X-Ray diffraction and scanning electron microscopy-energy dispersive spectroscopic analysis of ceramo-metal interface at different firing temperatures

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Abstract

Objective: Porcelain chipping from porcelain fused to metal restoration has been Achilles heel till date. There has been advent of newer ceramics in past but none of them has been a panacea for Porcelain fracture. An optimal firing is thus essential for the clinical success of the porcelain-fused to metal restoration. The aim of the present study was to evaluate ceramo-metal interface at different firing temperature using XRD and SEM-EDS analysis. Clinical implication of the study was to predict the optimal firing temperature at which porcelain should be fused with metal in order to possibly prevent the occasional failure of the porcelain fused to metal restorations. Materials and Methods: To meet the above-mentioned goal, porcelain was fused to metal at different firing temperatures (930–990°C) in vacuum. The microstructural observations of interface between porcelain and metal were evaluated using X-ray diffraction and scanning electron microscopy with energy dispersive spectroscopy. Results: Based on the experimental investigation of the interaction zone of porcelain fused to metal samples, it was observed that as the firing temperature was increased, the pores became less in number as well as the size of the pores decreased at the porcelain/metal interface upto 975°C but increased in size at 990°C. The least number of pores with least diameter were found in samples fired at 975°C. Several oxides like Cr2O3, NiO, and Al2O3 and intermetallic compounds (CrSi2, AlNi3) were also formed in the interaction zone. Conclusions: It is suggested that the presence of pores may trigger the crack propagation along the interface, causing the failure of the porcelain fused to metal restoration during masticatory action.

Keywords: Firing temperature, porcelain chipping, pores

Introduction

Occasional chipping of porcelain from metal surface in PFM restorations has been the continued problem till date. The failure of porcelain–metal bond leads to restoration failure. This failure can occur cohesively within porcelain, in metal or at porcelain–metal interface. Several studies have been conducted to determine the strength of porcelain–metal bonds[1-10] porcelain–metal interface,[11-15] fracture resistance of Porcelain Fused to Metal restorations,[16,17] porcelain-metal thermal compatibility,[18] effect of heat treatment and firing cycle,[19-21] adhesion of porcelain to other metal.[22,23] Present study deals with failure of porcelain metal interface. Porcelain fused to metal restoration failure can occur due to multiple reasons. This paper will focus on the effect of various firing temperatures on porcelain–metal interface.

Poorly controlled firing temperature is supposed to be potential cause to PFM restoration failure. An optimal firing temperature for porcelain is supposed to be one of the major factors for the restorations to be clinically successful. The aim of this study was to characterize the microstructure of oxide layer formed on metal surface before firing and after firing the PFM samples at different firing temperatures. The interaction zone formed along the interface was studied and evaluated.

The objective of the study was to predict the optimal firing temperature at which porcelain should be fused with metal in PFM restorations.

Material and Method

Casting of base metal alloy

Casting of base metal alloy was done [Chart 1]. Sample A was casted but not oxidised. Sample B was casted, oxidised but Porcelain was not applied. Sample C to G were casted, oxidised and Porcelain was applied. All the samples were evaluated microstructurally [Chart 2]. X-ray diffraction was done for Sample A, B and control sample. XRD and SEM-EDS analysis was done for samples C to G.

Results and Discussion

Porcelain fused to metal sample preparation (Samples C to G)

Figure 1 showed the relative X-ray diffraction (XRD) patterns for commercial base metal alloy (Niadur), Sample A and Sample B. Commercial base metal alloy showed the presence of delta phase chromium, nickel [δ(Cr, Ni)] in it.
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Chart 1: Casting of Base Metal Alloy.

*Begosol, Bego, Germany ‘NIOM – Made in Germany, DFS

Chart 2: Microstructural evaluation of sample.

