MICROSTRUCTURAL ANALYSIS OF THE INTERFACE BETWEEN SOME SUPERALLOYS AND COMPOSITE/CERAMIC MATERIALS

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ABSTRACT. The clinical success of aesthetic ceramic fused to metal or composite resin bonded to metal restorations depends on the quality and strength of composite/ceramic bonding. To investigate the ceramic and composite surface adhesion to the surface of the alloys, samples were prepared by metallographic techniques and then were analyzed by Scanning Electron Microscopy (SEM). We studied a total of four samples of superalloys, denoted S1, S2, S3, and S4. Each of these was treated with: Vita ceramic powders, Noritake ceramic powders, Premise Indirect composite and an indigenous composite C1. At a magnification level of x1500, the adherence between the layers and the surface irregularities of the layers that improve the adherence could be properly observed. It is worth noting that after the sample preparation procedure, samples S1, S2 and S4 were damaged, the only sample remaining in a good condition was sample S3.

Keywords: *Superalloys, Composite, Ceramic Materials, Microstructural Analysis, Scanning Electron Microscopy*

INTRODUCTION

Hybrid porcelain fused to metal (PFM) and metal-composite restorations are still the most popular type of fixed dental restorations [1,2] because of their good mechanical strength, high biocompatibility [3] and long-term satisfactory

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clinical performance [4]. Metal-composite restorations are not generally used for long spanning bridges because of their high fragility [5]. In such clinical situations, the restorative material requires a suitable mechanical strength, so conventional PFM bridges are still preferred to support the mastication forces for long-term clinical success. Their widely use has certified their clinical effectiveness due to many positive aspects of their properties, such as wetting behavior and interface adhesion that are directly linked to the bond-based metal and ceramic elements [6-8].

PFM restorations are comprised of a metallic framework, which confers mechanical resistance to the restoration, and a veneering ceramic layer which covers the metallic framework partially or completely [9]. The first non-noble alloys that have served in PFM restorations contained a composition of cobalt, chromium, iron, nickel and other metals [10,11]. Non-noble alloys show a lower resistance to corrosion by comparison to noble alloys, their fluidity is reduced and the mechanical processing is difficult, but they have a higher hardness and a high modulus of elasticity [12].

Co-Cr alloys have some advantages over Ni-Cr-Be alloys, due to their high degree of biocompatibility that derives from the lack of Ni, which is known to cause Ni-related allergic responses or Beryllium related toxic consequences [13], and greater resistance to corrosion generated by the higher concentration of chromium found in this type of alloys, which forms a protective oxide film on the surface of the framework [14]. The main causes of failure of PFM restorations are the corrosive degradation of alloys, mechanical wear and fatigue breakage [15].

The veneering ceramics used in PFM restorations convey optimum optical, mechanical and biocompatible properties to the final restoration due to their aesthetic color, low thermal conductivity, chemical resistance, high flexural strength, surface density and roughness, but these components also offer some disadvantages like: low tensile strength, further processing after glazing is nearly impossible because the machined surfaces become rough, the presence of internal and external cracks that lead to fracture and high cost [16-19].

The current investigations are aimed to study the way in which two commercially available feldspatic veneering ceramics, as well as a commercially available composite resin adhere onto the surface of Co-Cr superalloy frameworks, by comparison with an indigenous experimental composite C1 manufactured at ICCRR-Cluj-Napoca. The purpose of this study is to describe the adherence proprieties of the C1 composite by comparison with commercially available products that serve the same purpose in aesthetic hybrid restorations. For this purpose we are using scanning electron microscopy (SEM) which produces high-resolution images of sample surfaces. The images created by SEM have a three-dimensional black and white appearance, with a sharp focus over a great depth of field [20].

RESULTS AND DISCUSSION

After the preparation of the samples, it was observed that the deposited layers were peeling and cracking in samples S1, S2 and S4, while all the layers of sample S3 remained 90% intact.

