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Review

History and current state of metal adhesion systems used in prosthesis fabrication and placement

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Abstract: The adhesion techniques used in prosthetic dentistry have substantially improved with respect to retention of veneering resin to the metal framework of resin-veneered restorations and the bonding of resin-bonded fixed partial dentures (RBFPDs) to abutment teeth. In the early 1970s, prostheses relied on macromechanical retention for veneering surfaces and the retention holes of retainers. Later, retention was achieved by using small spherical particles. In addition, the use of small pits created by electrochemical corrosion was tested in resin-veneered restorations and RBFPDs. Thus, micromechanical retention gradually supplanted macromechanical retention. First-generation adhesive monomers were introduced at the end of the 1970s and were succeeded in the early 1980s by the marketing of adhesive resin cements, which were effective for use with non-noble alloys when surface oxidation procedures were used. In 1994, a second-generation adhesive primer for noble alloys was introduced, which prompted development of other adhesive primers. These primers were applied mainly to silver-palladium-copper-gold and type IV gold alloys and improved the reliability of RBFPDs. Recent studies have confirmed the effectiveness of such primers when used with high-gold-content metal ceramic alloys. Due to these developments, RBFPDs now have excellent esthetic characteristics.
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Introduction

A number of retention systems are used in prosthodontic practice to combine dental alloys with the tooth structure. Although such systems may utilize mechanical or adhesive retention, adhesive systems are now more common. Development of the bonding materials presently used in dental practice did not begin until the end of the 1970s. Previously, retention of dental alloys to the tooth structure depended on mechanical retention, and various systems were devised for this purpose. Such retention systems were mainly used in the fabrication of resin-veneered restorations and removable dentures. However, the need for more-accurate prostheses produced innovations that led to the transition from macromechanical to micromechanical retention systems.

At the end of the 1970s the first-generation adhesive monomers were synthesized. These adhesive monomers included 4-methacryloyloxyethyl trimellitate anhydride (4-META) and 10-methacryloyloxydecyl dihydrogen phosphate (MDP) and were shown to be effective for use with non-noble metal alloys. Attempts were made to use these monomers in fabricating restorations and placement of metal crowns on abutment teeth. However, because metal adhesion systems at that time were not fully established, the use of these adhesives was very limited. Second-generation adhesive monomers were introduced to clinical practice at the end of the 1980s and were effective for use with noble metal alloys. The

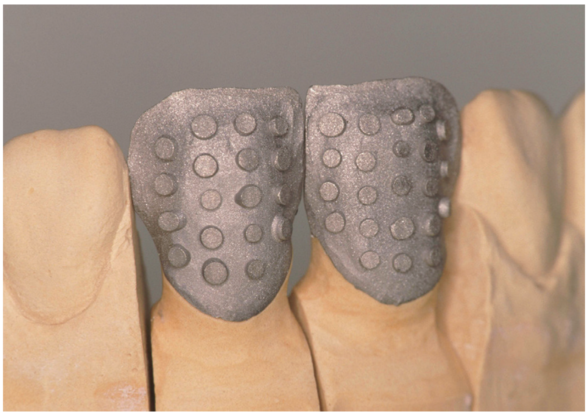

Fig. 1 Convex structures used for macromechanical retention on the facing surface. Reproduced from Tanaka T et al. DE (1977) 40, 1-5.

Fig. 2 Spherical particles used for retention of facing resins. Reproduced from Tanaka T et al. J Jpn Prosthodont Soc (1990) 34, 364-371.

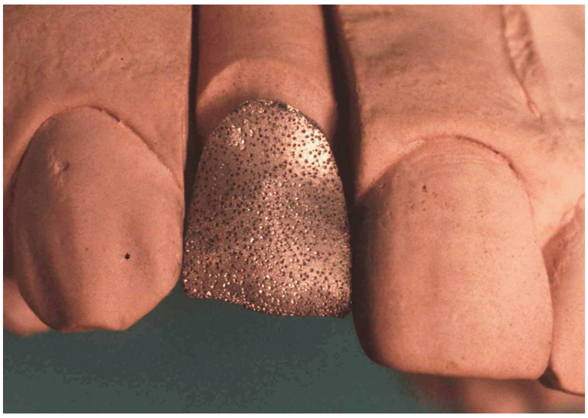

Fig. 3 Small pits formed on the facing surface by electrochemical corrosion. Reproduced from Tanaka T et al. J Prosthet Dent (1979) 42, 282-291.

