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# Influence of preoxidation cycle on the bond strength of CoCrMoSi–porcelain dental composites

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ABSTRACT

The purpose of this study was to evaluate the effect of preoxidation cycle on the shear bond strength (SBS) of CoCrMoSi alloy–porcelain dental composites. The porcelain was fired onto three types of metal surfaces: non-preoxidized, preoxidized and, preoxidized followed by grinding. The bond strength of metal–porcelain composites was investigated by the means of a shear test. The metal–ceramic interfaces and the fractured surfaces were analyzed using Optical Microscopy, Stereomicroscopy and SEM/EDS. Data was analyzed with Shapiro–Wilk test to test the assumption of normality. The *t*-test was used to compare shear bond strength results ($p<0.05$). The analysis of the three types of surfaces was performed prior to porcelain firing. It was also performed a complementary analysis of an alumina-blasted preoxidized CoCrMoSi surface. The greater metal–porcelain adhesion was obtained for non-preoxidized specimens.

Non-preoxidized specimens showed significantly ($p<0.05$) higher shear bond strength than preoxidized/ground specimens, $115.5 \pm 7.5$ MPa and $74.8 \pm 8.5$ MPa, respectively. Porcelain showed no adhesion to preoxidized specimens. All preoxidized specimens exhibited adhesive failure type while non-preoxidized presented both adhesive and mixed failure types. Preoxidation heat treatment revealed a detrimental effect on the adhesion of CoCrMoSi–porcelain composites for dental restorations. Hence, in order to enhance CoCrMoSi–porcelain adhesion, the preoxidation heat treatment conditions, as performed in this study, should not be performed.

## 1. Introduction

Despite the use of all-ceramic restorations is rapidly growing, porcelain fused to metal (PFM) restorations is still the most used technique within prosthetic dentistry. With its history of nearly 50 years serving dentistry, PFM technique is known to produce esthetic and reliable restorations proved by their great survival rates [1]. Some studies reported that up to 88.7% of metal–ceramic crowns and 80.2% of metal–ceramic fixed partial dentures (FPDs) were still in function after 10 years [2]. All-ceramic crowns are regarded to provide generally better esthetics for anterior teeth than metal–ceramic ones but they do not warrant the necessary strength to be used for posterior teeth. Although failure reports are decreasing over the last years, especially for pressed ceramics, its recent history does not allow drawing conclusions in respect to their long term clinical performance.

For many years gold based alloys were the primary choice for dental restorations because of their high biocompatibility. In 1971, the United States abandoned the gold standard and, as a result, its price together with other noble metals increased sharply over the next nine years. Because of the unstable price of the noble metals during this period, most dental laboratories started using alternative materials such as Ni–Cr and Co–Cr alloys. Besides their low price, the obvious advantages of base metal alloys are their lower weight, greater stiffness (elastic modulus) and other beneficial mechanical properties [3,4]. Co–Cr alloys have an advantage over Ni–Cr alloys based on its great biocompatibility relative to the allergenic potential of the nickel [4–6]. Studies are divergent about the bond strength of non-precious alloy systems. Anusavice [3], based on in vivo studies, states that there is no evidence of inferior or superior bond strength values of Ni–Cr or Co–Cr alloys, relative to those observed in noble metal alloys. He also reports no difference in failure incidence between metal and ceramic restorations made by base metal alloys and those obtained by noble metal alloys. On the contrary, Drumond et al. [7] found a significant decrease, in a range of 40%, in shear bond strength of nonprecious alloys–porcelain systems vs. gold–porcelain systems.

Base metal alloys are formed by elements that are able to be oxidized, especially chromium. Therefore, one of the challenges in this type of alloys is controlling the excessive formation of chromium oxide that results in lower bond strength between metal and porcelain [8–11].

The way this oxide interacts with porcelain during firing cycle has originated several theories. Klaus et al. [12] suggested that the adherent-to-metal oxide scale is wetted by the porcelain and becomes the transition zone between the two materials. Later, King et al. [13] believed that the layer of glass nearest the metal dissolves the oxide on the surface of the metal and that a layer of oxide-saturated glass bonds directly with the metal surface. This thinking was based on

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**Table 1**
Base alloy composition (wt.%) (according to manufacturer).

| Co | Cr | Mo | Si | Trace |
|---|---|---|---|---|
| 62 | 31 | 4 | 2.2 | Mn–Fe–W |

the premise that “few oxides are sufficiently adherent to their metals to produce excellent [porcelain] adherence”. This theory was later adopted by Pask and Fulrath [14] and Pask [15], although they do consider the possibility of existence of a discrete oxide layer at the interface and state that once it is present, it must be adherent to the metal.

Posterior studies performed by Miyagawa [16] and Ritchie et al. [17] have shown that a discrete oxide layer must be present at the interface. Therefore, Mackert et al. [9] tried to ascertain whether the oxides formed on dental PFM alloys were sufficiently adherent to their alloys to allow for excellent porcelain adherence and concluded that adherence between oxide formed on the metal surface and porcelain plays a dominant role in porcelain.

There are several oxidation heat treatments of the metal for different purposes: degassing removes the entrapped gas; outgassing eliminates surface contaminants and preoxidation creates an oxide scale [3]. Besides their main purpose, these treatments may cause collateral effects such as stress releases and framework distortions [18,19]. Wu et al. [20] determined the effect of oxidation heat treatment on porcelain bond strength in selected base metal alloys and concluded that it didn't have a significant effect on them.

