

## Scanning Electron Microscopy Study to Evaluate the Effect of Firing Temperature at Porcelain Metal Alloy Interface

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Conflict of interest: Nil

### Abstract:

**Purpose:** To probe in greater detail the changes at the ceramometal interface induced by heat energy absorption, using energy diffraction X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) and correlate these changes with the shear bond strength of porcelain to nickel chromium alloy.

**Materials and Methods:** Seventy-five strips of nickel-chromium alloy (20 mm long, 5 mm wide, 3 mm thick) were prepared and layered with porcelain, conforming to ANSI/ADA specification no. 38 (for Metal-Ceramic Dental Restorative Systems: 2010). These test specimens were divided equally into three groups. Specimens of each group (25) were fired to a specific temperature range, that is 700°C, 900°C, and 960°C. SEM and EDS were performed on all specimens, at the metal alloy/ceramic interface. Bonding of the ceramic layer to the metal alloy was evaluated by a shear bond strength test as per ANSI/ADA specification no. 38. The data were recorded and analyzed using one-way ANOVA and post hoc Tukey HSD test.

**Results:** SEM images of the porcelain/metal alloy interface revealed roughness of the metal alloy surface adjacent to the ceramic layer. EDS study revealed that an oxygen depletion zone was formed at the interface region, facilitating the formation of intermetallic compounds. The mean shear bond strength showed an upward trend until 900°C and decreased thereafter.

**Conclusion:** Formation of intermetallic compounds at the interface, in the presence of an oxygen depletion zone, was the prime factor in bonding of porcelain to metal alloy. This provides a new concept of ceramometal bonding. Porcelain-fused-to-metal (PFM) restorations are composite restorations that offer the high esthetic value of ceramics and the strength of metal alloy.

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### Introduction

The interface between the nickel chromium alloy scaffold and the ceramic overlay is of critical value in ensuring the long-term integrity of the restoration. The temperature gradient, through which the alloy thimble passes as porcelain is baked over it, has a profound effect on this interface. [1-4] This is due to a cascade of changes occurring both in the metal and porcelain, through the entire temperature range of the firing cycle. These changes are significant, because they may alter the desirable properties of PFM restorations. [5-10] Bonding of porcelain to metal alloy is vital to the success of PFM prostheses, especially under the rigors of oral function. Despite the advantages of PFM restorations, a considerable failure rate has been attributed to inadequate bonding between the two. [11-15] Hence, the basic mechanism of ceramometal bonding needs to be understood. Several research groups have tested the ceramometal bond strength by various shear and compressive test methods. Different types of

bonding occur between the porcelain mass and the metal coping, namely, chemical bonding, mechanical bonding, and to a lesser extent, a difference in thermal expansion between the metal alloy and porcelain. [16-21] Many other interfacial variables are responsible for the physico-chemical bonding, namely surface roughness, firing time, and vacuum level. It has been found that porcelain fractures easily at the interface region in alloys with smooth surface finish than rough alloy surfaces. This could be attributed to a lack of mechanical interlocking for porcelain on smooth finish alloys. The presence of oxygen in the firing chamber led to the formation of oxides, which weakened the bond between metal alloy and porcelain.<sup>28</sup> The present study was designed to investigate the changes at the ceramometal interface and bonding induced by heat energy absorption, using EDS, SEM, and shear bond strength test.<sup>1</sup>

