
Effect of interfacial variables on metal-porcelain bonding

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While ceramic-to-metal bonding has been used in many applications, the actual chemical and physical factors leading to optimum bond strength are not well understood. In this work, several variables affecting the bonding between dental porcelain and a palladium alloy (85% Pd, 10% Cu, and 5% Ga) were investigated: 1) precoating the metal by sputtering various oxides before porcelaining; 2) preoxidation of the metal base before porcelaining; 3) porcelaining under reducing atmosphere; and 4) surface roughening at controlled levels before porcelaining.

Using a modification of the push doughnut shear bond strength test to measure bond strength the following results were obtained. 1) Compared with standard

"control" samples, the aluminum oxide precoated specimens showed a bond strength improvement of 46%, while the copper, manganese, and tin oxide precoatings exhibited smaller effects. 2) Preoxidation of the metal base led to pronounced bond strengthening (152%) by surface roughening as well as oxide formation. 3) Porcelaining under a reducing atmosphere severely reduced bond strength (88% lower than the controls) indicating the role of oxidation during the standard firing cycle. 4) Mechanical roughening of the surface by controlled amounts gave pronounced improvements with greater notch depth. Coarse roughening produced the highest bond strength improvements (486%). © 1993 John Wiley & Sons, Inc.

INTRODUCTION AND OBJECTIVES

Dental research in ceramic-to-metal bonding has focused on two areas. First, the development and testing of alloy-porcelain systems for crowns and bridges and second, more basic research to understand the physical mechanisms involved in the bonding. The present study falls within the latter area.

There are three main factors that determine the success of a ceramic-metal bond: residual stress gradients, interfacial chemistry, and the interfacial morphology.

Much of the basic research has concentrated on residual stresses and thermal expansion compatibility. With large differences in thermal expansion coefficients, residual stress gradients will form across the interface during processing. These stresses can be so strong that either the bond fails at a much lower stress level or the porcelain spontaneously spalls off. Generally we attempt to limit differences in thermal

expansion coefficients between the ceramic and the metal. In this research the thermal expansion coefficients of the alloy and ceramic were matched to isolate the other factors—interfacial chemistry and interfacial morphology.

Researchers over the past 50 years have attempted to determine the chemical nature of the interface formed between ceramics and metals. Several theories¹⁻¹⁶ have been put forward; however, relatively little physical evidence has been available to support those theories.

Theories of the effects of interfacial morphology have been mixed.^{17,18} Some researchers believe that rough interface morphologies improve bond strength by mechanical attachment or by increased area for chemical bonding. However, others believe that roughness can weaken the interface by causing stress concentrations that could initiate fracture and others believe that roughness could cause incomplete contact between the metal and ceramic (and trapped gases), which could also reduce bond strength.

The purpose of this study was to determine relative effects of a range of interfacial treatments which fall

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within two categories: modifying the chemistry of the interface or modifying the morphology of the interface. In general, the purpose was to develop techniques that could be used to improve ceramic-to-metal bonding for porcelain-fused-to-metal dental crowns and bridges.

MATERIALS AND METHODS

Alloy and porcelain

To simplify interface reactions a single phased alloy with simple composition was necessary. It was also desirable for practical significance for the alloy to have similar composition to available dental alloys. Several alloys were developed and tested. An alloy composed of Pd-10%Cu-5%Ga was found to meet the requirements. The composition of this alloy is similar to that of the Pd-Cu dental alloys, examples of which include Liberty (J.F. Jelenko & Co., Div. Pennwalt Corp., Armonk, NY), Natural Lite (Jeneric Industries, Inc., Wallingford, CT), Option (J.M. Ney Co., Bloomfield, CT), and Spartan (Williams Dental Co., Inc., Buffalo, NY). The specimens were cast using standard dental techniques; then the specimens were finished to a 1 μm diamond polish before surface treatment.

The ceramic used in this study was a dental porcelain (Vita VMK 68 531 opaque porcelain, Vita Zahnfabrik, H. Rauter GmbH & Co. KG, Bad Säckingen, West Germany). It was applied to the alloy specimens (after the surface treatments) using standard dental porcelaining technique. For the mechanical test four layers of porcelain were applied and fired to build up the required thickness. The porcelain was fired using the manufacturer's directions for this porcelain.