*Lectra, UGIN, France, ‡KRISH (Cold setting compound liquid and powder) for metallurgical specimen mounting, Chennai, §Emery Paper No. 1/0,2/0, 3/0 <SIA> 1600 SAINOR B Swiss made; Emery Paper No. 4/0, John Oakley and Sons Limited, Made in England, ††ISO-DEBYEFLEX-2002, Germany †JEOL JSM-840

Sample A showed the presence of intermetallic compound Cr₂Ni, besides δ (Cr, Ni) phase whereas Sample B showed the presence of Cr₂Ni₃₄, nickel oxide (NiO), chromium oxide (Cr₂O₃) and delta phase. Since this sample was oxidized, the formation of these metallic oxides was quite reasonable.

The XRD pattern [Figures 2-6] and EDS patterns were recorded for samples C to G. [Table 1] shows the various oxides and intermetallic compounds formed in different samples and [Table 2] shows distribution of major elements.
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Figure 3: Diffraction pattern for sample D (opaque layer fired at 945°C)

Figure 4: Diffraction pattern for sample E (opaque layer fired at 960°C)

Figure 5: Diffraction pattern for sample F (opaque layer fired at 975°C)

Figure 6: Diffraction pattern for sample G (opaque layer fired at 990°C)

X-RAY DIFFRACTION (XRD) OBSERVATIONS

Table 1: Oxides and intermetallic compounds formed in different samples

| Sample       | Oxides       | Intermetallic compounds |
|--------------|--------------|-------------------------|
| Commercial base-metal alloy | –            | Delta (Cr, Ni)          |
| Sample A     | –            | Cr,Ni, Delta (Cr, Ni)   |
| Sample B     | NiO, Cr₂O₃   | Cr₃Ni₂, Delta (Cr, Ni)  |
| Sample C     | NiO, Cr₂O₃   | CrSi₂, AlNi₃           |
| Sample D     | Al₂O₃, Cr₂O₃, NiO | –                     |
| Sample E     | Al₂O₃, Cr₂O₃ | AlNi₃                  |
| Sample F     | Al₂O₃, Cr₂O₃, NiO | Al₂Cr₃            |
| Sample G     | Cr₂O₃, NiO, Al₂O₃ | –                     |

The EDS analysis was done for elemental recordings at the locations described above. The results were qualitatively correlated with XRD observations, which led to the evaluation of interaction zone.

Samples C–G showed the presence of oxides of Ni, Cr, and Al. Various intermetallic compounds like CrNi₂, CrSi₂, AlNi₃, and Al₂Cr₃ were also formed.

Table 2: Distribution of major elements observed in SEM-EDS analysis

| Sample | Interface region | Metal region | Porcelain region |
|--------|------------------|--------------|------------------|
| C      | Ni, Cr, O        | Ni, Cr, O    | Si, Al, K, O     |
| D      | Al, Ni, Cr, O    | Ni, Cr, O    | Si, Al, K, O     |
| E      | Ni, Cr, Al       | Ni, Cr       | Si, Al, K        |
| F      | Si, Al, O, Cr    | Ni, Cr, O    | Si, Al, O        |
| G      | Ni, Cr, O        | Ni, Cr, O    | Si, Al, K, O     |

The EDS analysis was done for elemental recordings at the locations described above. The results were qualitatively correlated with XRD observations, which led to the evaluation of interaction zone.
Sample E observations were well supported by the findings of Anusavice (1977) who showed Ni–Cr interactions with ceramic complexes. The presence of Al$_2$Cr$_3$ in Sample F further supported the studies of KJ Anusavice, RD Ringle, and CW Fairhurst,$^5$ who showed the presence of predominant Al-Cr interactions. The Cr ions were supplied by Cr$_2$O$_3$ oxide layer of metal surface and Al was provided by porcelain surface.

The XRD pattern and EDS analysis of various samples from A to G reconfirmed the fact that the oxidation of casted commercial base metal alloy led to the formation of oxides of major elements present in it (Ni, Cr) and during firing, the major elements from porcelain (K, Si, Al) interacted with metal oxide to form various oxides and intermetallic compounds. This resulted in the formation of interaction zone between metal and porcelain.

