of bonding by forming oxides, which dissolve in the porcelain during firing and give rise to cross-interface atomic bonding forces. In these high-gold alloys the trace elements involved in this oxide formation are indium, iron and tin. Copper is significant by its absence from this type of bonding gold as it tends to dissolve in the porcelain, giving it an unacceptable green tinge.

The second type of gold-rich alloy is a later development and, as seen in Figure 5, whilst half of it is gold, the other half is mainly palladium (another noble metal) with about 10% being silver (which, whilst corrosion resistant in the mouth, is not itself noble). In this alloy the trace metals that help bonding are cobalt, gallium and indium.

The price of palladium has fluctuated over the last five years. At one point in 2000 it was twice the price of gold, but in the spring of 2005 it was back down to being half the price of gold. As palladium is somewhat less dense than gold, these gold/palladium alloys produce a three-unit bridge framework for about two-thirds the cost of one in a high-gold alloy.

Palladium-based

Although silver is not itself a noble

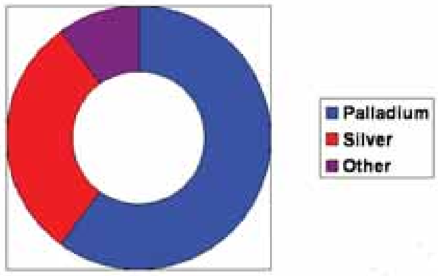

Figure 6. Typical composition of a palladium-silver metal-ceramic alloy.

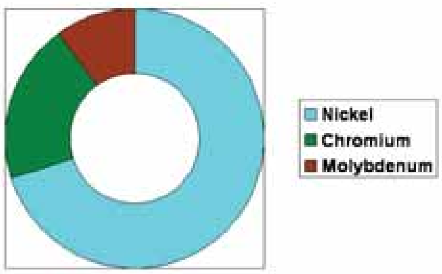

Figure 7. Typical composition of a nickel-chromium metal-ceramic alloy.

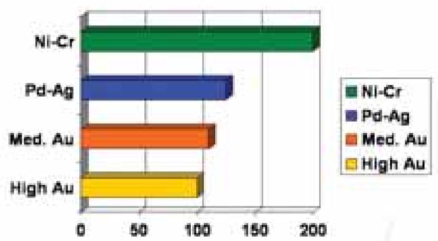

Figure 8. Elastic modulus in GN/m² of the four types of metal-ceramic bonding alloys available in 2005.

metal, mixing it with twice as much palladium (Figure 6) results in a corrosion-resistant alloy which casts into a three-unit bridge framework for about £15 (Figure 4). In these alloys the other minor constituents are indium and tin. Whilst these alloys are white in colour, there is some anxiety concerning the presence of silver, which had a reputation in the past of causing discoloration of the porcelain. Some complex silver-free alloys (not shown in the figures) have therefore been developed. These are three-quarters palladium with additions of cobalt, gallium, gold, indium, tin and ruthenium. Some even contain small amounts of copper, which is usually avoided. Modern casting procedures seem to have eliminated the discoloration challenge of copper and silver, and neither now appears to act in a deleterious way during the production of unsullied metal-ceramic bonds.

Nickel-based

These alloys derive their resistance to tarnish and corrosion from the presence of up to 20% chromium (Figure 7). Modern casting alloys based on nickel also contain up to 10% molybdenum to improve the corrosion resistance in the presence of the chloride ion, and often contain traces of aluminium, boron, carbon, cobalt, iron and manganese, many of which assist in the formation of the chemical component of the bond that forms between the substrate and the veneer.

Beryllium has been a constituent of these alloys in the past, in the belief that it improves castability. However, Bezzon *et al.*[3] have shown that it is not necessary, and as beryllium is a hazardous element to man and can be inhaled from the dust during the finishing of castings that contain it, the profession is better off without it. However, it is still permissible under international standards governing these alloys, but only if it represents no more than 0.02% of the mass fraction [BS EN ISO 16744:2003]. At such levels it is doubtful if it can do much more than act as a grain-refining element.

As the density of these alloys is low and the constituent base metals are not themselves expensive, the cost of a three-unit cast framework is under £3. What is more, because the inherent modulus of these alloys is twice that of a high-gold bonding alloy (Figure 8), very thin but rigid frameworks can be made.

Comparison of properties

Figure 9 compares the relative properties of the various categories of contemporary metal-ceramic bonding alloys described above. Recent research[4] compared the cytotoxicity of such alloys and suggested that the high-gold alloys continue to be the most biocompatible.

In a review in 2000 of the biocompatibility of dental casting alloys, Wataha suggests that the single most relevant property to biological safety of an alloy in the mouth is corrosion.[5] However, he indicates that there is little evidence supporting concerns that casting and bonding alloys cause systemic toxicity. In addition, the true risk of nickel and chromium, which have the potential to cause allergy, is undefined. He believes that it is just prudent to use those alloys that corrode the least.