Surface treatments

Precoatings. Several techniques to apply oxide precoatings were investigated and radio frequency sputtering was found to be most suitable.¹⁹⁻²² Specimens were sputter cleaned to remove any contaminants or oxides from the alloy surface. Then they were precoated with Al_2O_3 , Mn_2O_3 , CuO , or SnO_2 thin films (before the porcelain coating application). These oxides were chosen for their differences in physical properties. The primary properties of interest were the mechanical properties (based on hardness) and the stability (based on free energy of formation): CuO has the lowest hardness and stability, while Al_2O_3 has the highest hardness and stability. There are many other oxides that could be tested using these procedures. The standard precoating thickness was 100 nm; however, with the Al_2O_3 specimens three coating thicknesses were tested.

Furnace Treatments. There were two furnace treatments: preoxidation of the alloy before porcelain application, and porcelain firing under reducing conditions. To preoxidize specimens, alloy rods were placed in the furnace, heated to 982°C, and held in air for 5 min before porcelain application. This treatment produced a heavily oxidized surface. To eliminate the effect of oxidation, another set of specimens was coated with porcelain and fired under the reducing conditions of a 95% argon-5% hydrogen atmosphere. The specimens were placed in the furnace, a vacuum of 1 torr was applied, and the specimens were heated to 260°C and held for 1/2 h to drive off water. Then the Ar-5%H atmosphere was introduced at a flow rate of 150 cc/min and maintained throughout the firing cycle. The specimens were heated as with the normal firing cycle. However, after attaining the peak temperature, the specimens were then moved to a cool portion of the furnace and allowed to cool under the protective Ar-5%H atmosphere.

Roughness. A series of specimens with progressively rougher surfaces was produced.

The methods used to make these were: a) centerless grinding using 400 grit SiC paper; b) sand blasting with 25 μm alumina grit; and c) grooving with 1 mm deep and 1 mm wide cuts around the specimens. These were compared with the standard finish of 1 μm diamond polish.

Shear bond strength testing

There have been many mechanical tests developed for measuring the adhesion between ceramics and metals. For this study a simple shear test was chosen. As indicated by Anusavic et al.²³ the actual bond strength is difficult to determine with these tests because of nonuniform stress distributions. However, for this research the actual bond strength was not as important as the relative bond strengths resulting from the various treatments. In addition, the same alloy and porcelain were used for all specimens. Therefore the effects of thermal expansion incompatibility and differences in elastic moduli on bond strength were identical for all specimens and can be ignored when comparing the various treatments.

The bond strength test used in this research was a modification of the push doughnut test developed by Shell and Nielson and then later Asgar.^{24,25} The configuration of the test is shown in Figure 1. A 10 mm by 5 mm doughnut (torus) of porcelain was fired onto a 45 mm by 3 mm alloy rod. After the porcelain doughnut was fired in place on the rod, the area of the rod not covered by the porcelain was coated with a thin layer of wax (the wax prevented adhesion between the alloy rod and the stone). Then the rod and porcelain were encased in dental stone, a high-strength plaster of paris. The upper

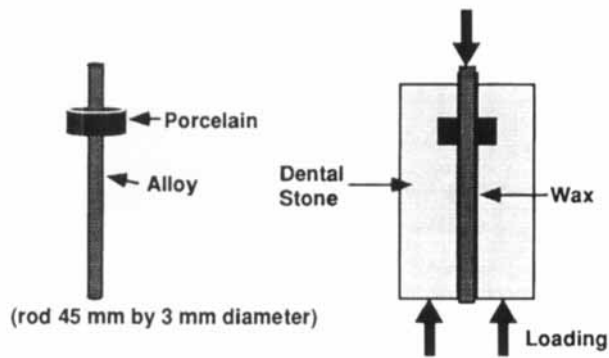


Figure 1. Configuration of the push doughnut test for measuring shear bond strength.

end of the rod was loaded in axial compression in a standard compression testing machine with a self-aligning head. Fracture occurred in shear between the doughnut of porcelain and the metal. Significance of differences in bond strength between materials were verified using ANOVA and the Bonferroni *t* procedure (both at $P \leq .05$).

Interface examination

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe fractured and intact specimens. Both microscopes were equipped for energy dispersive x-ray spectroscopy.

RESULTS

Effects of interface chemistry on bond strength

As shown in Table I, all the oxide precoatings improved bond strength over the controls (the controls had no precoatings, just polished surfaces). Statistically significant improvements were found with the Al_2O_3 precoatings, which improved bond strength by 46% ($P \leq .05$). Greater thickness of the Al precoatings improved bond strengths even further. The other oxides improved the bond strength by 24% for SnO_2 , and by 32% for Mn_2O_3 and CuO , but these improvements were not statistically significant.