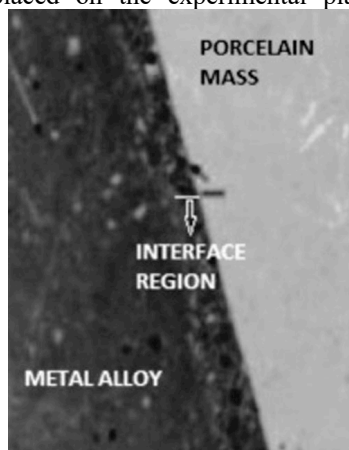
## Materials and Methods

Seventy-five strips of nickel-chromium alloy (20 mm long, 5mm wide, 3 mm thick) were prepared, conforming to ANSI /ADA specification no 38 (for Metal-Ceramic Dental Restorative Systems: 2010). These strips were surface finished similar to a metal coping and subsequently sandblasted (Sandstorm 2, Vaniman Sandstorm Expert; Vaniman Manufacturing Co., Fallbrook, CA) and oxidized by open atmosphere heating at 400°C for 10 minutes. The composition of the nickel-chromium alloy conformed to ANSI/ADA specification no. 38 (nickel 65.2%, chromium 22.5%, molybdenum 9.5%, iron, manganese, niobium, aluminum, and silicon <3%). Porcelain was layered (Ceramco; Dentsply, York, PA) on these oxidized nickel chromium strips to a length of 8 mm, a width of 3 mm, and a thickness of 1 mm (ANSI/ADA specification no. 38).

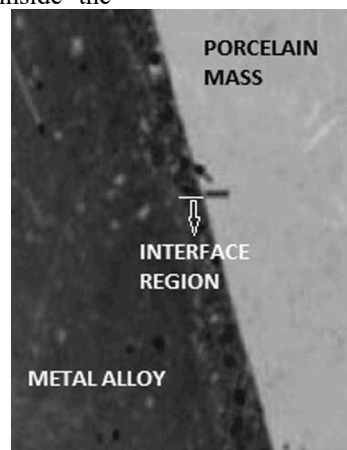
These test specimens were equally divided equally into three groups. Specimens of each group (25) were fired to a specific temperature range, that is 700°C, 900°C, and 960°C. SEM and EDS (S-4700 Scanning Electron Microscope; Hitachi, Tokyo, Japan) were performed on all specimens, at the metal alloy/ceramic junction. Each specimen was placed on the experimental platform inside the

scanning electron microscope, and an electron beam was made to scan the nickel chromium alloy/porcelain layer interface. When the electrons strike the specimen, specific signals characteristic of the specimen composition are generated. [22-26]

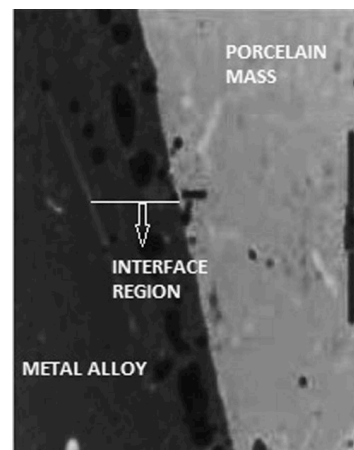
Secondary electrons, backscattered electrons, and X-rays are generated from the specimen. The X-rays emitted from the specimen have energy characteristic of the parent element. When the electron beam strikes different regions of the specimen, energies of different intensities characteristic of the elemental composition present in that particular region are generated. The magnification of the SEM was set at 2000×. The data was graphically recorded and analyzed. Bonding of the ceramic layer to the metal alloy was evaluate by a shear bond strength test as per ANSI/ADA specification no. 38. The metal alloy-ceramic strips of the three firing temperature groups were mounted, one at a time, on a jig and placed in a universal testing machine (Instron, Norwood, MA). Load was applied at the metal alloy/porcelain interface at a 0.5 mm/min crosshead speed to separate the two layers. The values were recorded and statistically analyzed (Fig.1).



