Metal ceramic restorations have been used successfully for many years in dentistry. Over the last several decades, noble alloys used in metal ceramic restorations have gradually been replaced by base metal alloys because of their lower cost and improved mechanical properties. Base metal alloys have desirable mechanical properties; nevertheless, they have disadvantages, including potential biologic hazards, low corrosion resistance, and difficult handling characteristics.

In recent years, titanium (Ti) and its alloys have become popular and are alternative substructure materials for metal ceramic restorations because of their superior properties, excellent biocompatibility, and relatively low cost. However, the bonding between titanium and dental porcelain is poor compared with the bonding of conventional metal ceramic restorations. One of the main causes of critical failures is the formation of a nonadherent and excessive titanium oxide layer during the porcelain firing. The weak porcelain bonding on titanium is mainly associated with this oxide layer.

To control the oxidation properties of titanium, various surface modification methods have been proposed, including airbone-particle abrasion, laser etching, chemical baths, silicon nitride, and chromium, ceramic, and gold coating. One of the surface treatments involves coating the surface of titanium or titanium alloys with an intermediate layer to prevent excessive oxidation at porcelain sintering temperatures to increase the bond strength between titanium substrate and porcelain.
Micro-arc oxidation (MAO), also called plasma electrolytic oxidation or anodic spark oxidation, is a relatively new anodic oxidation technique used to deposit ceramic coatings onto the surface of valve metals, including aluminum, titanium, zirconium, magnesium, and their alloys.23-26 MAO processes are characteristically defined by the circumstance of electrical discharge on the anode in the aqueous solution.25 The MAO technique that provides adhesion strength and wear resistance is used to form a nanometer-sized porous surface, high micro-hardness, and high quality coatings.25,26 An MAO coating, which can limit the formation of an excessive oxide layer by acting as a barrier to the diffusion of oxygen during the dental porcelain firing process, can enhance the bonding of porcelain to titanium.22

One method of developing the titanium-porcelain bonding may be the use of intermediate coatings of hydroxyapatite (HA) by means of electrospay deposition between the titanium substrate and porcelain. HA has been widely used as a biocompatible ceramic in many areas of medicine.27 HA coating of biomaterials improves the corrosion resistance at the same time as promoting its bone bonding ability.28,29 HA coating formed by electrospay deposition, which could mask the color of the metal substructure, might be effective in enhancing the bond strength between titanium and porcelain.

The purpose of this in vitro study was to assess the effects of coating a titanium alloy surface with the MAO and hydroxyapatite on titanium-porcelain bonding and to examine changes on the surface of titanium. The null hypothesis was that coating a titanium alloy surface with MAO and HA improves the adhesion of porcelain to titanium.

MATERIAL AND METHODS

One hundred twenty machined titanium specimens 25x3x0.5 mm were prepared from titanium grade 5 (CopraTi-5; Whitepeaks Dental Solutions GmbH) as the metal substrate. Specimens were wet ground with 80, 120, 320, 600, 800, 1000, and 1200 grit silicon carbide papers, using a grinding and polishing machine (Mini-tech 233; Fresi UK Ltd) to achieve flat and smooth surfaces. The surface of the titanium specimens on which Noritake Super Porcelain Ti-22 would be fired were airborne-particle abraded with 50-μm alumina (Korox; Bego) according to the manufacturers’ instructions. The other specimens on which Vita Titankeramik would be fired were airborne-particle abraded with 110-μm alumina (Korox, Bego). The roughened titanium specimens were ultrasonically rinsed in acetone for 15 minutes (Professional Ultrasonic Cleaner CD-4800; Shenzhen Codyson Electrical Co, Ltd) and then dried with high-pressure steam.

On the basis of data from a pilot study, the sample size (n=10) was estimated with a power analysis to provide statistical significance (α=.05 at .80). Specimens were divided into 6 groups (n=20) according to the surface treatment used: airborne-particle abraded (control), coated with MAO for 5 minutes, coated with MAO for 15 minutes, coated with MAO for 30 minutes, coated with HA, and coated with a combination of MAO and HA. Each group was further equally divided into 2 subgroups (n=10) according to the type of porcelain used, Noritake Ti-22 or Vita Titankeramik. All test groups and their codes are listed in Table 1.