Next a technique commonly used in dentistry, pre-oxidation, was tried. Here the formation of a heavily oxidized surface resulted in a 152% improvement in bond strength (statistically significant at $P \leq .05$). This improvement is probably not solely due to the change in interface chemistry, but may be due to increased interface roughness (as will be discussed later).

It was found that the alloy in all the previous cases oxidized during porcelaining. Therefore, to eliminate the effect of oxidation, uncoated polished specimens were fired under the reducing conditions of an Ar-5%H atmosphere. This resulted in very significant reductions in bond strengths (-88%).

Effects of roughness on bond strength

Evidence both from electron microscopy of the previously mentioned specimens and from the

TABLE I
Bond Strengths Resulting from Various Treatments

Treatment	Bond Strength (MPa)	Standard Deviation (MPa)	Sample Size
Control	23.7	3.9	7
Preoxidized	59.7	13.1	7
100 nm oxide precoatings			
SnO_2	29.5	11.4	6
Mn_2O_3	31.3	8.5	5
CuO	31.3	2.2	3
Al_2O_3	34.6	5.7	7
Increased thickness of precoating			
Al_2O_3 , 100 nm	34.6	5.7	7
Al_2O_3 , 175 nm	39.0	7.8	5
Al_2O_3 , 350 nm	46.9	2.6	2
Roughness series			
Control	23.7	3.9	7
400 grit SiC paper	64.5	6.1	6
Sandblasted	81.1	2.2	2
Notched	139.0	4.1	3
Reducing atmosphere series			
Control, reduced	2.9		1
Al_2O_3 , reduced	2.6		1
Preoxidized, reduced	15.7		1
Sandblasted, reduced	25.0		1

literature indicates that roughening the interface will affect bond strength. Therefore a series of specimens with different interfacial roughness was tested. Table I shows that there is a strong correlation between the roughness and bond strength. The roughest finish showed the highest bond strengths (139.0 MPa, 486% higher than the controls), while the smoothest finish showed much lower bond strengths (controls, 23.7 MPa).

Effects of combined treatments

All specimens (controls, precoated, or roughened) that were fired under the reducing atmosphere showed lower bond strengths than their counterparts fired under "normal" conditions. This change in strength ranged from a 13-fold decrease in strength for Al_2O_3 precoated specimen to a 3-fold decrease in strength for a sandblasted specimen. As expected, the decrease in bond strength from firing under the reducing conditions were more pronounced for specimens with smooth interfaces.

Examination of interface structures

Before porcelaining, the specimens were examined using SEM. They showed varying degrees of roughness as a result of the different pretreatments. The control specimens and sputter precoated specimens had very smooth finishes while the preoxidized specimens and the roughness series had greater surface roughness.

After porcelaining, the specimens were viewed in cross-section using SEM and TEM. Interfaces appeared intact in all cases. However, several features should be noted. The sputtered films dissolved into the porcelain and were no longer identifiable even at very high magnifications (Fig. 2). All the specimens fired under the "normal" atmosphere showed some degree of internal oxidation at the surface of the alloy. The internally oxidized layer (Fig. 3), showed large amounts of gallium oxide (as determined by energy dispersive x-ray spectroscopy). The formation of this oxide caused significant roughening of the surface of the alloy. Greater amounts of internal oxidation were observed with the preoxidized specimens, while the specimens fired under the Ar-5%H atmosphere showed no internal oxidation.

Fractured cross-sections were observed after mechanical testing. In all specimens that had relatively smooth finishes, the fracture occurred primarily at the interface between the metal and the porcelain, with a few small islands of porcelain adhering to the alloy fracture surface (Fig. 4). However, with specimens that had coarse finishes (sandblasted and notched) in-

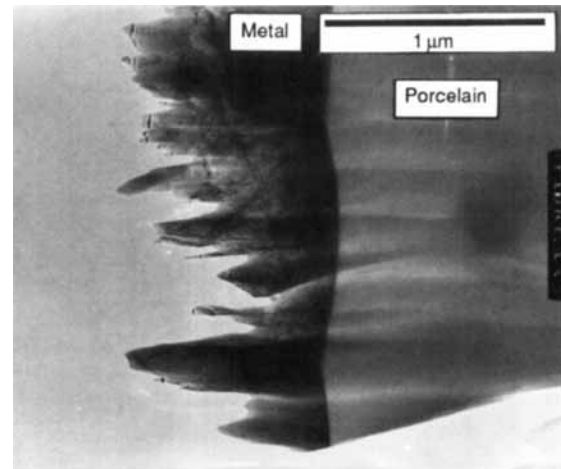


Figure 2. Cross-section of preoxidized specimen before porcelaining, showing the gallium phase formed in the metal (the medium gray phase).

creased amounts of adherent porcelain were observed with the increased roughness (Fig. 5).