**Figure 1:** The region on the specimen the where the shear load was applied



**Figure 2:** SEM image of the specimen fired at 700°C



**Figure 3:** SEM image of fired at 900°C.

## Results

SEM images of the interface of porcelain and metal alloy revealed roughness of the metal alloy surface adjacent to the ceramic layer. These irregularities were produced during sandblasting of the metal alloy strips (Figs 2–4). Energy diffraction spectroscopy showed that ions from silica (Si, O) and alumina (Al, O) of the porcelain mass and nickel and chromium ions from the metal alloy were released simultaneously when specimens were fired at temperatures of 700°C, 900°C, and 960°C (Fig 5). A striking feature observed in the graph obtained from the spectroscopic analysis for all three firing

temperatures was that there was formation of an oxygen depletion zone at the interface. Figure 5 illustrates that regions I and III showed the presence of oxygen ions whereas region II, the interface area, showed an absence of oxygen ions.

Due to the formation of this zone, metal ions (nickel and chromium ions) from the alloy could not react to form any oxides in region II, and instead reacted with silicon and aluminum ions from the ceramic layer, to form intermetallic compounds (Table 1). This was evident from the interpretation of the intensity peaks of all three groups obtained on the energy dispersion graph. When the energy beams

fall on the specimen at an angle of 20, a graph is generated depending on the compound the beams strike. Figure 5 shows the various peaks obtained at different firing temperatures (shown as A, B, and C), with interpretation for ease of comprehension. The relative weight percent of the elements present can be inferred depending on the intensity of the peaks obtained. The shear bond strength values of porcelain to nickelchromium alloy at different firing temperatures (700°C, 900°C, 960°C) are summarized in Table 2. Mean shear bond strength increased from a mean value of 20.41 MPa at 700°C to a mean of 35.19MPa at 900°C and thereafter decreased to a mean value of 30.35 MPa at 960°C.

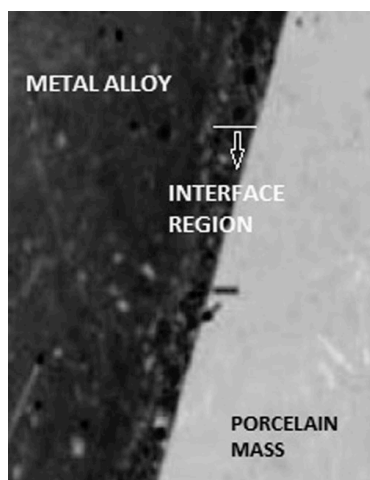


Figure 4: SEM image of the specimen fired at 960°C

Of the three firing temperatures used in this experiment, maximum shear bond strength was seen at 900°C. The ceramic layer never completely separated, but fractured under shear load, leaving a thin layer adhered to the metal alloy surface, as reported earlier.<sup>31</sup> Evaluating the effect of temperature on shear bond strength, ANOVA revealed a significant effect of temperature on shear bond strength ( $F = 2275.00, p < 0.001$ ) (Table 2). Further, comparing the mean shear bond strength between the temperatures, a Tukey test showed significantly different ( $p < 0.001$ ) and higher shear bond strength at 900°C, compared to both 700°C and 960°C.

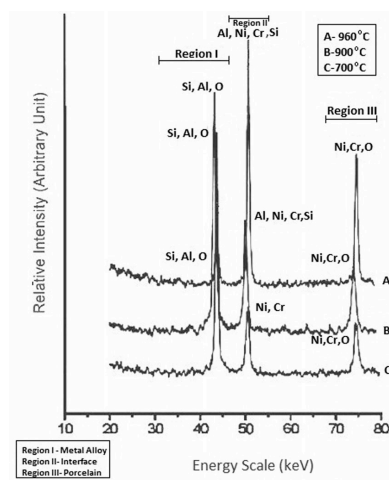


Figure 5: Energy dispersion spectroscopy of the different specimens with respect different firing temperatures.