Examination of samples in group S1 revealed that approximately 90% of the Vita ceramic layer was removed. Small portions that remained attached to the alloy indicate that Vita ceramic material (V1) is adherent to the support of the super alloy. Figure 1 indicates how the ceramic material V1 has adhered to the support. At the interface between the V1 layer and the alloy, the oxide layer can be distinguished. Note that some parts of the ceramic material did not adhere to the alloy, due to the presence of elongated cracks that formed parallel to the metal-ceramic interface. The difference between the oxide layer and the cracks can be observed in the form of a thin, white reaction layer that has formed only near the oxide layer.
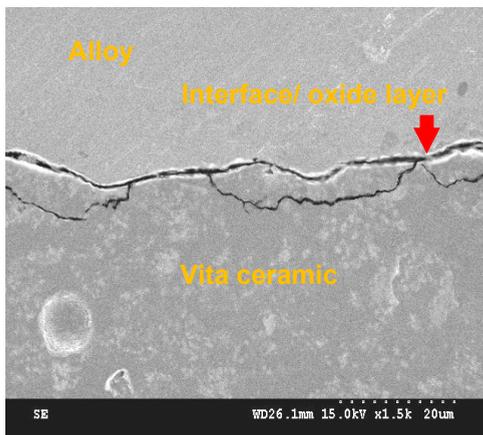
Figure 1. Adhesion of Vita ceramic material, sample group S1 X 1500. The super alloy is in the upper part of the image
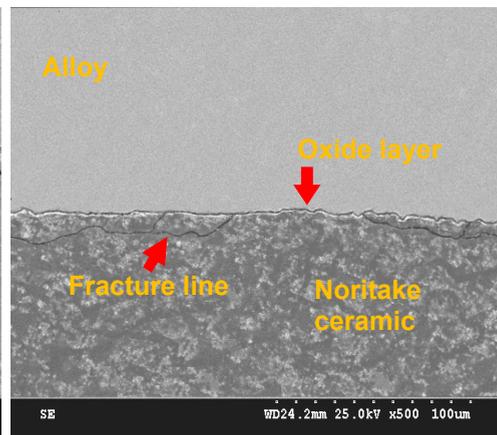
Figure 2. Appearance of the interface between Noritake- Alloy, sample S1 X 500

The Noritake ceramic (N1) layer was also removed from the S1 sample in approximately the same proportion as the V1 ceramic, as it can be observed in Figure 2. An oxide layer can be distinguished at the metal-ceramic junction. This layer has been formed during the oxide firing of the metal framework. For this sample, between the ceramic and the super alloy, a similar but thinner black belt that represents the space between the super alloy and the ceramic support was observed. Thin fracture lines can be observed in the ceramic veneering material near the metal-ceramic junction.

Aspects of composite adhesion to the metal framework are displayed in Figure 3, where the boundary between the two layers is shown- the Premise Indirect composite (P1), in the upper right of the image, presenting air pockets) and the indigenous composite (C1), on the left of the picture, presenting a uniform appearance. Detaching from the support alloy is clearly visible. In depth viewing of the border between the two composites and the metal framework shows that both composite materials have adhered to the supporting material in small areas, which are encircled in Figure 3. In Figure 4, a portion of Premise Indirect composite is shown penetrating the surface irregularities and massive peeling can be observed at the top of the image, due to the crack that propagates along the boundary.
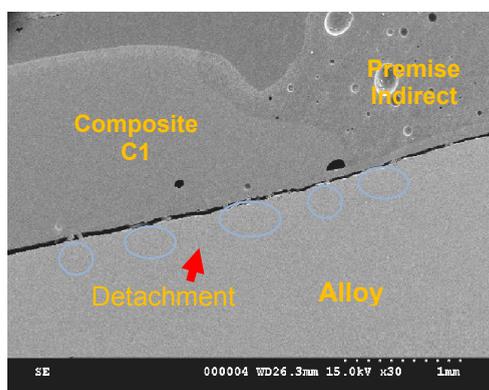
Figure 3. Adhesion of C1 and P1 composites to the surface of the alloy. Adherent areas are encircled, sample S1 X30
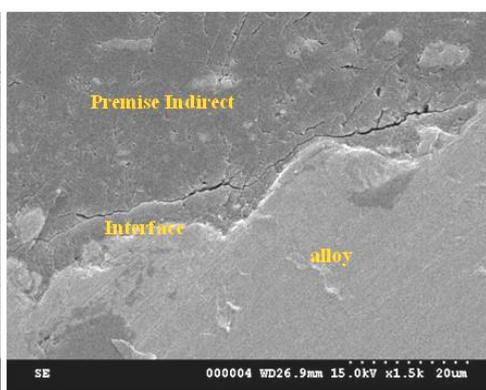
Figure 4. Adhesion of Premise Indirect to the metallic alloy, sample S1 X 1500

Adhesion was also revealed in the case of the indigenous composite, which besides peeling presented cracks, as displayed in Figure 5. Besides the peeling from the supporting layer, penetration of surface irregularities and patches of adherent composite material can be seen (metal framework is at the bottom of the image).