For the MAO treatment, Ti specimens were used as the anode, and a stainless steel bar was used as the cathode in an electrolytic bath. In this bath, an aqueous solution containing 12 g/L NaAlO₂ and 2 g/L KOH was used as an electrolyte. The surface of the titanium specimens was coated using the MAO method under constant electrical parameters and with the same electrolytic composition for 5, 15, and 30 minutes. After the coating process the specimens were washed with distilled water and dried at room temperature.

Electrospray was used for the deposition of HA onto titanium specimens as coatings at room temperature. HA suspension was applied through the needle with an automated syringe pump at a flow rate of 0.02 mL/min. In this procedure, a voltage of 8 kV and a spraying time of 1 minute was used. The needle-to-titanium substrate distance was kept at 70 mm. The electrospray deposition method produced uniform HA coating.29

After all specimen-surface-coating processes were completed, microstructure analysis of the titanium-porcelain systems was conducted with a scanning electron microscope (SEM) (XL-30; Philips). One specimen from each group was selected, and the titanium surface was examined by SEM. Surfaces of titanium specimens were imaged at magnifications of ×500. After being
subjected to bond strength test, 1 specimen from each group was selected to investigate the interface of the metal substrate-porcelain and the fracture surfaces by SEM (XL-30; Philips) at ×250 magnification. For other specimens, the fracture sites were observed using a stereomicroscope (SZTP; Olympus Corp) at ×40 magnification to identify the mode of failure.

Before porcelain firing, the surface roughness and the roughness average (Ra) of all the investigated titanium specimens were measured with a surface profilometer (Dektak 8 Advanced Development Profiler; Veeco). Measurements were performed in 3 different areas and then the mean roughness average was calculated. The average values obtained from all specimens were compared with 1-way ANOVA and Tukey honest significant differences multiple comparison tests.

In the center of the specimens, porcelain was built up to the dimension of 8×3×1 mm according to the ISO standard.22 A custom-designed split metal mold was used to apply porcelain onto the titanium specimens. For each type of porcelain, a thin layer of bonder porcelain was applied, followed by a second opaque layer and a dentin body layer; according to the manufacturer’s instructions; each layer was fired separately in a dental vacuum porcelain furnace (Programat P 300; Ivoclar Vivadent AG).

The bond strength was tested on a universal testing machine (Shimadzu AGS-X; Shimadzu Corp) according to the ISO standard.22 (Fig. 1). The titanium-porcelain specimens were positioned on supports with 20-mm span distances, with the porcelain layer facing the bottom. The load was applied at the midline of the titanium bar by the metal rod at a crosshead speed of 0.5 mm/min until fracture, which indicated bond failure (Fig. 1). The bond failure was recorded digitally in Newtons (N) with computer software, and the bond strength (in MPa) was calculated according to the following formula, which was specified in the ISO certificate:31

\[ T_b = kxF \]

where \( T_b \) equals the bond strength in MPa, \( F \) equals the maximum force, \( k \) equals the coefficient calculated according to the Young modulus of the metal substrate and the thickness of the specimens, and \( T_b \) shows the bond strength in MPa.

**RESULTS**

Two-way ANOVA of the bond testing data (type of porcelain and surface treatment) revealed that bond strength was significantly affected by the type of surface treatment and porcelain (\( P=.001 \)) (Table 2). Means ± standard deviations bond strength measurements between titanium and dental porcelain (in MPa) are presented in Figure 2. For both of the porcelain groups, the 30-minute MAO groups showed higher bond strength values than the control groups (\( P<.05 \)) (Table 3).

For both of the porcelain groups, the surface morphologies of the metal substrates after different surface treatment methods are shown in Figure 3. The surface morphology of the MAO coating layer was composed of micropores with protrusions. Figure 3E illustrates the surface morphology of the metal substrate after HA coating. The HA-coated specimens showed uniform microporous surface morphology. Figure 3F shows the surface morphology test specimen after coating with the MAO and HA combination. The specimens showed irregularities and microcracks.