Although many patients are nickel-sensitive when patch tested, there is a growing body of evidence that suggests there are mechanisms within the mouth that will tolerate the presence of alloys that contain nickel without producing an allergic response.[6] Many nickel-sensitive patients are also sensitive to palladium; however, there are no well-documented cases of adverse biological reactions to palladium ions in the mouth. This is further helped by the low dissolution rate of palladium ions from dental alloys.[7]

Table 1 lists the suppliers of metal-ceramic bonding alloys in the UK.

Contemporary metal-ceramic alloys – recent developments

Titanium and its alloys

Whilst titanium and its alloys are both biocompatible and corrosion resistant and can be used to produce the strongest frameworks using the superplastic

Property	Ideal Material	High Gold	Gold-Palladium	Palladium - Silver	Nickel-Chromium
Biocompatible	☺☺☺	☺☺☺	☺☺	☺☺	☺
Corrosion resistant	☺☺☺	☺☺☺	☺☺	☺☺	☺☺
High modulus	☺☺☺	☹	☺	☺☺	☺☺☺
Forms strong bond	☺☺☺	☺☺	☺☺	☺☺	☺☺
Low cost	☺☺☺	☹	☺	☺☺	☺☺☺

☺good ☺☺very good ☺☺☺excellent ☹poor

Figure 9. The properties of the four types of metal-ceramic bonding alloys available in 2005 compared.

Bracon Ltd	Etchingham	TN19 7AL	www.bracon.co.uk
Chaperlin & Jacobs	Sutton	SM3 9QR	www.chaperlin.co.uk
Cookson Preciosu Metals	Birmingham	B1 3NZ	www.cooksongold.com
Degussa Ltd	Macclesfield	SK11 0LP	www.degudent.com
Dental Directory	Witham	CM8 3SX	www.dental-directory
Dentsply Ltd	Weybridge	KT15 2SE	www.dentsply.co.uk
Engelhard-CLAL	Chessington	KT9 1TD	www.engelhard-clal.fr
Heraeus Kulzer Ltd	Newbury	RG14 1DL	www.heraeus-kulzer.com
Ivoclar-Vivadent Ltd	Leicester	LE191WY	www.ivoclarvivadent.co.uk
Metalor Dental Products	London	EC1N 8HB	www.metalor.com
Metrodent Ltd	Huddersfield	HD3 4EP	www.metrodent.com
National Dental Supplies	Southport	PR9 7SA	www.ndsonline.co.uk
Panadent Ltd	Orpington	BR5 3AQ	www.panadent.net
Schottlander Ltd	Letchworth	SG6 2WD	www.schottlander.co.uk
Skillbond Direct Ltd	High Wycombe	HP13 6EQ	www.skilbond.com
Williams-Precious Metals	Amherst	NY 14228	www.ivoclarvivadent.us.com
Wright Cottrell & Co	Dundee	DD2 3QD	wwww.wright-cottrell.com
Zahn Laboratory	Gillingham	ME8 0SB	www.henryschein.co.uk

Table 1. A list of the suppliers of metal-ceramic bonding alloys.

forming process described by Soo *et al*.[8], with a modulus of 100 GN/m^2 for commercially-pure titanium and 115 GN/m^2 for the sophisticated titanium-aluminium-vanadium alloys, they are at a distinct disadvantage when it comes to retaining veneering porcelain on thin sections.

Titanium alloys have been used successfully to produce single crowns using the *Procera* system, which is undergoing continuous evolution. In the earlier *Procera AllTitan* process the exterior curves of the titanium substrates were milled to the correct dimensions using computer-assisted equipment and the interior surface was shaped via spark erosion using graphite electrodes, which were also made by a CAD/CAM process. More recently, the *Procera* titanium copings have been made by a pressed powder metallurgical technique.[9] Multi-unit substructures, which may include a titanium pontic, can be made by laser welding several units together. Whatever the method of manufacture, the titanium substrates are completed by the addition of a veneer of low-fusing porcelain.

Alloying titanium with elements such as chromium, palladium, silver or copper produced casting alloys with modestly improved elastic moduli, which formed bonds with porcelain just within the limits set by the international standard.[10]

Foils are back

Over the years, several attempts have been made to use metallic foils to act as a means of preventing the propagation of cracks through porcelain by bonding it to a thin metal substrate. By electroplating platinum foil with tin and allowing a layer of tin oxide to form on the surface, McLean and Sced[11] produced considerable reinforcement when the porcelain veneer wetted the surface and bonded to it. However, the grey appearance of the tin oxide tended to show through the porcelain, making it difficult for the technician to produce the good aesthetics required for anterior crowns.

A system which leaves a layer of gold in contact with the porcelain, and is thus said to be warmer in appearance, is the *Captek* system (Altamonte Springs, Fla, USA). This produces a thin metal framework by 'diffusion bonding'. In this process a layer of wax, which is impregnated with particles of a gold – 4% palladium – 4% platinum alloy is adapted to a refractory die and fired in a porcelain furnace. The alloy particles sinter together and a porous structure is thus produced. On to this another metal-filled wax layer is adapted. This contains particles of pure gold, which melt below the fusing temperature of the Au-Pd-Pt alloy, and the molten gold flows into the porous structure. This produces a thin coping – 250 microns thick for anterior crowns and 350 microns thick for posterior ones, on to which the porcelain is applied and fired.[12]

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