**Discussion**

Interactions at the metal/porcelain interface with regard to an array of factors namely shear strength, [2,3,16,19] thermal coefficient, [6] and varied permutations and combinations of metal alloys and ceramic types [12-15] have been researched previously. This study aimed to elucidate various heat energy induced elemental level transformations at the metal alloy/porcelain interface, using SEM and EDS. SEM images magnified the interface region for a clear understanding of the changes taking place. Sandblasting brought about roughness on the surface of the alloy, enhancing the wetting of the metal surface by the porcelain. The porcelain mass interlocked itself into these irregularities. Prior to this attempt to study the porcelain/nickel

chromium alloy, many researchers had concluded that surface irregularities on the surface of the alloy helped in mechanical interlocking of the porcelain mass as the two were fired in a porcelain furnace. [3,12,16] Earlier concepts of bonding postulated that ionic bonding and weak van der Waal’s forces were solely responsible for the ceramometal bond. [12,16] The porcelain overlay was believed to bond to the oxide layer formed on the metal alloys surface. The present study found that intermetallic compounds were formed precisely at the alloy/porcelain interface (region II), which was many times stronger than van derWaal’s forces.<sup>29</sup> Regions I and III, which formed the periphery of the interface, were found to have metallic oxides, whereas region II had an oxygen depletion zone, which led to the formation

**Table 1: Compounds released at different regions at various firing temperatures**

	Porcelain mass	Interface region	Metal alloy
Group A (700°C)	Si, Al, O	Ni, Cr	Ni, Cr, O
Group B (900°C)	Si, Al	Al, Cr, Ni	Ni, Cr
Group C (960°C)	Si, Al, O	Al, Cr	Ni, Cr, O

**Table 2: Shear bond strength (MPa) of porcelain (Mean  $\pm$  SD, n = 25) at different firing temperatures**

700°C	900°C	960°C	F value	p value
20.41 $\pm$ 0.93	35.19 $\pm$ 0.71	30.35 $\pm$ 0.94	2275.00	<0.001

of intermetallic compounds instead of the weaker metallic oxides. Metal oxides, chemically, have a terminal oxygen atom that can be easily removed, whereas in case of intermetallic compounds, a sufficient amount of energy is required to break the bond between the two.<sup>30</sup> Earlier researchers [1,3,6] concluded that a metal oxide layer was formed at the interface of porcelain and the metal alloy, imparting bond strength, and that excessive oxidation decreased bond strength. Extensive studies performed by Borm et al [3] and Pask et al [1,6] proved that the porcelain dissolved from the interface region leaving behind a layer of metal-oxide-saturated porcelain in thermodynamic equilibrium. This metal oxide layer in turn was in thermodynamic equilibrium with the metal alloy, thus forming a continuous electronic structure, whereas, in our study, we found that the metal oxide layer was formed just adjacent to the interface region, and intermetallic compounds were formed precisely at the porcelain/metal alloy junction.

Intermetallic compounds are superior in bond strength due to their long-branched microstructure. The line C in Figure 5 represents the specimens fired at 700°C, which shows relatively higher weight percentages of Si, Al, and O in region I compared to Ni and Cr of region II. This is an incomplete phase wherein the porcelain particles start to coalesce and the process of chemical bonding is initiated. Line B depicts the changes in intensity of energy dispersion for specimens fired at 900°C. Region II of this peak is seen to have all four metallic elements (Al, Ni, Cr, Si) along with absence of oxygen, which would definitely facilitate the formation of intermetallic compounds, because the elements are unstable and would have to react with each other to attain stability. Depending on the electronic configuration of the metal ions, chromium would react with silicon to form CrSi<sub>2</sub>, and aluminum would react with nickel to form AlNi<sub>3</sub>. Both are strong inter-metallic compounds. Line A represents the energy dispersion changes occurring in specimens fired at 960°C.

The same changes are seen at this temperature when compared to the specimens fired at 900°C. The interpretation of the graph obtained from EDS shows the various ions released from different regions of the alloy/ceramic interface, at the three firing temperatures in the experiment (700°C, 900°C, 960°C). The interface displayed three distinct regions:

Region I: adjacent to the porcelain layer, it contained aluminum (Al), silicon (Si), and oxygen (O) ions.