The 1-way ANOVA of the surface roughness data revealed that surface roughness was significantly affected by the type of surface treatment (\( df=6, F=79.830, P<.001 \)) (Table 4). The test results are listed in Table 5. The NC group (50-μm airborne-particle abrasion; 1.49) was not significantly different from the VC group (110 μm airborne-particle abrasion; 1.56). The 30-minute MAO group showed the highest surface roughness (μm) (3.02) among all the groups (\( P<.05 \)).

Figure 4 shows the SEM image of the cross-sectioned metal substrate-porcelain specimens treated with MAO for 15 minutes for the Noritake porcelain group. Although, as seen in Figure 5A, no air bubbles or microcracks were seen in the cross-sectional image, shown in Figure 5B, some air bubbles and microcracks in the bonder porcelain were observed. The thickness of the oxide layer was approximately 13 to 15 μm. When the cross-sectioned views were evaluated in the HA-coated groups, the HA-coated layer could not be seen in either the Noritake group or the Vita-Titankeramik group. Modes of failure are presented in Table 6. The mode of failure was mainly a combination of adhesive

**Table 2. Two-way ANOVA of bond testing data**

<table>
<thead>
<tr>
<th>Material</th>
<th>df</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porcelain</td>
<td>1</td>
<td>34.57</td>
<td>&lt;.001</td>
</tr>
<tr>
<td>Surface treatment</td>
<td>5</td>
<td>20.19</td>
<td>&lt;.001</td>
</tr>
<tr>
<td>Porcelain type*</td>
<td>5</td>
<td>6.23</td>
<td>&lt;.001</td>
</tr>
</tbody>
</table>

*Surface treatment.

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and cohesive failures. For both of the porcelain groups, the combination of cohesive and adhesive failure was most prevalent in groups N30M and V30M (60%). Although more cohesive type fractures were seen than adhesive type fractures in the Noritake groups, in the Vita Titankeramik groups adhesive type fractures occurred more often than cohesive type fractures.

DISCUSSION

Within the limitations of this in vitro study, the null hypothesis that titanium coated with MAO and HA would not alter the porcelain adhesion to titanium alloy was rejected. The experimental results demonstrated that the use of MAO and HA coating techniques on milled, noncast Ti-alloy surfaces increased the bond strength between Ti and the porcelain phases before porcelain sintering.

Although titanium and its alloys have many superior properties, the bonding between titanium and dental porcelain is poor compared with the bonding in conventional metal ceramic restorations. In metal-porcelain systems, the bond strength is primarily related to chemical and mechanical bonding. Obtaining an acceptable bond strength depends on the properties of both the metal substrate and the dental porcelain. Titanium has great affinity for oxygen, and its oxidation rate increases gradually at porcelain sintering temperatures. The oxide layer that is thick, unsuitable, and nonadherent for porcelain bonding formed on the titanium surface. Various types of surface treatments have been used to solve this oxidation problem and improve titanium-porcelain adhesion. Some investigators have suggested covering the titanium with a layer to prevent overoxidation on the surface of titanium. The application of an intermediate layer significantly improves the bonding between titanium and dental porcelains.

In this study, an intermediate layer was applied using HA coating and MAO techniques. MAO is a relatively new anodic oxidation technique that is used to form ceramic coating on the surface of valve metals, such as titanium and its alloys. A previous study emphasized that an MAO coating can control the formation of an excessive and nonadherent oxide layer by acting as a barrier to the oxygen diffusion.

Table 3. Means (±SD) of bond strength (MPa) for Ti6Al4V surfaces modified with different methods

<table>
<thead>
<tr>
<th>Surface Treatment</th>
<th>Noritake Ti-22</th>
<th>Vita Titankeramik</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>27.12 (±7.16)</td>
<td>29.55 (±5.54)</td>
</tr>
<tr>
<td>MAO for 5 min</td>
<td>39.25 (±4.34)</td>
<td>30.08 (±4.66)</td>
</tr>
<tr>
<td>MAO for 15 min</td>
<td>43.57 (±4.91)</td>
<td>35.88 (±4.84)</td>
</tr>
<tr>
<td>MAO for 30 min</td>
<td>44.42 (±7.47)</td>
<td>45.48 (±4.59)</td>
</tr>
<tr>
<td>HA</td>
<td>41.8 (±7.07)</td>
<td>31.99 (±3.71)</td>
</tr>
<tr>
<td>Combination of MAO and HA</td>
<td>40.62 (±6.25)</td>
<td>27.87 (±4.88)</td>
</tr>
</tbody>
</table>

