THE DENTAL CLINICS OF NORTH AMERICA

Dent Clin N Am 51 (2007) 433–451

Adhesion to Porcelain and Metal

Raymond L. Bertolotti, DDS, PhD*

University of California, San Francisco School of Dentistry, Parnassus Avenue, San Francisco, CA 94143, USA

Advances in adhesion monomers and surface preparation techniques permit strong bonding of resins to metals and to porcelains. Most "pressed ceramics" bond in a manner similar to that of porcelains. The bond strengths to these materials can easily exceed the typical bond of resin to phosphoric-acid–etched enamel [1]. Using the strong bonds to these restorative materials, many innovations in tooth-conservative procedures are possible.

When we consider that tooth reduction correlates with need for subsequent endodontic treatment [2], the preferred treatment option often is one that relies on minimal tooth reduction. Adhesion, with less need for tooth reduction, is a highly desirable shift away from tooth preparation for mechanical retention.

This paper first presents some clinical examples where the use of adhesives clearly provides compelling advantages compared with mechanical retention and cementation. Then methods and materials to achieve resin adhesion to metal and porcelain are reviewed. Based on these methods and materials and the author's own clinical experience, specific adhesion protocols are given for some complex clinical applications.

The clinical advantages of using porcelain and metal adhesion

If we examine the cross section of a typical molar (Fig. 1), the distance from the occlusal surface to the pulp chamber is about 7 mm. A 3-mm occlusal reduction therefore leaves about 4 mm of remaining dentin thickness (Fig. 2). On the other hand, axial reduction of 2 mm leaves <1 mm of remaining dentin (Fig. 3). The 2-mm axial reduction is within current pressed ceramic manufacturers' instructions for tooth preparation.

Raymond L. Bertolotti owns stock in Danville Materials Inc.

* 188 Beechwood Drive, Oakland, CA 94618.

E-mail address: rbertolott@aol.com

0011-8532/07/$ - see front matter © 2007 Published by Elsevier Inc.
doi:10.1016/j.cden.2006.12.003

Fig. 1. Cross section of a molar.

With porcelain, metal, and even dentin adhesion equivalent to etched enamel adhesion, the obvious clinical application is the adhesion onlay. The onlay may be made of metal, porcelain, or pressed ceramic (Figs. 4 and 5). In these examples shown in Figs. 4 and 5, there is no intentionally cut retention form (Fig. 6). The "preparation" of the teeth was actually done by the patient through years of abrasion. No additional tooth modification was made before taking the final impression. Last photographed at 5 years and 3 months, this case remains successful after nearly 10 years.

While metal adhesion onlays have been successful for many years [3], clinicians have been reluctant to place occlusal porcelain onlays on molars. Presumably the reluctance results from reports of clinical failure of all porcelain molar crowns. However, a recent study [4], where 2 mm of pressed ceramic (Empress; Ivoclar/Vivadent, Schaan, Leichtenstein) was bonded to the occlusal surfaces of molars (partial onlays, not crowns), reported 100% success at 33 months. These onlays used 2 mm of pressed ceramic, like those demonstrated on the previous case. The high success rate is

Fig. 2. Shaded area shows 3-mm occlusal reduction.

Fig. 3. Shaded area shows 3-mm occlusal reduction and 2-mm axial reduction.

presumed to be due to the ceramic being placed in compression during function, well supported by bonding to enamel and dentin.

Another tooth-conserving example is the cantilevered adhesion bridge (Figs. 7–9) of porcelain fused to metal, bonded to enamel. This is similar to the ''Maryland bridge'' but the ''Yamashita adhesion bridge'' uses resistance channels placed in enamel [5]. Such mesial and distal channels produce a highly successful result [6] when the metal is bonded to phosphoric-acid–etched enamel.

Porcelain veneers are a third compelling application of adhesives. The adherends are porcelain and enamel, porcelain and dentin, or porcelain and both enamel and dentin. Veneers can be done successfully with minimal intra-enamel tooth reduction [7]. The survival rate in most reports exceeds 90% at 10 years. The high success rates can be attributed to durable bonding and support for the porcelain provided by tooth structures (Figs. 10–13).

