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Original Article

Evaluating the effect of varying the temperature and duration of oxidation heat treatment on the shear bond strength of porcelain to Co-Cr alloy: An invitro study

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Abstract

Background: Metal ceramic restorations are popular in restorative dentistry due to their better esthetics and strength. Plaque removal is easier when gingival tissues are in contact with vacuum-fired glazed porcelain. However, failures due to cohesive fracture within porcelain or adhesive fracture at porcelain-metal-phase boundary are frequent.

Aims and Objectives: The aim of this paper is to find out if varying the temperature and the duration of oxidation heat treatment would have any effect on the shear bond strength of porcelain to Co-Cr alloy.

Materials and methods: 80 samples of wax pattern of 6.4mm diameter and 1.6mm thick were casted cleaned and polished using silicon carbide papers of different grits. The samples were divided in different groups and were subjected to oxidation heat treatment at 920˚C, 950˚C, 980˚C and 1010˚C for a duration of 3, 4, 5 and 6 minutes respectively. Then single layers of wash opaque, opaque and dentinal porcelain were applied to form a porcelain cylinder, which was later subjected to shear bond test in a Universal testing machine.

Results: The statistical analysis showed that the samples subjected to the oxidation heat treatment at 980˚C for duration of 5 minutes exhibited the highest bond strength with the Mean of the Maximum Load value of 414.69640 N. The samples fired at 950˚C and 980˚C showed higher bond strength as compared to the samples fired at 920˚C and 1010˚C. The samples fired for the duration of 4 to 5 minutes showed better strength than the samples fired for the duration of 3 or 6 minutes.

Conclusion: From this study we can say that the variation in time and temperature has an effect on the bond strength of porcelain to metal and the cohesive failure seen within porcelain fired at 980˚C for 3, 4 and 5 minutes suggests sufficient bond between porcelain and metal.

Key words: Oxidation Heat Treatment, Shear bond strength, Porcelain and Co-Cr alloy

Introduction

The success of metal-ceramic restoration depends on the firmness of the ceramic bond over the metal. It is generally recognized that three modes of bonding are applicable to varying degrees in PFM system- mechanical interlocking, the chemical bonding and a variant of chemical bonding termed Van der Waals bonding[1, 2, 3]. In all the various mechanisms of bonding of porcelain-to-metal, metal oxide layer plays a vital role. The thickness of the oxide layer depends on the temperature and in the duration of heat treatment to which these metals are subjected to. Earlier studies have shown that the degassing or oxidation firing formed the oxide layer which is required for bonding[1]. Oxidation firing time and temperature must be sufficient to produce an adequate layer for bonding. Excessive oxidation results in a non-adherent oxide layer and a poor metal-ceramic bond.[1] In case of base-metal alloys, NiO or Cr_2O_3 were predominant after oxidation at high temperature of 1000˚C[4]. The strength of the bond between dental porcelain and base metal alloy containing Cr or Ni is adversely influenced by the formation of Cr_2O_3 and NiO[5]. When these oxides are combined in the dental porcelain; they reduce

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the thermal expansion co-efficient of porcelain, thus, incurring danger of a high degree residual stress at the bond[5].

On the other hand, if an oxide layer is lacking or is of insufficient thickness to prevent complete dissolution by the fusing porcelain, the porcelain comes into direct contact with the alloy surface and the adherence is poor[6]. In case of base metal alloys, the excessive formation of oxide is not easily controllable because all the elements in it are oxidizable[7].

The purpose of this study was

1. To study the effect that the temperature changes of oxidation heat treatment has on the shear bond strength between Co-Cr alloy and porcelain.
2. To determine the effect that varying the duration of oxidation heat treatment will have on the shear bond strength between Co-Cr alloy and porcelain.
3. To find out the optimum temperature and duration of oxidation heat treatment at which the Co-Cr alloys can be subjected to before porcelain firing so as to achieve the maximum bonding between porcelain to metal.
4. To find out the temperature and duration of heat treatment that gives the maximum bond strength.