The procedure of sample preparation in the case of group S2 resulted in separation of the layers deposited on the metal frame. V1 veneering ceramic is detached from the metal framework on approximately 90% of the length of the layer and presents multiple surface cracks (Figure 6), however small patches of adherent ceramic material can also be observed.

At the interface between the V1 ceramic and the metal framework, small irregularities and air pockets are visible.

In the case of the N1 veneering ceramic, sample preparation resulted in peeling and cracking of the ceramic material from the surface of the super alloy, in a similar manner to the V1 veneering.

The composite materials have been affected in a small degree by the preparation procedure, as seen in Figure 7. The Premise Indirect composite (P1), which contains air pockets, is located in the upper right of image, while the indigenous composite (C1) is located on left. Adhesion-wise, both composites have adhered to the surface of the super alloy, discontinues and in thin layers.

Adherence to the metal frame has occurred only in a thickness of 2 to 8 µm, given the fact that the remaining thickness of the layer was separated by the cracks caused by the sample preparation technique. Adherence of the indigenous composite (C1) has also been discontinues, in a layer thickness of 2 to 8 µm, as seen in Figure 7.
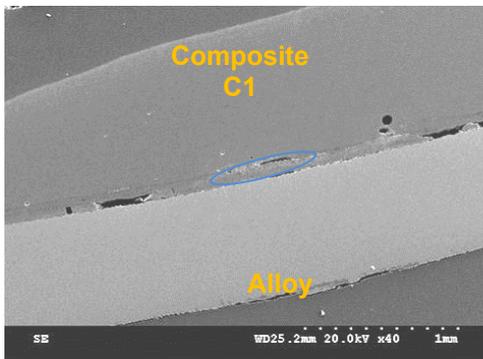
Figure 5. Boundry between C1 and alloy. Peeling area and fracture line is encircled. Sample S2 X40
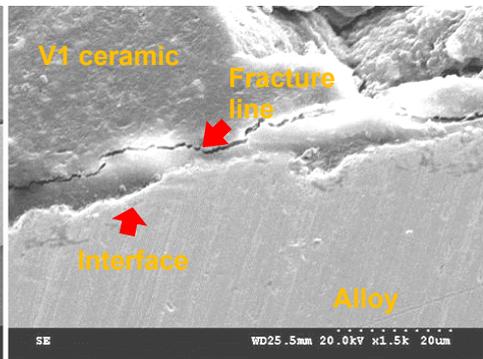
Figure 6. Interface between V1 ceramic and alloy. Sample S1 X1500
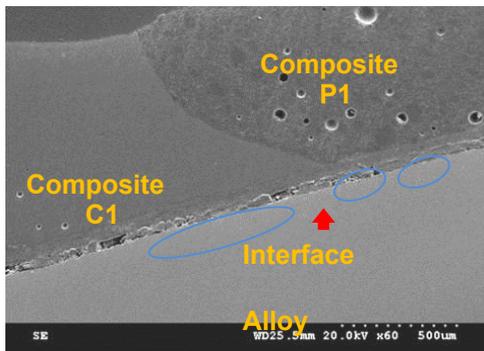
Figure 7. Adhesion of C1 and P1 compo-sites to the metal framework. Fracture lines and air pockets are encircled. Sample S2 x60
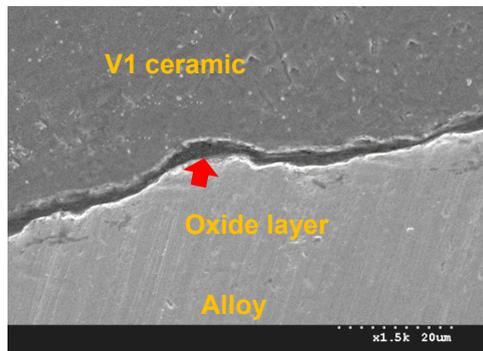
Figure 8. Interface between V1 ceramic and alloy. Sample S3 X1500

Examination of sample group S3 reveals that the prepartion technique used had a small effect on the adherence of the different veneering materials used, given the fact that the materials adherent to the alloy on almost the entire lenght. The layer of V1 veneering ceramic contains a small number of cracks and the adherence to the metal frame is proven to be good, as seen in Figure 8.