HA, hydroxyapatite; MAO, micro-arc oxidation.
Same superscript letters indicate no statistical differences (P > .05).
The effects of the MAO coating technique is surface wettability. Surface wettability is known to be one of the characteristics of the interaction between porcelain and a metal surface. The coated surfaces showed hydrophilic properties, and this factor improves the adhesion of the porcelain to the titanium surface. In this study, HA coating was another method that was used to form the intermediate layer. HA coating is widely used to improve the chemical bond with bone in orthopedics and dentistry because of its excellent biocompatibility. HA may mask the color of the metal substructure, and better adhesion effects could be obtained by using it on a metal substrate surface.

To assess the bond strength between the metal substrate and dental porcelain, various test methods have been described, including the push-pull test, the shear test, the flexure test, and the tensile test. The 3-point bend test was found with finite element stress analysis to be the most reliable among the many available methods. The International Organization for Standardization (ISO) standard for metal-ceramic systems also advocates a 3-point bending test. Therefore, in the present study, the bond strength was tested with the 3-point flexure bond test according to the ISO standard.

According to the test results, the MAO group with a 30-minute coating showed higher bond strength values than the control groups for both types of low-fusing porcelains. This may be because the coating layer also increased the strength of the test material, so higher test results were obtained. As expected, the HA-coated

---

**Table 4. One-way ANOVA of surface roughness data**

<table>
<thead>
<tr>
<th>Data</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between groups</td>
<td>41.896</td>
<td>6</td>
<td>6.983</td>
<td>79.830</td>
<td>&lt;.001</td>
</tr>
<tr>
<td>Within groups</td>
<td>5.511</td>
<td>63</td>
<td>.087</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>47.406</td>
<td>69</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5. Means (±SD) of the surface roughness for Ti6Al4V surfaces modified with different methods**

<table>
<thead>
<tr>
<th>Surface Treatments</th>
<th>Surface Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noritake Ti-22 control (50 μm)</td>
<td>1.49 (±0.12)</td>
</tr>
<tr>
<td>Vita Titankeramik control (110 μm)</td>
<td>1.56 (±0.10)</td>
</tr>
<tr>
<td>MAO for 5 min</td>
<td>2.66 (±0.26)</td>
</tr>
<tr>
<td>MAO for 15 min</td>
<td>3.01 (±0.37)</td>
</tr>
<tr>
<td>MAO for 30 min</td>
<td>3.83 (±0.30)</td>
</tr>
<tr>
<td>HA</td>
<td>2.78 (±0.42)</td>
</tr>
<tr>
<td>Combination of MAO and HA</td>
<td>3.02 (±0.34)</td>
</tr>
</tbody>
</table>

HA, hydroxyapatite; MAO, micro-arc oxidation. Same letter indicates no statistical differences (P>.05).
specimens showed higher test results than the control groups and can be used to achieve a thinner layer on the titanium surface. The HA coating treatment increased the Ti surface resistance to oxidation during the porcelain sintering treatment, so this point significantly improved the bonding properties between the Ti and porcelain. However, the test specimens did not reach the bond strength values of the MAO-coated test specimens. When the SEM views were evaluated, some microcracks were seen on the coating surface, and this resulted in bonding weakness between the porcelain and titanium.

In the present study, the Ra values increased in all the coated test groups compared with the control groups. SEM observations also showed that the combined MAO and HA coating creates a uniformly coated surface with micropores. The MAO groups that were coated for 30 minutes presented the highest Ra values of all the groups. The surface structure and increased surface hydrophilicity influence the micromechanical interlock between the porcelain and the titanium alloy in the MAO groups, as mentioned in a previous study. Previous studies have observed that the roughness of the surface enhances the mechanical interlocking of titanium with porcelain, which is a significant factor that could affect titanium–porcelain adhesion.