All the clinical examples illustrated above can generally be accomplished in a straightforward manner by following manufacturers' instructions for

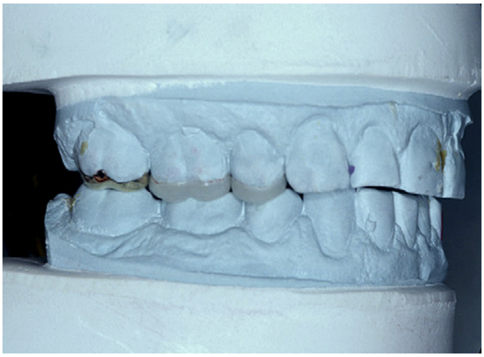

Fig. 4. Occlusal ''adhesion onlays'' of gold alloy and pressed ceramic.

Fig. 5. Onlay 5 years and 3 months after completion.

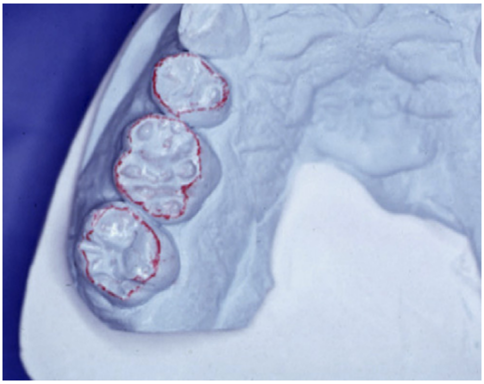

Fig. 6. Occlusal surface of cast with margins marked in red.

Fig. 7. Completed Yamashita adhesion bridge bonded to enamel.

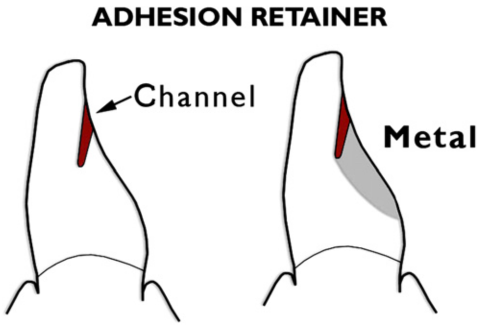

Fig. 8. Retainer preparation using intra-enamel channels.

the adhesive. While sometimes not as straightforward, porcelain repairs can also be highly successful. Some repairs require bonds to several dissimilar surfaces. After the discussion of metal adhesion and porcelain adhesion, some repair applications are illustrated and specific clinical protocols given for adhesion to multiple surfaces.

Metal adhesion

Mechanical retention

Adhesion to metal has long been a goal in dentistry. Resin-bonded "Rochette" [8] retainers were described in 1973. Retention was provided mechanically by composite resin locking into tapered perforations in the metal. A different approach to mechanical retention, using electrolytic etching to produce a microscopically retentive surface on the entire inner surface of the metal, was subsequently reported [9]. This etched metal is used for what is usually called the "Maryland bridge." Using the microscopic approach, two critical factors for successful adhesion to a metal substrate

Fig. 9. Adhesion retainer on cast, lingual view.

Fig. 10. Intra-enamel tooth preparations for a conventional veneer on the lateral incisor and "sectional" mesial veneer on the cuspid.

are (1) using an adhesive liquid with excellent wetting characteristics and (2) providing a high-energy metal surface to promote good wetting.