On the contrary, Dekon et al. [21] and Rokni and Baradaran [8] found a significant difference in NiCr–porcelain bond strength between oxidized and non-oxidized samples but with divergent results. The former author registered the best results for non-oxidized samples and the latter for oxidized ones. Wagner et al. [22] found an improvement of 152% on bond strength for preoxidized palladium alloys. Daftary et al. [23] used different pretreatments on noble and base metal alloys to evaluate their effect on metal-porcelain bond strength. They found significant differences between the different metals and pointed out that each alloy should be treated differently.

This study evaluated the effect of preoxidation heat treatment on the bond strength of a commercial CoCrMoSi alloy to porcelain. It was developed an integrated investigation in terms of the element diffusion profiles at the interaction zone, the ceramic fracture types and the alumina-blasting surface treatment for oxide removal.

## 2. Material and methods

### 2.1. Specimens composition and preparation

For this work a CoCrMoSi dental alloy [24] (Nobil 4000, Nobilmetal, Villafranca d'Asti, Italy) and a dental opaque ceramic [25] (Ceramco3, Dentsply, York, USA) (batch number: 08004925) was used. The chemical composition of the commercial base alloy Nobil 4000 is presented in Table 1. Every alloying element plays a specific role in this alloy. Hence, cobalt is the main constituent in this alloy and chromium is added to provide strength and corrosion resistance via passivation [26,27]. Molybdenum, iron and tungsten are added for solid solution hardening [4,28]. Molybdenum has the added benefit of influencing the coefficient of thermal expansion [4,29]. Silicon imparts good casting properties and increases alloy ductility [30].

In Table 2 is presented the chemical composition of Ceramco3 Opaque porcelain. This porcelain was selected for this study because of its recognized mechanical properties [31] and due to its suitability to bond to CoCr dental alloys [24,25].

**Table 2**
Porcelain chemical composition (wt.%).

| $SiO_2$ | $Al_2O_3$ | $K_2O$ | $SnO_2$ | $ZrO_2$ | CaO | $P_2O_5$ | $Na_2O$ | Others |
|---|---|---|---|---|---|---|---|---|
| 41.3 | 14.5 | 14.0 | 11.9 | 5.8 | 4.1 | 4.1 | 3.0 | MgO, $SO_3$, ZnO, $Cr_2O_3$, $Fe_2O_3$, CuO, $Rb_2O$ |

Metal substrates were directly produced from metal rods supplied by the manufacturer. Rods were machined to a diameter of 4.5 mm and then cut into several 4 mm high substrates using a precision cut-off machine (Minitom, Struers). Afterwards, all substrates were finely ground with 2400-grit SiC paper, ultrasonically cleaned in an alcohol bath for 10 min and rinsed in distilled water for 10 min to remove contaminants. Then they were dried with adsorbent paper towels.

Metal substrates were split in two groups: non-preoxidized and preoxidized substrates. Preoxidation heat treatment comprised a 10 min stage in air at 1000 °C. After preoxidation, substrates were again split in two groups. Part of them were stored with the oxide scale formed during preoxidation cycle and the rest was light ground with 2400-grit SiC paper to remove the non-adherent oxide layer formed on metal surface. Indeed, manufacturer instructions recommended a light alumina blasting of metal's surface to remove the oxide scale. The grit-blasting, however, would introduce a substantial amount of surface roughness, which is very important in metal–ceramic adherence but was not desired for this study. In order to avoid the introduction of this new variable (roughness), it was decided to perform this study without the influence of complicating surface-roughness effects, thus this step (grit-blasting) was omitted and replaced by a fine grinding of the surface (2400-grit SiC paper) that would not introduce any surface roughness. This allows the study of the influence of the preoxidation heat treatment on the chemical bonding between the metal and the porcelain without the effect of mechanical interlocking provided by metal surface roughness.

In order to guarantee a flawless interface, porcelain powders were hot pressed onto the metal substrate. First, graphite die was painted with $ZrO_2$ in order to impede carbon diffusion to specimen. Then, the metal substrate was placed in die's cavity followed by the porcelain powder. Finally, the set was heated up to 970 °C at a heating rate of approximately 60 °C/min and remained at that temperature for 2 min. Hot pressing was performed under vacuum ($\sim 10^{-2}$ mBar) and at a pressure of ~20 MPa.

A SEM-EDS analysis was performed on the surface of the following specimens: (1) non-preoxidized; (2) preoxidized and (3) preoxidized specimens followed by oxide removal with P2400-grit SiC paper. Although sandblasting effect had been omitted for bond strength purposes, it was decided to conduct a broad surface analysis also on an (4) alumina blasted preoxidized specimen comprising a mechanical (surface hardness and roughness) and a chemical (SEM-EDS) component. Alumina blasting of the preoxidized metal surface was performed according to manufacturer's instructions with Ø110 μm grains at a pressure of 0.5 bar (Protempomatic, Bego, Germany). After sandblasting, samples were ultrasonically cleaned in an alcohol bath for 10 min and rinsed in distilled water for another 10 min. Amongst other things, this step allowed to quantify the oxidation level of the CoCrMoSi surface after sandblasting treatment.

### 2.2. Shear bond strength tests

Metal–porcelain bond strength was assessed by the means of shear bond strength test. Several tests have been used to assess metal–ceramic bond strength, namely the Schwickerath crack initiation test used in ISO 9693:1999, the three-point-flexure test, the four-point-flexure test, the biaxial flexure test, etc. However, based on literature data, all of them show great variability in the mean bond strength values with large standard deviations [3,32,33]. The planar interface shear bond strength test used in this study is not influenced by the Young's modulus of the alloy as happens in bending tests and is considered to be suitable for evaluation of metal–ceramic bonds [32,34].

The current standards that indicate the minimum acceptable bond strength for metal–ceramic composites are ANSI/ADA Specifications Nº38 (2000) and ISO Standard 9693 (1999). Both employ