DISCUSSION

Mechanical effects

Roughening the alloy surface was the most effective treatment for improving bond strength. The roughest surface treatment, cut notches, produced 139.0 MPa bond strengths. This value is very close to the published shear strength of dental porcelains and examination of the fractured interface showed that most of the fracture actually occurred in the porcelain (Fig. 6). A less rough surface (sandblasted) showed similar effects although to a lesser degree. The other

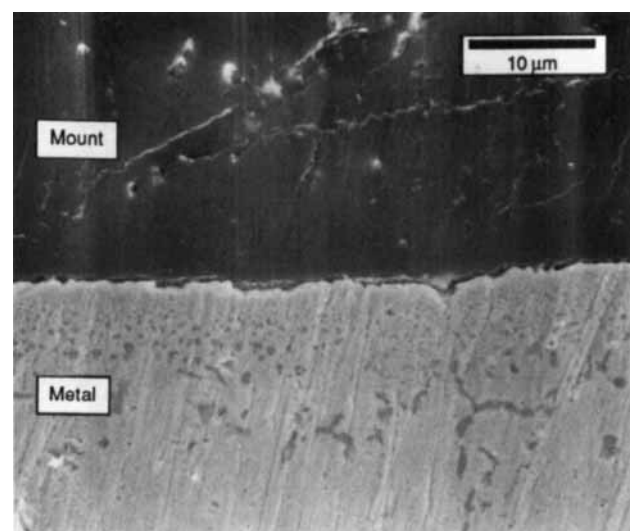


Figure 3. Transmission electron micrograph at 35,000 \times magnification. No second phases or sputtered films are visible at the porcelain-metal interface.

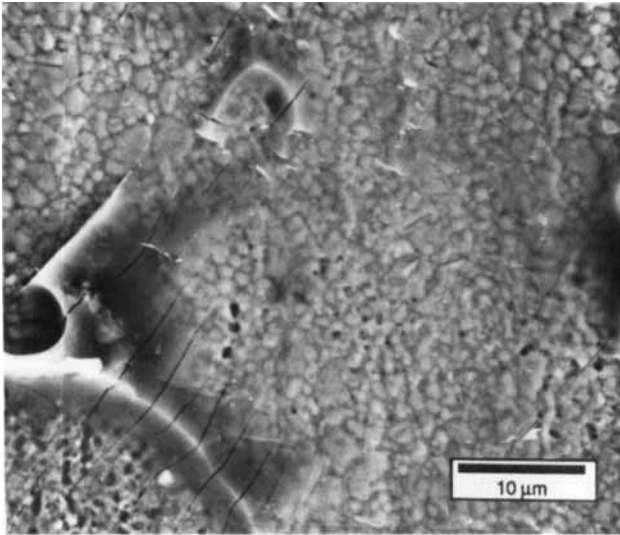


Figure 4. SEM of control specimen fracture surface showing islands of adhering porcelain on metal.

specimens with smoother surfaces all showed fracture at the interface with little adherent porcelain on the alloy fracture surface (Fig. 7).

The mechanism responsible for this strength increase is probably that the roughness causes the fracture path to deviate into the porcelain. When the shear strength of the porcelain is stronger than that of the interface, and fracture occurs in the porcelain (as with the rougher specimens), the bond strength is increased. In addition, interfacial roughness causes the fracture path to deviate, increasing the fracture surface area and the total energy required for failure.