Substrate modification

Several researchers took a different approach to modifying the adherend metal surface. By itself or in conjunction with other procedures, sandblasting with aluminum oxide has become an almost universal procedure. Sandblasting with aluminum oxide can be done extraorally or intraorally. Sandblasting provides a fresh and uncontaminated surface that is high in surface energy and can be easily wetted by suitable metal bonding agents. Some other reported adherend modifications are high-temperature oxidation, immersion in an oxidizing agent, anodizing, and alloying the surface with a liquid gallium–tin alloy. In contemporary dental practices, these modifications do not appear to be used often. A different and more popular approach is adding a SiO_{x}-C coating by injecting a solution through a special flame [10]. Then a special silane is applied to the coated surface. This

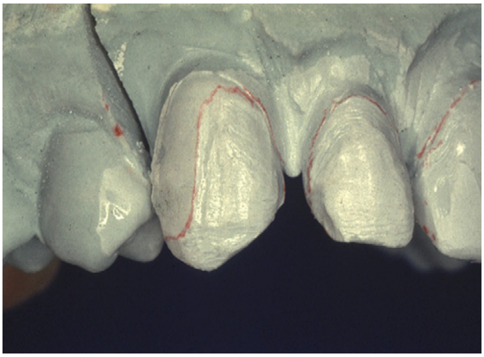

Fig. 11. Cast showing tooth preparations by marked margins.

Fig. 12. Immediate result after veneers were bonded.

method is known as Silicoater (Heraeus Kulzer, Hanau, Germany). A more recent approach, widely used, is known commercially as Rocatec in the laboratory and CoJet chairside (3M ESPE AG, Seefeld, Germany). With this method, a tribochemical silica coating is sandblasted onto the metal surface to provide ultrafine mechanical retention. When treated with the silica-coating system, the surface is not only "abraded," but becomes embedded with a silica coating derived from silica-coated aluminum oxide particles. Metal and many other surfaces may be abraded with 30-μm grain size CoJet-Sand. Intraoral application is done with an intraoral sandblaster (Fig. 14), such as the Microetcher (Danville Materials, San Ramon, California). A specialized silane coupling agent is then applied.

Chemical modification of filled resins

Modification of the chemistry of resin to create affinity for metals is another approach taken to strongly adhere resins to metals. Following the development in 1978 of a new adhesive monomer, 4-META [11], a commercial

Fig. 13. Veneer 8.5 years after bonding.

Fig. 14. Microetcher ERC II sandblaster with intraoral, contra-angle tip attached.

powder and liquid acryliclike product, Super Bond C&B (Sun Medical Co., Ltd., Kyoto City, Japan) was introduced in 1982 for adhesion to dental alloys and to tooth structures [12]. To improve mechanical properties of the adhesive resin and to change the handling characteristics, another approach was taken, which resulted in the product Panavia Ex (Kuraray, Osaka, Japan) [13]. It is a low-viscosity, quartz-filled composite resin containing a phosphate monomer known as M-10-P. Panavia is known to bond well to sandblasted base metals, but its bond to noble metals decreases when stored in water. To overcome this bond instability, the manufacturer developed a laboratory tin–plating apparatus, known as the Kura-Ace. It is used on noble metal alloys after sandblasting. Subsequently, two manufacturers produced portable tin platers capable of intraoral use [1]. These are Kura-Ace Mini (Kuraray) and Microtin (Danville Materials). A more recent product, similar to Panavia but using a different adhesion monomer, is Bistite II DC (Tokuyama, Tokyo, Japan). Tin plating has been challenged by the use of metal primers, presumably because metal primers are more expedient to

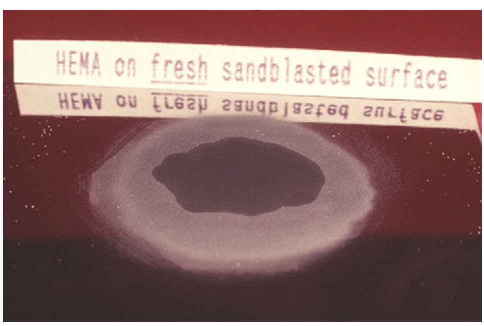

Fig. 15. Hydroxyethyl methacrylate on freshly sandblasted gold alloy surface. (*Courtesy of* Tom Blake, San Ramon, CA.)