Fig. 4 Lingual view of Rochette bridge. Retainers have countersunk holes for macromechanical retention. Reproduced from Tanaka et al. Quintessence of Dental Technology (1985) 10, 276-296.

best-known example was 6-(4-vinylbenzyl-n-propyl) amino-1,3,5-triazine-2,4-dithiol (VBATDT). Recently, in addition to better bonding performance, their applicability has remarkably improved. Moreover, they can be used with a variety of metal alloys, including noble and non-noble metal alloys. This article describes the history of metal adhesion systems used in the fabrication of restorations and placement of fixed partial dentures and presents clinical prosthodontic cases that illustrate the latest metal adhesion techniques.

The era of mechanical retention systems

Use in fabricating prosthetic restorations

The resin-veneered restoration is a representative crown restoration and combines a polymer material with a metal. Macromechanical retention was used before the development of systems that could bond metal and polymer materials. Beginning in the early 1970s, convex structures were applied to veneering surfaces to assist in retaining veneering resins (Fig. 1).

Due to their superior esthetics and reduced marginal leakage, powders made up of small spherical particles replaced retention devices in the fabrication of resin-veneered restorations (1) and their use is now widely accepted (Fig. 2).

Another method of retaining veneering resin utilizes electrochemical corrosion (2) to produce numerous small pits on the veneering surface of nickel-chromium alloy, without a need for convex structures (Fig. 3). This method was not used for veneer retention in resin-veneered restorations but as a surface treatment for the retainers of resin-bonded fixed partial dentures (RBFPDs). This was the start of RBFPD development, which has continued up to the present.

Use in bridge placement

Another representative crown restoration combines a polymer material with metal and is also considered an RBFPD. Various types of RBFPDs and implants can be chosen for patients with one missing tooth and intact

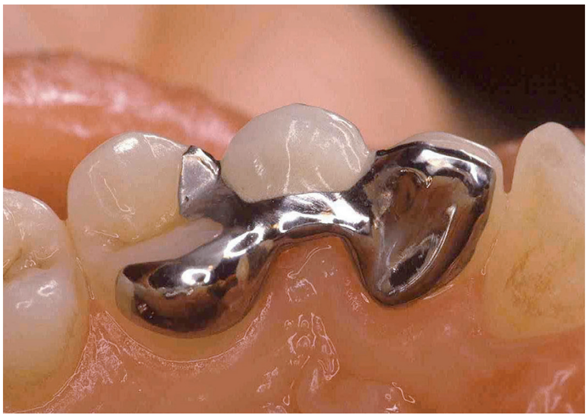

Fig. 5 Lingual view of Maryland bridge. Reproduced from Tanaka T et al. Dental Outlook (1984) 63, 753-767.

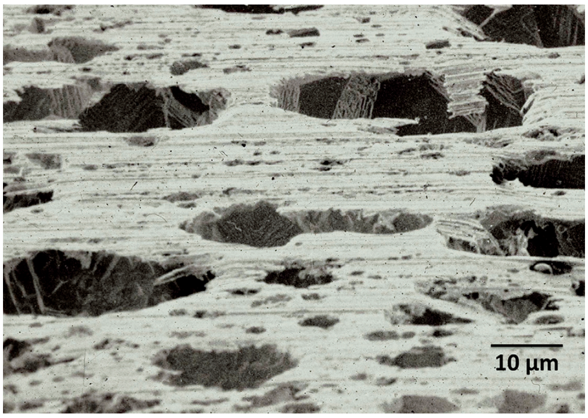

Fig. 6 SEM view of electrolytically etched surface for micromechanical retention (original magnification ×400).

Fig. 7 Tin plating procedure and plating device for RBFPD retainers. Reproduced from Tanaka T et al. Dental Outlook (1984) 63, 753-767.

Fig. 8 RBFPD that underwent surface oxidation by heat treatment. Reproduced from Tanaka T et al. J Prosthet Dent (1988) 60, 271-279.

adjacent teeth.

The Rochette bridge was introduced for temporary use in 1973 and is considered the origin of the RBFPD (3). This bridge was placed onto the etched enamel of abutment teeth, using retainers with countersunk holes for retention and a chemical polymerizing composite resin for filling (Fig. 4). Although the composite resin adhered to the etched enamel, the retainer had holes that were filled with composite resin, to facilitate macromechanical retention. This concept is comparable to the macromechanical retention achieved by veneering resin in the fabrication of resin-veneered restorations.

The Rochette bridge had disadvantages, including risk of fracture due to insufficient retainer strength and the fact that considerable skill was required during placement because of the short polymerization time of the composite resin. To address these problems, the Maryland bridge was developed at the end of the 1970s (4) (Fig. 5). The intaglio of the retainer was electrolytically etched to form numerous undercuts (Fig. 6) that ensured micromechanical retention of composite resin. The procedure was very similar to the pitting corrosion used in fabricating resin-veneered restorations. The Maryland bridge was easy to place and strong, as it does not use retention holes on the retainers. However, it also had disadvantages: it required a complicated electrolytic etching procedure and only nickel-chromium alloys could be used.