There was no evidence of the maladies cited in the literature, either stress raisers caused by rough interface or trapped gases in the valleys, causing lowered

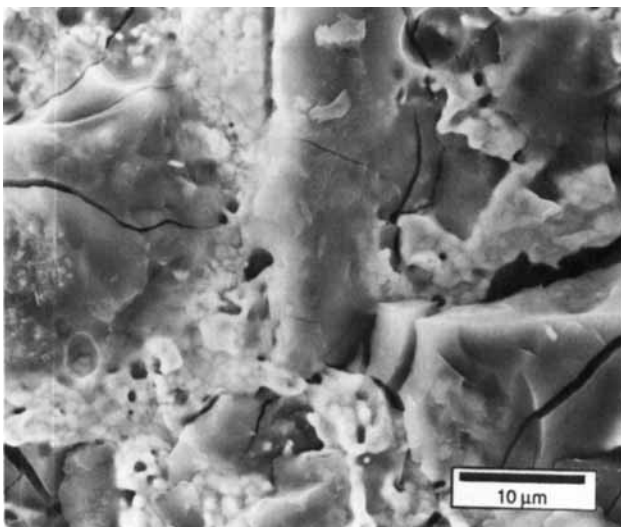


Figure 5. SEM of sandblasted specimen fracture surface showing large amounts of adhering porcelain.

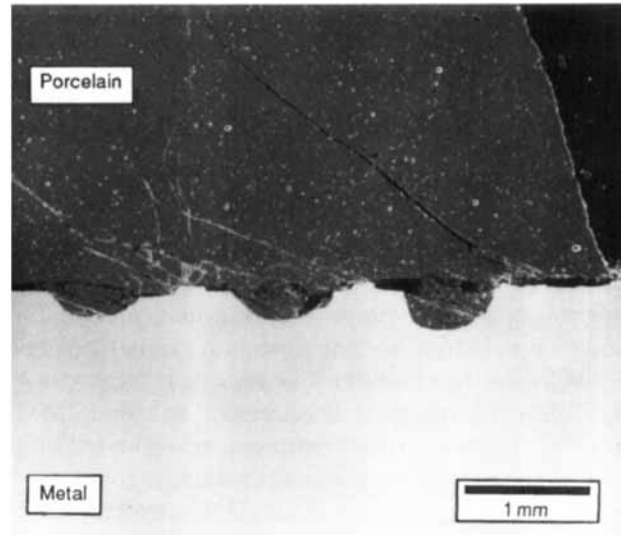


Figure 6. SEM of cross-section of notched specimen after shear testing. Most of the fracture occurred in the porcelain.

bond strengths. Instead, it appears that the roughness is entirely beneficial to porcelain-metal bonding.

Chemical effects

Before continuing, it should be pointed out that no specimens showed a second phase along the interface except for the gallium oxide phase formed in the alloy near the interface (Fig. 2). This was established using electron microscopy (TEM or SEM) at magnifications to 160,000 \times (Fig. 3).

Perhaps the most significant outcome of this study was the effect of furnace atmosphere. Here 3- to 13-fold differences in bond strength were found depending on the history of the specimens. Firing in

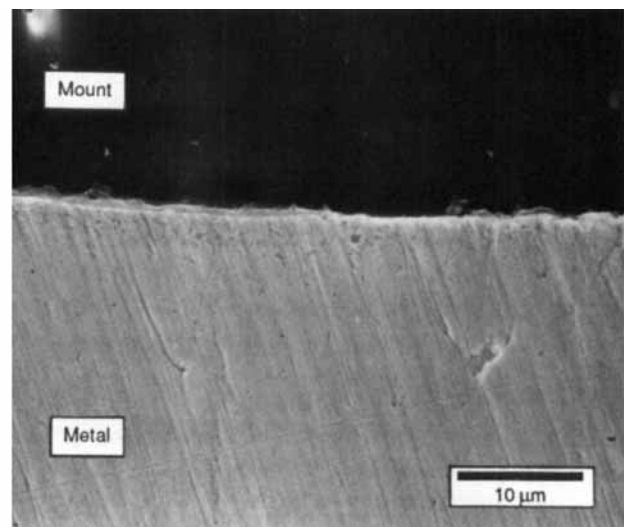


Figure 7. SEM of cross-section of control sample showing only small amounts of adherent porcelain.

an argon-5% hydrogen atmosphere produced much weaker bonding in all cases that produced by the standard firing atmosphere (the hydrogen in the argon-5% hydrogen atmosphere immediately removes any free oxygen that could become involved in reactions at the interface). This indicates that the presence of oxygen is critical for strong bonding.

While some of the effects of the reducing atmosphere may have been due to changes in the porcelain itself, this probably plays only a minor part in the reduced bond strength. The porcelain rarely fractured in specimens fired under the reducing atmosphere (only with the roughest specimens), and qualitative (indenter crack) fracture toughness tests showed only a minor decrease in the porcelain's fracture toughness.