Region II: the interface, contained aluminum (Al) silicon (Si), nickel (Ni), and chromium (Cr) ions.

Region III: adjacent to the metal alloy, it contained nickel (Ni), chromium (Cr), and oxygen (O) ions.

The striking feature of the spectroscopic analysis was the presence of an intermediate oxygen depletion zone wherein only Al, Si, Ni, and Cr ions were detected at all three firing temperatures. The vacuum environment of the furnace and this intermediate region of oxygen depletion initiated the formation of two intermetallic compounds in this region. An oxygen depletion zone was formed in the interface region at all three firing temperatures, which initiated the formation of inter-metallic compounds rather than formation of oxides.

This was evident from the EDS graphs, which clearly depicted the elements present at different regions of the three specimen groups. The shear bond strength values further substantiated the results interpreted from the EDS graphs. A rough estimate of the relative weight percentages of the elements could be interpreted depending on the intensity of the peaks. The higher the peak, the greater the relative weight percentage of the element. The presence of oxygen in the firing chamber would annul the formation of metallic compounds at the interface and lead to failure of the PFM restoration. Intermetallic compounds are long-range ordered alloys with a defined stoichiometry and ordered crystal structure. Intermetallic compounds resemble alloys except that the bonding is partly ionic.

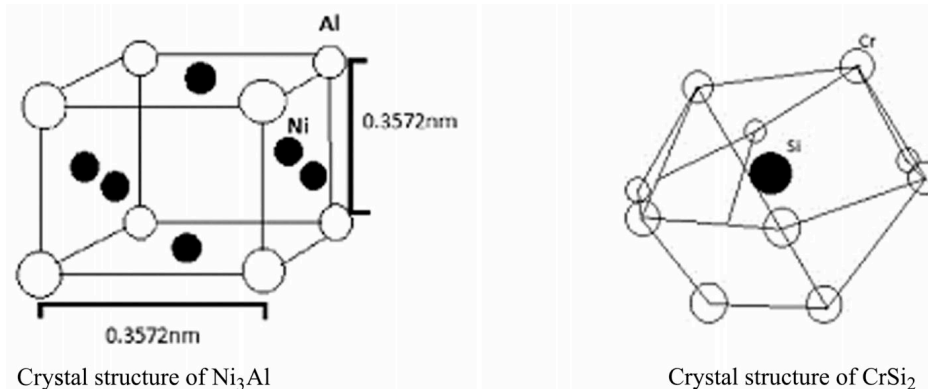
Elements with similar electro negativities tend to form alloys, whereas those with a large difference in electronegativities form more ionic bonds. A characteristic feature of these compounds is that they have a high melting point, because they are generally solid-state compounds. The formation of intermetallic compounds depends on the reactivity series and the metallic character. The reactivity of a metal increases as one goes up the periodic table, whereas the metallic character increases from right to left of the periodic table. The Aufbau principle also plays a role in bonding. According to this, the electrons of an atom occupy quantum levels or orbitals starting from the lowest energy level proceeding to the highest. Nickel and chromium belong to groups VIII B and VIB, respectively, and are known as transition metals.

Aluminum belongs to group IIIB, and silicon is a semimetal belonging to group IVA. The nickel and chromium ions from the metal alloy come in contact with aluminum and silicon ions (from the ceramic) when porcelain is fired at an increasing temperature gradient in the firing chamber. [22-24] Nickel bonds with aluminum and chromium bonds with silicon to form Ni<sub>3</sub>Al and CrSi<sub>2</sub> in the absence of oxygen.

Vacuum builds up in the porcelain furnace to facilitate the formation of intermetallic compounds instead of metal oxides. Ni<sub>3</sub>Al and CrSi<sub>2</sub> are very strong intermetallic compounds (Fig 6).