First-generation metal adhesion systems

The adhesive 4-META was developed in 1978 and was the first adhesive monomer to be effective for use with dental metal alloys. It prompted the launch in 1982 of Super-Bond C&B (Sun Medical Co., Ltd., Moriyama, Japan), which contained 4-META, and the development in 1983 of Panavia EX (Kuraray Co., Ltd., Osaka, Japan), which contained MDP. These adhesive resin cements were combined with the retainers of the Maryland bridges. Because these adhesive monomers are able to firmly adhere to non-noble metal alloys (5-7), cobalt-chromium and nickel-chromium alloys could be used in

Fig. 9 Intaglio of gold-platinum alloy onlay before surface oxidation.

Fig. 10 Intaglio of onlay after surface oxidation by heating.

Fig. 11 Onlay bonded to abutment tooth. The onlay can be easily polished after bonding.

fabricating metal frameworks.

Nevertheless, development of adhesive primers that could be used with noble metal alloys was desirable due to the negative esthetics and allergenic effects of non-noble metal alloys. Before the development of adhesive primers for noble alloys, techniques were developed to produce an oxidized layer on the surface of noble metal alloys, as this allowed subsequent application of adhesive monomers that contained 4-META and MDP. These techniques included tin plating (8-10) and formation of an oxide layer by heating (11) the surface of the noble metal alloy. Figure 7 shows the procedure used for tin plating (8-10) the retainers of an RBFPD. Tin plating required a proprietary device and plating liquid. In addition, the procedure was quite complicated and the shelf life of the plating liquid was limited. Figure 8 shows a bridge that has undergone surface oxidation treatment by heating (11). The oxidation procedure usually required a furnace; thus, it was impossible to veneer with composite resins. Strong bonding of the restoration to the tooth structure enabled maximal conservation of intact tooth structure (Figs. 9-11) in cases of large cavities.

Second-generation metal adhesion systems

The first adhesive monomer for noble metal alloys was VBATDT (12-15), an ingredient in V-Primer (Sun Medical Co., Ltd.), which was first marketed in 1994. VBATDT is also an ingredient in Alloy Primer (Kuraray Medical Inc., Tokyo, Japan), which is available for both noble and non-noble metal alloys. These primers are applied to the fresh metal surface.

Other adhesive monomers were developed after VBATDT, and adhesive primers for noble metal alloys have been developed and marketed (Table 1). Figure 12 shows the chemical structures of the adhesive monomers contained in each primer. All adhesive monomers for noble metal alloys have a sulfur-containing component, which is believed to react with the noble metal alloy.

However, sulfur-containing monomers inhibit polymerization of resins initiated by the BPO-amine redox system. Therefore, Super-Bond C&B is preferred as an adhesive resin cement for combined use with sulfur-containing primers, as it uses partially oxidized tri-n-butylborane (TBBO) as an initiator.

Current state of adhesive primers for noble metal alloys

Because adhesive primers for noble metal alloys are effective for use with silver-palladium-copper-gold alloy and type IV gold alloy (14,16-19), these alloys are frequently used for the retainers of RBFPDs. However, because the effectiveness of these primers for each metal element was unclear, the effects of these primers with pure gold (Au), silver (Ag), copper (Cu), and palladium (Pd) (the metal elements in silver-palladium-copper-gold alloy) were evaluated (20). The results (Fig. 13)

Table 1 Primers available for noble metal alloys

Adhesive monomer	Typical commercial product	Indication	Manufacturer
MEPS	Metal Primer II	Noble and non-noble metal alloys	GC Corp., Tokyo, Japan
VBATDT	V-Primer	Noble metal alloys	Sun Medical Co., Ltd., Moriyama, Japan
	Alloy Primer	Noble and non-noble metal alloys	Kuraray Medical Inc., Tokyo, Japan
MTU-6	Metaltite	Noble metal alloys	Tokuyama Dental Corp., Tokyo, Japan
MDDT	M.L. Primer	Noble and non-noble metal alloys	Shofu Inc., Kyoto, Japan

MEPS: thiophosphate methacryloyloxyalkyl derivatives
VBATDT: 6-(4-vinylbenzyl-n-propyl) amino-1,3,5-triazine-2,4-dithiol
MTU-6: 6-methacryloyloxyhexyl 2-thiouracil-5-carboxylate
MDDT: 10-methacryloyloxydecyl-6, 6-dithiooctanoate