Preoxidizing specimens resulted in substantial improvements in bond strength. Electron microscopy of the interface (Fig. 3) showed an internally oxidized structure consisting of a gallium oxide phase within 20 μm of the surface of the alloy. In addition, it was found that porcelain penetrated into the metal where the phase was present at the surface. These results show that the preoxidizing process causes internal oxidation and roughening of the alloy surface. The approximate roughness (as determined by SEM) created by preoxidation is close to that created by the 400 grit SiC paper roughening treatment. The bond strengths are also close, which indicates that the improvement in bond strength after preoxidation is primarily caused by roughening, not the presence of additional oxides.

The improvements in bond strength with the 100 nm oxide precoated specimens ranged from 24% to 46% over the controls. Observation of the interface indicates that the precoatings completely dissolved into the porcelain, although they may persist at the atomic level at the interface. Therefore, it seems likely that the precoatings had a transient effect during the porcelain firing or perhaps a change in porcelain composition was responsible for the improvements in bond strength. Another factor should be considered—the specimens were sputter cleaned before the precoatings were applied and this has been shown to slightly improve bonding.

Other researchers have also observed improved bond strengths as a result of oxide precoatings. McLean and Sced²⁶ electroplated a variety of metal coatings on Pt, which were subsequently thermally oxidized. The oxidized coatings of Sn, In, Co, Ni, and Zn produced the strongest bond strengths to porcelain. Allard²⁷ reactive ion plated SnO₂ and Al₂O₃ coatings onto base metal specimens followed by applying porcelain and found improved bonding with Al₂O₃, but not with the SnO₂. Most recently Bullard et al.²⁸ sputter deposited coatings of Al₂O₃, In, and Sn on a dental gold alloy (the In and Sn coatings were subsequently oxidized).

They found significant improvements in adhesion of porcelain with Al₂O₃ and In₂O₃, but not with SnO₂.

While the techniques to apply the coatings and the metal substrates differ in these studies and our research, there is general agreement that Al₂O₃ coatings significantly improve bonding. Others have shown that In coatings can significantly improve bonding. The strong improvements in bond strength observed by McLean and Sced²⁵ with Sn coatings was not observed by any other group; however, their coating thicknesses were about five times thicker than the rest.

Combined chemical and mechanical effects

To determine the mechanisms by which the various treatments affected bonding, some were combined. Most importantly, the effects of a reducing atmosphere in combination with other treatments were tested.

To compare the effects of roughness to that of porcelain firing atmosphere, specimens were sandblasted, porcelain was applied, and then the specimens were fired in the Ar-5%H atmosphere. Here a large decrease in bond strength was found (69% lower than samples fired under normal conditions), although this bond strength was still much higher than that of the control fired under the same conditions. This shows that both firing atmosphere and roughness are important in determining the bond strength.

Preoxidation followed by firing in the Ar-5%H atmosphere caused a 74% reduction in bond strength over preoxidized samples fired in the "normal" atmosphere. The oxides that had been on the surface appeared to be reduced, producing a metallic appearing surface. However, the surface had a frosted appearance—perhaps roughness produced by the preoxidation treatment. Again the data indicate the importance of both roughness and firing atmosphere.

CONCLUSION

Roughened surfaces resulted in the highest bond strengths. A direct correlation between roughness and bond strength was found with greater roughness leading to higher bond strength.

Changing porcelain firing atmosphere strongly affected bond strength. Firing in a reducing atmosphere (Ar-5%H) dramatically reduced bond strength (reductions between 69% and 88%) as compared to specimens fired in a "normal" firing atmosphere. The amount of strength decrease was dependent on the pretreatment.

All sputtered oxide precoatings improved bond strengths over the controls. However, the only statistically significant increase was with the Al₂O₃ films, which produced a 46% improvement. Increasing

the thickness of these Al₂O₃ precoatings improved the strength even further.

Preoxidizing the specimens improved bond strength 152%. The preoxidation treatment resulted in the formation of an internal oxide, gallium oxide, and roughening of the interface between the alloy and porcelain.

Several people were very helpful or essential in the development of the techniques used in this project. Hal Estry provided the electronics knowledge required for designing the radio frequency sputterer. Haru Wada and Leya Wang supplied the hydrogen furnace and help in using it. The dental technology expertise of Edward R. Dootz and Gary P. Mora was indispensable for many phases of this project.

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