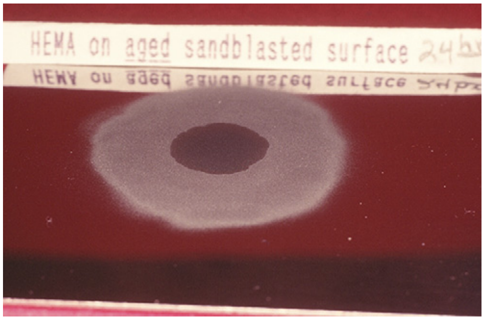

Fig. 16. Hydroxyethyl methacrylate on 24-hours–aged sandblasted gold alloy surface. (*Courtesy of* Tom Blake, San Ramon, CA.)

use. One recent study [14] compared the adhesive primers Alloy Primer (Kuraray), Metal Primer II (GC America, Alsip, Illinois), and Metaltite (Tokuyama) and the resin cements Bistite II (Tokuyama), Panavia F and Super-Bond C&B. All combinations appear to be potentially successful for the bonding of prosthodontic restorations, although there were reported differences in bond stability.

Unfilled ''universal'' bonding resins

As opposed to using a chemically modified filled resin, another method is to use a ''universal'' bonding agent, such as the All-Bond 2 System (Bisco, Inc., Schaumburg, Illinois), and then add a layer of filled resin. Primer B of the All Bond 2 System can function as a metal primer [15]. According to the manufacturer, when using the All-Bond 2 System, tin plating does not improve the bond strength of composite resin to sandblasted noble alloys. Similarly Clearfil (Kuraray) adhesives, such as Photo Bond and SE Bond, provide excellent metal bonding agents owing to the inclusion of the same adhesion monomer (M-10-P) as in Panavia.

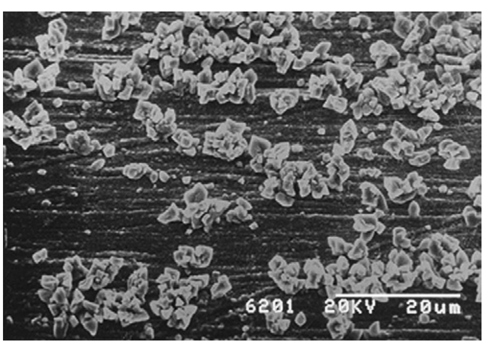

Fig. 17. Tin plate on sandpaper-treated gold alloy.

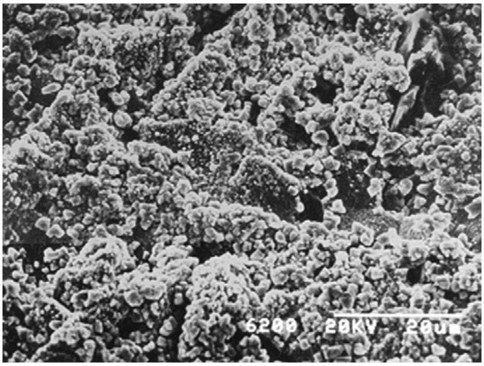

Fig. 18. Tin plate on gold alloy sandblasted with aluminum oxide.

Metal surface preparation

Contaminants on metal surfaces reduce surface energy and may compromise the bond strength to all resins. Sandblasting can remove such contaminants, creating a fresh, clean, and microscopically irregular surface with high surface energy. A high-energy surface is more wettable than a low-energy surface. An investigator, Tom Blake, looked at the effect of a delay after sandblasting, before the adhesive was applied. Blake, Director of Research at Danville Engineering, reported to the author in 2006 that the delay has a significant effect on wetting. Figs. 15 and 16 show the wetting of hydroxyethyl methacrylate (HEMA), a component of many bonding agents, at two elapsed times after sandblasting. When a measured drop of HEMA was applied to the "freshly" sandblasted gold alloy surface, a low contact angle and good wetting was observed. When the time was delayed for 24 hours after sandblasting, the HEMA did not wet as well, presumably because an absorbed layer on the metal surface lowered the surface energy.