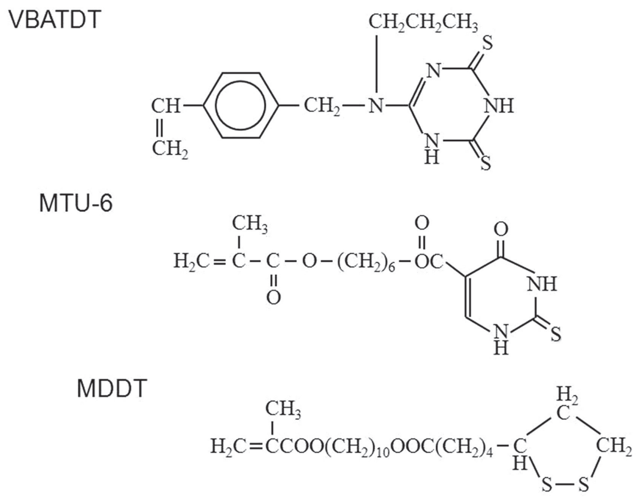

Fig. 12 Chemical structure of adhesive monomers used with noble metal alloys.

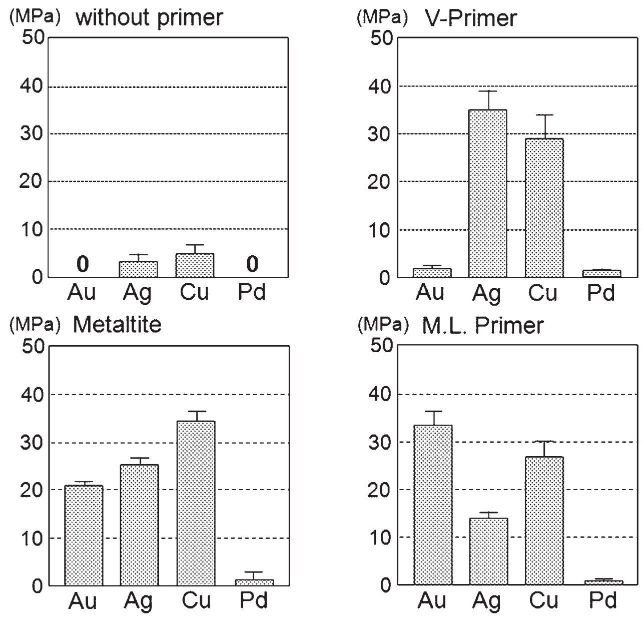

Fig. 13 Shear bond strength of Super-Bond C&B to each element metal after 2000 thermal cycles. Error bars denote standard deviations.

confirmed the effectiveness of V-primer for Ag, Metaltite for Cu, and M.L. Primer for Au. None of the primers was effective for Pd.

The disadvantage of RBFPDs fabricated from silver-palladium-copper-gold alloy or type IV gold alloy is that the pontic must be veneered with prosthetic composite resin. To address this problem, the pontic may be faced with porcelain. In particular, the use of noble metal ceramic alloys has superior biocompatibility and workability. However, this technique has not been introduced to clinical practice because there was some suspicion that metal primers for noble alloys would not work well with noble metal ceramic alloys. The reason for this belief is that Cu, which has high reactivity with adhesive monomers (Fig. 13), is not used in noble metal ceramic alloys, so as to prevent porcelain discoloration during firing. In addition, noble metal ceramic alloys contain only a small amount of Ag (which is also reactive to adhesive monomers), (Fig. 13) because it too provokes discoloration during firing. Thus, in addition to tin plating, the Silicoater MD (21,22) and Rocatec (21) have been studied for surface treatment of noble metal ceramic alloys. However, because both of these systems require proprietary devices, a simple and effective bonding procedure was still needed.

As part of the continued examination of the effects of primers on element metals (Fig. 13), the effects of primers on alloys of varying gold content (12-88%) (Table 2) were studied (23). When primed with M.L. Primer, high-gold-content alloys, including IFK88 and W85, maintained their bond strength after 50,000 thermal cycles. Indeed, the values were equivalent to those obtained with silver-palladium-copper-gold alloy (Fig. 14).