Review of literature

Kautz (1936)[8] mentioned about the oxide layer theory which says that a layer of metal oxide is considered to be tightly bonded both to the metal and to the porcelain, thus forming an intermediate layer responsible for porcelain-metal bond. Their belief that few oxides are sufficiently adhered to their metals to produce excellent porcelain adherence, compelled them to propose 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.

McLean JW and Sced IR (1973b)[9], found out that cobalt-chromium and nickel-chromium based alloys had been pre-oxidized before porcelain application developed stronger bond than those not pre-oxidized under conditions expected to suppress metal oxidation. However, they also showed in their study that the strength of the bond between dental porcelain and base metal alloys containing chromium and nickel is adversely influenced by the formation of chromium and nickel oxide. The study suggested that potassium oxide, sodium oxide and stannous oxide in the porcelain are reduced by chromium in the alloy, and that chromium oxide and also nickel oxide diffuses into porcelain. The modified porcelain then has a reduced coefficient of thermal expansion and a state of residual stress results at the interface, which weakens the adherence.

Wight TA, Bauman JC et al (1977)[10] studied the effect on 4 processing variables on the bond strength of porcelain to a non-precious alloy. They found that the metal preparation (grinding, sandblasting, etc) and degassing temperature variation had little measurable effect on the bond strength. The firing temperature of opaque porcelain however has a profound effect on the bond strength. Increasing the maximum firing temperature from 1790°F to 1840°F for opaque layer caused a doubling of the bond strength values. They also reported that if degassing time was increased, the bond strength appear to decrease. Complete bond between porcelain and non-precious metals were demonstrated when fracture occurred at the interface.

GR Baran (1984)[5] his study was conducted on 5 Ni-Cr alloys in order to identify the compounds formed on the alloy surface during oxidation under conditions similar to those encountered during dental laboratory procedures prior to application of porcelain. Oxides of nearly all elements contained by the alloys were found after low temperature (650°C) oxidation, while NiO and particularly Cr_2O_3 were predominant after oxidation at high temperature 1000°C.

Craig RC (1985)[11] in Restorative Dental Materials has said that oxidation firing time and temperature must be sufficient to produce an adequate oxide layer for bonding. Excessive oxidation results in a non-adherent oxide layer and a poor metal ceramic bond.

Howes VR (1968)[12] found out that pure chromium which forms poorly adherent oxide is responsible for loss of oxide adherence in Cr- containing alloys.

Sced IR and McLean JW (1972)[13] conducted a study to assess the effect of Cr_2O_3 on the opaque porcelain adjoining the metal/porcelain interface. They said that the formation of chromium oxide at the interface poses a doubt for any successful bond between the current base metal alloys and dental porcelain. Chromium oxides reduce the expansion coefficient of dental porcelain to an unacceptably low level. Thus, base metal alloy failure invariably occurs at the metal- porcelain interface.

Mackert JR. Jr, Ringelle RD et al (1988)[7] found out that if an oxide layer is lacking or is of insufficient thickness to prevent complete dissolution by the fusing porcelain, the porcelain comes into direct contact with the alloy surface and the adherence is poor. This situation is observed in the fusion of porcelain to some noble metal alloys where the surface becomes covered with a metallic layer deposited by diffusional creep and no surface oxide is present.

Ihab Adel Hammad, Robert Sheldon Stein et al (1990)[14], in their study have stated the ceramometal bond to be a direct result of oxide formation at the ceramoalloy interface. Sub minimal or excessive oxide formation at the ceramometal interface produces a weaker bond. However, for base metal alloys, the excessive formation of oxides is not easily controllable because all of the elements in the base alloys are oxidizable. The ceramo-metal bond was considered to be direct result of oxide formation at the ceramo-metal interface. Thick oxide layers had less coherent strength than thin oxide layers. Conversely, if the oxide layer was absent, a much weaker Van der Waals bond was produced. They have postulated that the increased bond strength was due to increased wettability of the metal by the porcelain (Van Der Waals adhesion). The increased wettability of the metal in turn increased the mechanical adherence and elevated the shear bond strength. This effect might be caused by an increase in the pyroplasticity of porcelain at the higher temperatures. Alternatively, increased diffusion across the bond might produce oxide intrusion and greater adhesion at the interface.