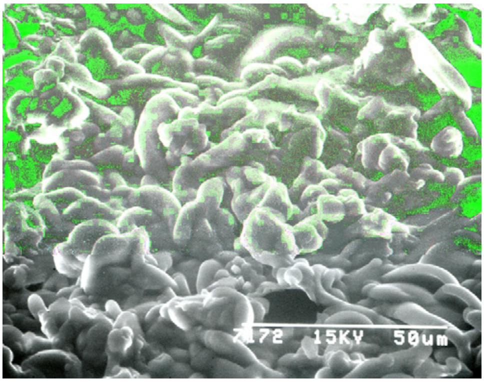

Fig. 19. Hydrofluoric-acid–etched porcelain. (*Courtesy of* Tom Blake, San Ramon, CA.)

Fig. 20. Three components of Clearfil Porcelain Bond, which are mixed before use.

Clearly there is an advantage to having sandblast capability at chairside to freshly sandblast metals just before applying adhesive. It is common for dentists in North America to use such sandblasting. Outside North America, use is far lower but, according to the manufacturer of CoJet, many dentists worldwide use similar sandblasters to apply CoJet sand.

Sandblasting is generally used before tin plating of noble metals. In addition to providing added mechanical retention, the sandblasting activates the metal surface and makes it more receptive to tin plating. Somewhat analogous to the above HEMA wetting experiment is the tin plating activity on the sandblasted surface compared with a surface polished with fine abrasive paper. Plating tin onto an aluminum-oxide–sandblasted gold alloy surface results in tiny crystals covering the entire surface. In contrast, tin plating after abrasive paper treatment results in large crystals growing out of a few active spots. Therefore, it appears that the best tin plating results by electroplating a freshly sandblasted surface (Figs. 17 and 18).

Fig. 21. Before repair.

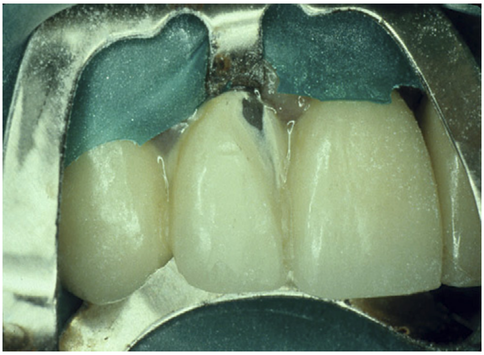

Fig. 22. Isolation.

The character of the tin crystal may play a role in the adhesion of resins to tin-plated metals. It may be that tin provides the enhanced mechanical retention or that a chemical bonding link to resin is established. In any event, the author's clinical experience with Panavia on tin-plated gold strongly suggests that the tin-plated metal-to-Panavia bond is superior to the Panavia-to-enamel bond. Debonds, although rare, invariably occur adhesively at the enamel-to-resin interface when Panavia is properly used. This observation is supported by shear bond testing [1]. It is interesting to note that "onlays" bonded with Panavia, when stressed to failure in a dislodgement test, broke the teeth cohesively rather than debond [13].

In summary, metal adhesion relies on an adhesive liquid with excellent wetting characteristics and a high-energy metal surface to promote good wetting. Modification of the adherend metal and modification of resin chemistry both play roles in achieving high bond strength and durability, important for clinical success.

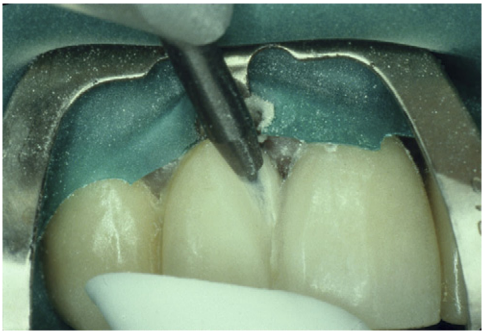

Fig. 23. Sandblasting of porcelain and metal with aluminum oxide.