Similar results were obtained when using the Noritake ceramic veneering material (Figure 9). The layer of ceramic is continues and presents a good adherence to the surface of the super alloy with a small number of micron sized air-pockets present near boundary between the super alloy and the ceramic layer.
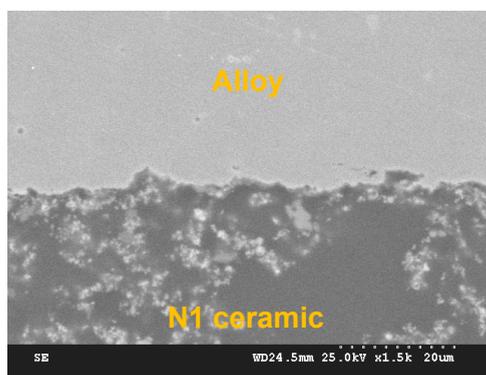
Figure 9. Boundary between N1 veneering ceramic and alloy. S3 X1500
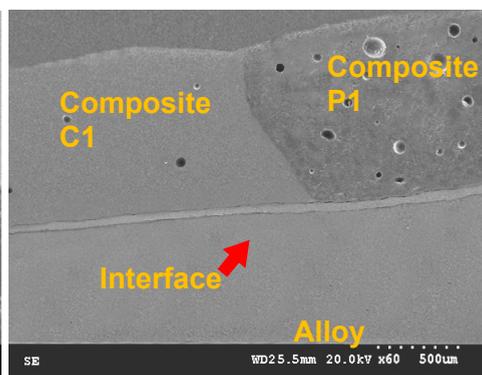
Figure 10. Adhesion of C1 and P1 composites to the surface of the alloy. S3 x60

The Premise Indirect composite and indigenous composite had a good and very good adherence to the super alloy. In Figure 10, the separation limit between the two types of composite is presented (composite C1 on the left and Bellglass composite on the right), with the metal support located at the bottom of the figure. The layer of Premise Indirect presented in this sample also contains embedded air pockets. Adherence of the two composites to the metal frame is illustrated in Figure 11 and 12. In both Figures the super alloy frame is located at the top of the image.

During sample preparation of group S4, about 90% of the thickness of the veneering materials has been removed. After sample preparation, approximately 10% of the thickness of the Vita ceramic veneering material has remained adherent to the surface of the super alloy, this remaining portion of the V1 layer contains micron sized voids and presents a similar adhesion to the metal frame as the samples in group S1 and S2.
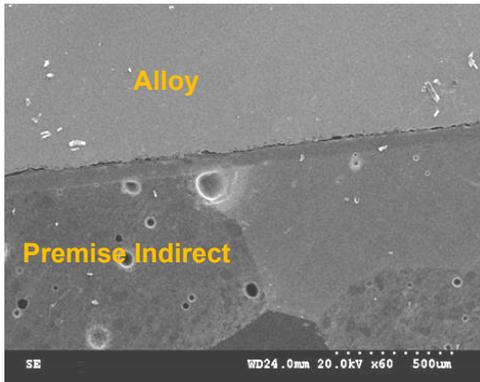
Figure 11. Separation limit between the composite materials- alloy. S3 X60
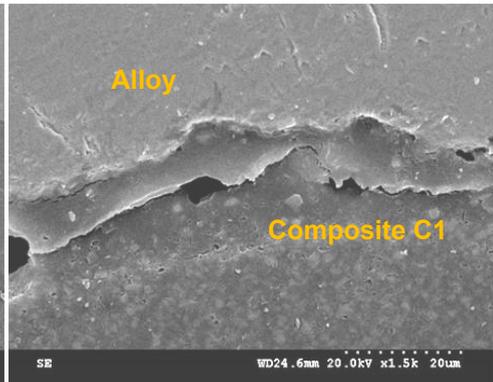
Figure 12. Adherence of indigenous composite to the super alloy sample. S3 X 1500

The Noritake veneering ceramic was removed in about 85% of thickness during sample preparation and presented similar appearance and characteristics with the samples in S1 and S2 groups.