The bond strength achieved by combined use of IFK88 and M.L. Primer was then evaluated after a longer duration of thermal cycling. The results showed that bond

Table 2 Dental gold alloys

Material	Brand name	Composition (w%)	Manufacturer	Code
Metal-ceramic gold alloy	Super Metal W-85	Au (78), Pt (7.1), Pd (9.8), Ag (2.4)	Noritake Co., Ltd., Nagoya, Japan	W85
	IFK88 GR	Au (88), Pt(9.8)	Ishifuku Metal Industry Co., Ltd., Tokyo, Japan	IFK88
Metal-ceramic palladium alloy	Super Metal N-40	Pd (44), Au (43), Ag (2)	Noritake Co., Ltd., Nagoya, Japan	N40
Silver-palladium-copper-gold alloy	Castwell M.C.12	Ag (46), Pd (20), Cu (20), Au (12)	GC Corp., Tokyo, Japan	MC12

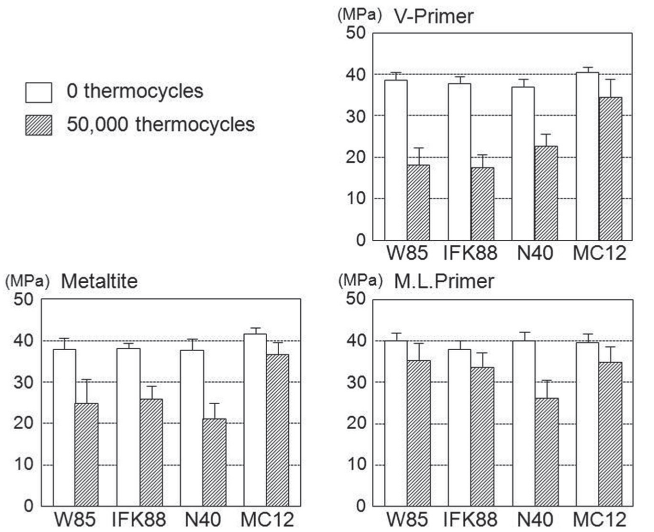

Fig. 14 Shear bond strength of Super-Bond C&B to alloys with varying gold content. Error bars denote standard deviations.

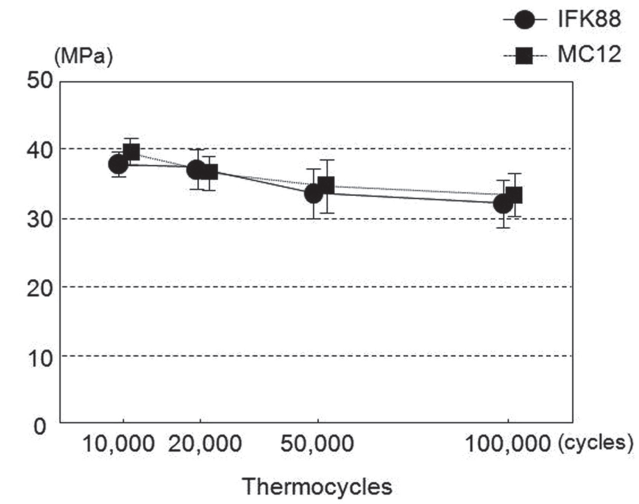

Fig. 15 Shear bond strength of Super-Bind C&B to high-gold-content alloy after extended thermal cycling. Error bars denote standard deviations.

Fig. 16 Buccal view of RBFPD fabricated from high-gold-content alloy and faced with porcelain. Reproduced from Tanaka T. QDT Art & Practice (2012) 37, 50-58.

Fig. 17 Lingual view of RBFPD fabricated from high-gold-content alloy and faced with porcelain. Reproduced from Tanaka T. QDT Art & Practice (2012) 37, 50-58.

strength after 100,000 thermal cycles (32 MPa) was equivalent to that of silver-palladium-copper-gold alloy (Fig. 15), which confirmed the clinical utility of the bonding procedures used for fabricating RBFPDs from high-gold-content metal ceramic alloys.

An example of the clinical application of an RBFPD fabricated from high-gold-content alloy and faced with porcelain is shown in Figs. 16 and 17. The esthetic appearance of the pontic is enhanced by porcelain facing. The time required is similar to that needed for fabricating an RBFPD using a silver-palladium-copper-gold alloy retainer and composite resin veneer. In addition, the bridge can be installed using routine procedure, i.e., airborne particle abrasion with alumina particles followed by application of M.L. Primer to the retainers and bonding with Super-Bond C&B.

Implant treatment has become popular in the prosthetic treatment of missing teeth, as it results in satisfactory esthetics with no reduction of adjacent teeth. However, the clinical procedures required to fabricate RBFPDs using high-gold-content metal ceramic alloys are no different from those used for conventional RBFPDs. As compared with implant treatment, RBFPDs are advantageous with respect to time and fabrication cost. Therefore, the RBFPD should be considered a useful option in prosthetic treatment, due to its minimal invasiveness and optimal metal adhesion system.

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