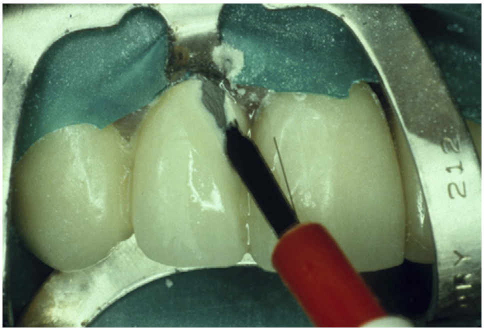

Fig. 24. Phosphoric acid cleansing of repair surface, followed by wash and dry.

Porcelain adhesion

Etchable porcelains and pressed ceramics

"Feldspathic" porcelain (eg, Ceramco 2; Dentsply, York, Pennsylvania) and pressed leucite– or lithium-disilicate–reinforced ceramics (eg, IPS Empress and Empress II; Ivoclar/Vivadent) are treated in similar ways before bonding. Being etchable with hydrofluoric acid and other fluorides (eg, acidulated phosphate fluoride and ammonium bifluoride), a strong resin bond can result from mechanical interlocking. Hydrofluoric acid (HF) solutions between 2.5% and 10% applied for 2 to 3 minutes are commonly used on porcelain and many pressed ceramics. The exact etching time depends on the substrate and the acid concentration. The glassy matrix of the porcelain is selectively removed and crystalline structures are exposed, creating a rough surface (Fig. 19). Some low-fusing porcelains and pressable ceramics do not etch well due to the low volume of acid-resistant crystalline structure.

Generally, etching is followed by application of a silane coupling agent. In addition to enhancing the wettability of the surface, the silane provides a chemical bond to the silica-based ceramic surface. Being bifunctional

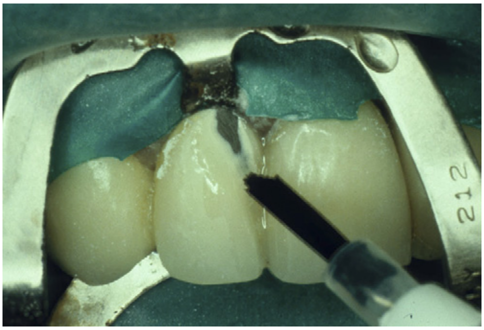

Fig. 25. Application of three-component Clearfil Porcelain Bond.

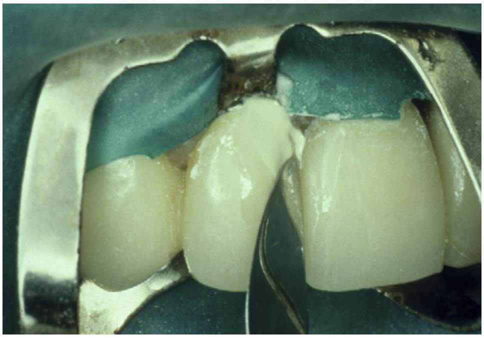

Fig. 26. Opaquer being applied, followed by light activation.

molecules, silanes bond to the silicon dioxide as well as copolymerize with the resins in the composite bonding agent that is subsequently applied. However clinical success has been reported [16] for bonding of etched porcelain veneers that had no silane applied. Presumably that success can be attributed to sufficient mechanical interlocking to resin created by etching of the porcelain surface.

Nonetchable ceramics

Nonetchable aluminum oxide or zirconium oxide surfaces (eg, Inceram; Vident, Brea, California) are not to be confused with HF-etchable porcelains. Since these oxides are not etchable with HF, they will not achieve a strong and stable bond by the same method as that used for porcelain [17]. Instead, certain adhesion monomers, such as M-10-P in Panavia, may be used to create a strong and stable bond. Likewise, Rocatec and Co-Jet are known to promote adhesion to these surfaces [17].

A little-known [18] product line called Clearfil (Kuraray) bonds silica-based ceramics without the need for HF etching; it only uses sandblasting.