The layers of P1 and C1 composite materials were also affected by the sample preparation procedure. The adherence of the two composite materials to the super alloy framework is presented in Figure 13 and 14. Good adherence of the P1 composite has been observed in a thin layer, separated from the much thicker layer by a crack formed parallel to the metal-composite boundary.
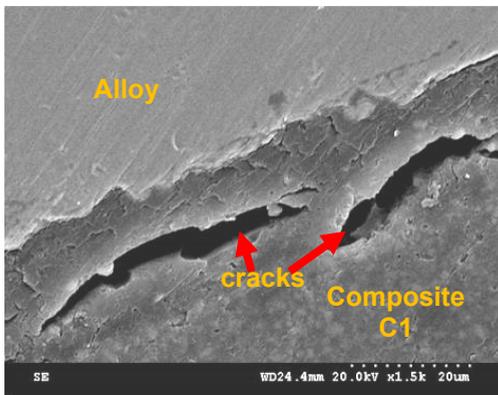
Figure 13. Boundary between C1 composite and alloy. Multiple cracks in the C1 layer. Sample S4 X1500
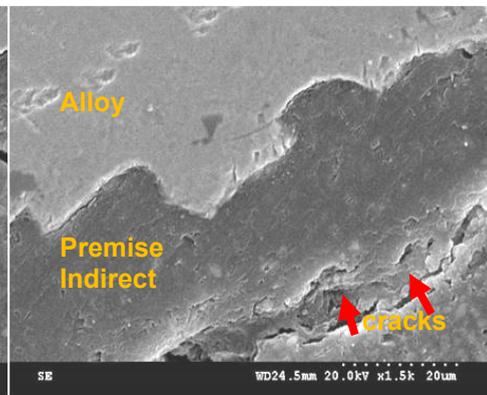
Figure 14. Adherence of the P1 layer to the metal framework. Sample S4 X1500

The adherence of the indigenous composite, which can be observed in figure 12, is observed only in a thinner layer, which is separated from the underlying layer by numerous cracks with lengths of about 40 microns and appreciable width of about 2-4 microns.

CONCLUSIONS

Scanning Electron Microscopy examination with a degree of magnification of between x30 to x1500 of the veneering ceramic and composite layers on the super alloy led to the conclusion that in all of the cases, the studied materials have adhered, in large or small quantities, to the surface of the super alloys.

At a magnification degree of X1500, the adherence between the layers and the irregularities present on the surface of the layers that improve the adherence could be best observed. In addition, the appearance of an oxide layer with a different structure and coloration from the rest of the metallic layer has been noted. The oxide layer may act as a buffer layer. It is worth noting that after the sample preparation procedure, samples S1, S2 and S4 were damaged, the only sample remaining in a good condition is sample S3.

EXPERIMENTAL SECTION

In order to investigate the morphological surface adhesion of the veneering materials to the superalloy frameworks, the Co-Cr superalloy specimens were fabricated by conventional casting technique. For this purpose, four groups consisting of four wax patterns (N=16) in the form of a bar with dimensions of 0.5 mm × 3 mm × 25 mm (IQ sticks, Yeti Dental) were invested with phosphate-bonded investment (BellaVest SH, BEGO). The indigenous composite C1 is manufactured at ICCRR, Cluj Napoca and based on glass with Zn (40% SiO_2; 30% ZnO; 10% Al_2O_3; 10% B_2O_3; 5% CaO; 5% Na_2O melting temperature: 1350^0C) and quartz, colloidal silica as inorganic phase. For organic phase: monomers mixture consists of BisGMA (ICCRR-synthesis, TEGDMA (Aldrich) and UDMA (urethane dimethacrylate, Aldrich) with photo-baro-thermo polymerization system.

The molds were heated at 1050 °C and cast with the superalloys at 1450°C using a centrifugal- induction casting machine (OrcaCast, п Dental)- one mold per superalloy-molds were left to cool down to room temperature and the specimens were then divested and cleaned by sandblasting with alumina particles (110 µm). The specimens were then coated with the four veneering materials, according to the manufacturers instructions.

After veneering, the samples were embedded in a self-curing acrylic resin and then they were mechanically polished with SiC sandpaper (220–2000 grit) under continuous water cooling using a diamond paste (DP Paste, Struers). Between each polishing step, the specimens are rinsed with distilled water and ultrasonically cleaned for 1 min in order to remove remnants of polishing debris and pastes. After polishing, a thin layer of 10 nm of gold coating was deposited on the samples using a sputter coater (B7341, Agar Scientific), before observation with the scanning electron microscopy SEM (HitachiS-2600N).

We studied a total of four groups, denoted S1, S2, S3 and S4. Each of these groups contained four samples which were treated with: Vita VMK Master ceramic (V1), Noritake EX-3 ceramic (N1) Kerr Premise Indirect- a commercially available composite (P1) and an indigenous composite –C1 (C1).

ACKNOWLEDGMENTS

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