SEM image [Figure 7] of porcelain fused to metal sample C (opaque porcelain layer fired at 930°C) showed large number of pores ranging from 25–30. The size of average diameter of observed pores was found to be 43 μm. These large-sized pores were triangular to irregular in shape [Figure 8]. This observation can be explained by the studies of Anusavice.$^{24}$ They observed that during firing, the voids between porcelain particles were occupied by the furnace atmosphere. The vacuum, created during firing, pushes the air out of the porcelain particles. During firing, porcelain particles bond at their point of contact as the sintering of porcelain particles occur. The sintered porcelain particles try to flow and fill up the pore spaces. It might be presumed that large number of pores in this sample were due to incomplete sintering of porcelain particles and inability of particles to flow and fill up the air spaces completely. This can be also predicted from the fact that the commercial porcelain, used in the present study, is usually densified/sintered in the temperature range of 850–1100°C. Therefore, it can be said that due to lower temperature of 930°C, the sintering of porcelain particles was not complete, which resulted in large-sized pore formation.

As the firing temperature was increased to 975°C (sample F), both the number of pore and average diameter of pores [Figure 9] and [Figure 10] decreased due to better fusion of porcelain particles. Also, the flow of particles was increased causing increased filling of air space among the particles. In sample G, the number of pore and average diameter of pores did not decrease because fusion ability of porcelain particle did not increase at this temperature and tend to remain constant. On the contrary, pore size was increased. It was
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Clearly noted that as the firing temperature was increased, the pores became less in number as well as the size of pores decreased. The least number of pores with least diameter were found at 975°C. It shows that porcelain particles flowed and filled up the air spaces between them optimally at 975°C, which results in better sintering, leading to very few numbers of pores. Another reason of the observation of less number of pores at 975°C might be the optimal match of coefficient of thermal expansion of porcelain and metal.

Also noted was the fact that the pores were present only in the porcelain side and not in the metal side. The pores present in porcelain side are susceptible to crack formation at the edges. These cracks can form when PFM restoration comes under pressure; for example, during mastication, during which an average load of 2 N is transferred along the long axis of PFM crown or bridge. During mastication, the presence of pores can lead to the formation of cracks from its edges. These cracks possibly can coalesce together to form a longer crack. These longer cracks can subsequently propagate parallel to the interface, potentially leading to chipping of the porcelain layer, and hence, failure of the PFM restorations. Slow crack growth phenomenon is most commonly observed in samples with large-sized pores as compared to samples with small-sized pores.

Scope for Future Work

The firing of porcelain on metal in inert atmosphere like argon can be done to observe the influence of different atmosphere on the microstructural changes in the interaction zone. Studies correlating mechanical properties such as strength, with voids number and size can be performed in future to evaluate the nature of porcelain–metal interface.

Conclusions

Based on the experimental investigations of the interaction zone of porcelain fused to metal samples, the following conclusions can be drawn:

1. XRD and SEM – EDS analysis indicated that porcelain–metal interaction occurred during the firing of opaque porcelain layer at varying temperatures of 930°C to 990°C. Another important observation was the presence of pores of varying size, shape, and numbers on the porcelain side at the interaction zone, dependent on firing temperatures of opaque porcelain layers. As the firing temperature was increased, the pores became less in number as well as the size of the pores decreased. The least number of pores with least diameter was found for the sample in which opaque porcelain layer fired at 975°C.

2. Several oxides like Cr$_2$O$_3$, NiO, and Al$_2$O$_3$ and intermetallic compounds (CrSi$_2$, AlNi$_3$) were formed in the interaction zone.

3. The experimental studies indicate that an optimum firing temperature of 975°C is preferred for better adhesion properties of porcelain to Ni–Cr base metal alloy.

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