Fig. 27. Application of composite, followed by light activation and polishing.

Fig. 28. Completed repair.

The porcelain bonds are equal to those achieved by HF etching followed by the best silanes [19]. Clearfil products are not the only ones capable of such porcelain bonds. However, unlike the other products, Clearfil products also simultaneously (with only one mix of material) bond to metals, etched enamel, and etched dentin. Clinical use of one of these products, Clearfil Photo Bond base and catalyst mixed with Clearfil Porcelain Bond Activator (Fig. 20), is illustrated later for simultaneous bonding to multiple substrates. This combination of three components is known as Clearfil Porcelain Bond. All Clearfil products are also capable of bonding to alumina and zirconia due to the Panavia monomer M-10-P in their formulas.

Complex clinical applications

Porcelain repair

Clinicians often face challenging cases where adhesion to multiple surfaces is required. Such a case is illustrated by the fractured porcelain on

Fig. 29. Tooth loss, before replacement.

Fig. 30. Porcelain removed from distal abutment.

a five-unit fixed partial denture (Fig. 21). Successful repair with composite resin requires simultaneous adhesion to a base metal alloy and also to porcelain. Many similar situations also involve adjacent dentin and enamel (eg, an endodontic opening in a crown) where there would be metal, porcelain, dentin, and, perhaps, enamel. Illustrated below is a clinical example [1] where Clearfil Photo Bond (a sort of dual-cure "prime and bond") mixed with the Clearfil Porcelain Bond Activator is used to bond to all surfaces simultaneously (Figs. 22–28).

Pontic addition

Another challenging situation is the loss of a tooth adjacent to a relatively new three-unit fixed partial denture. With the capability for intraoral sandblasting and tin plating, the replacement of this lost tooth is easy. Porcelain is removed from the distal tooth of the existing restoration to create a preparation that will draw occlusally, in alignment with the preparation of the natural tooth distal abutment. A three-unit repair is prepared in the

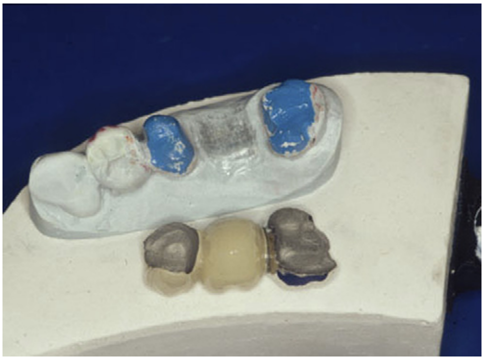

Fig. 31. Repair base metal casting with porcelain applied.

Fig. 32. Microtin plater with contact ring for intraoral connection.

laboratory. Since the existing metal is a noble alloy, sandblasting and intraoral tin plating is used to condition the prepared abutment. The repair casting only requires sandblasting since it is fabricated with a base metal alloy. The natural tooth abutment distal to the missing tooth is treated with self-etching ED Primer (Kuraray) before bonding with Panavia F. The Panavia F bonds to the ED Primer as well as to both conditioned metals (Figs. 29–34).

Other uses

Following techniques similar to those used in the aforementioned tooth replacement, a procedure for replacement of a missing acrylic facing on a gold-acrylic crown has been published [20]. Again, intraoral sandblasting and tin plating were used to condition the metal. Panavia was then used to bond a fully opaqued Artglass (Heraeus Kulzer) facing the conditioned metal. Using similar technology, modification of existing gold occlusals by intraoral bonding of new occlusal gold was reported [21].

Fig. 33. Intraoral tin plating of sandblasted metal surface.

Fig. 34. Tooth replacement complete.

Summary

Development of adhesives and modification of adherends have made it possible to bond to metal and porcelain with enamel-like adhesion. Maximum tooth conservation is the compelling advantage in using these materials and methods.

References

[1] Bertolotti RL, Lacy AM, Watanabe LG. Adhesive monomers for porcelain repair. Int J Prosthodont 1989;2:483–9.