In titanium–porcelain systems, the porcelain firing process should be performed at temperatures below 883°C to minimize excessive oxidation on the metal surface. Therefore, types of porcelain that are usually low-fusing were selected for the titanium alloys. In this research, porcelain application was also performed by using Noritake and Vita Titankeramik low-fusing porcelains at temperatures under 800°C according to the manufacturers’ instructions. For the groups that used Vita Titankeramik porcelain, the group coated with MAO for 30 minutes showed significantly higher bond strength values than those of the control group and the other coating groups. However, the use of a combination of MAO and HA or the use of only HA did not significantly improve the adhesion of porcelain to the titanium surface compared with the control group. However, for the groups that used Noritake, the control group showed the lowest bond strength values of all the groups. The use of a combination of MAO and HA or the use of only HA significantly improved the adhesion of porcelain to the titanium surface compared with the control group. The bond strength differences between the porcelain types can result in different applications onto the titanium surface. A bonding agent must be applied to an alloy surface before porcelain slurry condensing can occur, and, for Noritake Porcelain, this bonding agent is a flowable material that can be uniformly applied onto the titanium alloy; however, Vita Titakeramik porcelain has a greater viscosity so it should be applied with a hand instrument. This finding was supported by the SEM images (Fig. 5B), which showed some interfacial porosity and air bubbles in the Vita Titakeramik groups. We thought that these bubbles caused some microcracks to form at the interface and decreased the bonding strength.

Investigations have indicated the bond strength values between pure titanium or titanium alloys and dental porcelains below 25 MPa, which was the acceptable minimum value as determined by the ISO 9693 specification. In this in vitro study, the bond strength values of all the test groups exceeded 25 MPa, including the control groups. In these groups, the mean bond strength was found to be 27.12 MPa for Noritake-Ti22 and 29.55 MPa for Vita Titakeramik, which were similar to the results of the study conducted by Lin et al. Similar findings were noted in different in vitro studies. In related publications, earlier studies suggest that the application of a coating layer on the Ti surface considerably increases the bonding between titanium and dental porcelains. Studies have reported that the coatings (such as, SiO2–TiO2 and gold) on Ti surfaces considerably increase the titanium-porcelain bond strength (approximately 36 MPa). Zhang et al have shown variations in bond strength of ZrSiN-coated Ti specimens with different Si concentration from 32.7 MPa to 57.3 MPa. In this in vitro study, similar test results were obtained in the coated specimens. When the related literature evaluated HA coating of biomaterials is widely applied to improve the corrosion resistance at the same time as promoting its bone bonding ability in orthopedic and dental implants however there is no study in the literature that investigated the effects of this coating process on Ti/porcelain bond strength. Also no study compares MAO technique treatment times. The application of the MAO technique significantly improves the bonding between titanium and porcelain. Although the researchers prefer only a 3 minute surface treatment time, they did not discuss this
When the coating duration increased, the coating layer thickness also increased. Every minute of coating causes approximately a 1 mm-increase in the oxide layer on the titanium alloy surface. In this research, a thick MAO layer was expected to cause bonding failure; however, the results showed that the higher duration time of coating process showed higher bonding values in test specimens.

Titanium or its alloys that are used in dentistry can be produced by various methods, including casting and milling. Previous studies have indicated that the bond strength values between porcelain and titanium or its alloys were not significantly different between cast and machined titanium specimens. In addition, grade 5 titanium is the most widely used titanium alloy because of its hardness and high flexural and fatigue strength and because it has better physical and mechanical properties than CpTi. In several studies that used both the CpTi alloy and Grade 5 titanium as the metal substrate, the bond strength values of the grade 5 titanium–porcelain systems were considerably higher than those of the CpTi–porcelain systems. A limitation of the present study was that only milled Grade 5 titanium was used as the metal substrate.

Further studies should evaluate the effect of electrolyte content in coatings on the bond strength of porcelain and a metal alloy in order to investigate the optimal electrolyte solution that can be used in the MAO technique and different metal alloys should be coated and tested using the MAO technique to evaluate porcelain-metal bonding.

**CONCLUSIONS**

Within the limitations of this in vitro study, the following results were drawn:

1. Both MAO and HA coating techniques had a positive effect on porcelain–titanium bonding.
2. Porous, compact, and stable TiO₂ coating can be achieved using the MAO technique.
3. A high viscosity porcelain bonding agent application before porcelain slurry condensing decreased the bond strength values between the porcelain and the alloy as shown by the presence of air bubbles in the bonding agent layer interface.

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