Both these compounds are oxidation resistant to temperatures of nearly 1000°C to 1200°C. Ni<sub>3</sub>Al

has an ordered face-centered cubic structure with a melting point of 1390°C, a density of 7.5 g/cm<sup>3</sup>, and Young's modulus of 337GPa. [26] CrSi<sub>2</sub> has an ordered hexagonal structure exhibiting stacking. This belongs to the polytypic family. Each Si atom is linked to 10 Cr neighbors (2+3 close Cr neighbors and 2+3 neighbors at a 2.48Å and 2.56Å). [27]



**Figure 6: Crystal lattice structures of Ni<sub>3</sub>Al (left) and CrSi<sub>2</sub> (right).**

Tesket al<sup>8</sup> hypothesized that an interfacial diffusion zone was most likely created at the ceramic/alloy interface with properties dissimilar to both metal and porcelain, and that this layer was responsible for bonding. The current study proved the existence of the interfacial diffusion zone through SEM and the composition of this zone through EDS. In this study, intermetallic compounds were formed at the junction of the porcelain and metal layer, predominantly an interaction of aluminum, nickel, chromium, and silicon. This was mainly responsible for the bonding of the porcelain mass to the metal alloy. [28-31]

Chemically, other factors like van der Waal's forces and difference in surface tension affected ceramometal bonding to a lesser extent. Mechanical interlocking due to surface roughness on the metal alloy aided in the formation of a stronger bond. The porcelain mass, once heated to an optimum firing temperature, got interlocked in those minor surface irregularities and resisted shear and compressive forces. Scolaro et al [27] studied the shear bond strength between ceramic and silver-palladium alloy using a universal testing machine. They concluded that bond strength must be enough to resist the cyclic masticatory forces exerted by the opposing dentition on the PFM restoration. Son et al<sup>26</sup> used similar equipment to study the shear bond strength between ceramic and nickel-chromium alloy, and inferred that an optimum amount of surface roughness in the alloy was an essential factor in the increased shear strength of the interface region. [32]

Bertolotti<sup>7</sup> formulated a method to predict the interfacial stress as a function of temperature. The stress was assessed in terms of the deflection/deformation of the biomaterial strips. The

method used in this study was based on microstructural changes and oxide formation between the metal alloy and porcelain. The average shear bond strength was highest at 900°C, followed by 960°C and 700°C. The specimens fired at 700°C displayed weak ceramometal bonding. The porcelain particles did not form a homogenous mass at 700°C; hence this group had the lowest shear bond strength values. At 960°C, the components of porcelain got over-dessicated and friable, leading to decreased shear bond strength. [33,34]

The shear bond strength values could be correlated with the EDS graphs obtained. The lack of formation of intermetallic compounds in region II (Fig 5) of line C (700°C) justified the decreased shear bond strength of the specimens of that group. At 900°C and 960°C, the EDS graph trends were almost similar, but a slight difference was observed in shear bond strength values. Previous studies<sup>32-34</sup> have shown that when fired at 960°C the components of the porcelain mass become over-dessicated and friable, explaining the slight decrease in the shear bond strength of specimens fired at 960°C, compared to the specimens fired at 900°C.

### Conclusion

The dental porcelain/alloy interface has been studied using scanning electron microscopy and energy diffraction spectroscopy in the present study. An oxygen depletion zone was formed at the ceramometal interface at the designated firing temperatures, preventing formation of oxides and leading to the formation of intermetallic compounds at the interface, and was the prime factor in ceramometal bonding. The findings of this study have elucidated a new concept of bonding of

porcelain and metal alloy. The formation of an oxygen depletion zone at the ceramometal interface and reaction between metallic ions released from the two surfaces to form intermetallic compounds (never reported in the literature before) has provided a comprehensive understanding of the ceramometal bond. Also, shear bond strength tests revealed that the mean strength value increased for specimens fired at 700°C to specimens fired at 900°C and then decreased for specimens fired at 960°C. Shear bond strength values could be correlated with the formation of intermetallic compounds as seen in the EDS graph.

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