[2] Zollner A, Gaengler P. Pulp reactions to different preparation techniques on teeth exhibiting periodontal disease. J Oral Rehabil 2000;27:93–102.

[3] Uchiyama Y. Adhesion in prosthetic restorations. In: Gettleman L, Vrijhoef MMA, Uchiyama Y, editors. Adhesive prosthodontics. Chicago (IL): Academy of Dental Materials; 1986. p. 21–31.

[4] Guess PC, Stappert CF, Strub JR. Clinical study of press ceramic and cerec partial coverage restorations. Presented at the International Association for Dental Research 84th General Session. Brisbane, Australia, June 28–July 1, 2006. Abstract number 1639.

[5] Yamashita A, Yamani T. Adhesion bridge, background and clinical procedure. In: Gettleman L, Vrijhoef MMA, Uchiyama Y, editors. Adhesive prosthodontics. Chicago (IL): Academy of Dental Materials; 1986. p. 61–76.

[6] Botelho MG, Lai SCN, Ha WK, et al. Two-unit cantilevered resin-bonded fixed partial dentures—a retrospective, preliminary clinical investigation. Int J Prosthodont 2000;13:25–8.

[7] Freedman MJ. Porcelain veneer restorations: a clinician's opinion about a disturbing trend. J Esthet Restor Dent 2001;13:318–27.

[8] Rochette AL. Attachment of a splint to enamel of lower anterior teeth. J Prosthet Dent 1973; 37:28–31.

[9] Livaditis GL, Thompson VP. Etched castings: an improved retentive mechanism for resin-bonded retainers. J Prosthet Dent 1982;47:52–8.

[10] Vojvodic D, Predanic-Gasparac H, Brkic H, et al. The bond strength of polymers and metal surfaces using the 'silicoater' technique. J Oral Rehabil 1995;22:493–9.

[11] Takeyama M, Kashibuchi S, Nakabayashi N, et al. Studies on dental self-curing resins. Adhesion of PMMA with bovine enamel or dental alloys. Shika Rikogaku Zasshi 1978; 19(47):179–85 [in Japanese].

[12] Nakabayashi N, Takeyama M, Kojima K, et al. Studies on dental self-curing resins—adhesion of 4-META/MMA-TBB resin to pretreated dentine. Shika Rikogaku Zasshi 1982; 23(61):29–33 [in Japanese].
[13] Wada T. Development of a new adhesive material and its properties. In: Gettleman L, Vrijhoef MMA, Uchiyama Y, editors. Adhesive prosthodontics. Chicago (IL): Academy of Dental Materials; 1986. p. 9–19.
[14] Yoshida K, Kamada K, Sawase T, et al. Effect of three adhesive primers for a noble metal on the shear bond strengths of three resin cements. J Oral Rehabil 2001;28:14–9.
[15] Cinione FA, Stojkovich L, Suh BI. Resin:metal adhesion and the all bond 2 system. Esthetic Dent Update 1993;4:38–47.
[16] Freedman MJ. A 15-year review of porcelain veneer failure: a clinicians observations. Compendium Cont Dental Educ Dent 1998;19:625–8, 630, 632.
[17] Kern M, Thompson VP. Bonding of glass infiltrated alumina ceramic: adhesive methods and their durability. J Prosthet Dent 1995;73:240–9.
[18] Bertolotti RL. Bonding to porcelain (forum). Practical Periodontics and Aesthetic Dentistry 2005;17:232.
[19] Llobell A, Nichols JI, Kois JC, et al. Fatigue span of porcelain repair systems. Int J Prosthodont 1992;5:205–13.
[20] Bertolotti RL, Miller D. Gold-acrylic facing replaced by intraoral bonding of a polyglass: a case report. Quintessence Int 1999;30:557–9.
[21] Bertolotti RL, DeLuca SS, DeLuca S. Intraoral metal adhesion utilized for occlusal rehabilitation. Quintessence Int 1994;25:525–9.