McLean JW (1983)[15] has said that the problem of base metal alloy is that they readily oxidize. At high temperature, Cr_2O_3 can form in quite thick layers and will produce a weak layer of a dark green oxide. Controlling the thickness of oxide layer is a major problem for the ceramist since it has also been shown that if Cr or Ni are combined in the porcelain, they reduce the thermal expansion of porcelain thus incurring the danger of a high degree of residual stress at the bond. It had also been argued that a lowering of expansion may improve the strength of the bond by inducing greater compressive stresses. It is the authors opinion that the ideal state should be one in which minimal stresses occur at the bond.

Reduction of the firing temperature of the porcelain might reduce the risk of excessive oxide production in Cr- containing alloys.

Materials and methods

Inlay casting wax was used to prepare 80 samples of wax patterns of 6.4mm in diameter and 1.6mm thick[16,17,18]. Sprues were attached to all the 80 samples. They were then invested and then wax burn out was carried out. Casting was done and after it cooled down, the samples were retrieved. Sandblasting was done to further remove the fragments of the investment material attached to the samples. The attached sprues were cut away. After cleaning was done, they were sequentially polished with 220, 320 and 400 grit silicon carbide papers. Eighty samples were randomly categorized into four groups (A, B, C and D) with twenty samples each, to be used in accordance to the temperature variation of 920˚C, 950˚C, 980˚C and 1010˚C. Each group was further subdivided into 4 subgroups, with 5 samples in each, according to the time variation of 3 minutes (Subgroup A^1, B^1, C^1, D^1), 4 minutes (Subgroup A^2, B^2, C^2, D^2), 5 minutes (Subgroup A^3, B^3, C^3, D^3), and 6 minutes (Subgroup A^4, B^4, C^4, D^4).(Table1). All eighty samples were cleaned under running water and dried.

Each group (A, B, C and D) was then subjected to oxidation heat treatment at 920˚C, 950˚C, 980˚C and 1010˚C by varying the time duration of 3, 4, 5 and 6 minutes as shown in Table 1. Following that, single layers of wash opaque, opaque and dentinal porcelain were applied at the center of the 80 samples as per the manufactures instructions so as to obtain the porcelain cylinder of the height of 9.5mm and the diameter of 3.2mm.

All 80 samples were then mounted on acrylic blocks as shown in Fig. 3. They were then subjected to shear bond test in Universal Testing Machine. The zig was made to fall on the metal at the cross head speed of 0.02inch/min (Fig. 3) The maximum load at which the delamination or fracture of porcelain from the metal occurred was noted down for all the eighty samples as shown in Table 2. The delaminated metal discs were examined visually and microscopically with Scanning Electron Microscope to see the level of fracture.

The entire recorded maximum load was then subjected to statistical analysis using Kruskal Wallis Test and Mann-Whitney ‘U’ test.

Observation and results

The statistical analysis showed that the samples subjected to the oxidation heat treatment at 980˚C for duration of 5 minutes exhibited the highest bond strength with the Mean of the Maximum Load value of 414.69640 N. We also observed that the samples fired at 950˚C and 980˚C showed higher bond strength as compared to the samples fired at 920˚C and 1010˚C. It shows that the samples fired for the duration of 4 to 5 minutes showed better strength than the samples fired for the duration of 3 or 6 minutes.

Statistical analysis

For the statistical analysis, **Mean and Standard Deviation** was calculated using the formula as mentioned below.

1. Mean = $\frac{\text{Sum of all the values}}{\text{No. of samples}}$

2. Standard Deviation $= \sqrt{\frac{(x\text{-}x)^z}{n}}$

x = Individual value
x = Mean
n = Number of samples

Kruskal Wallis Test was done to evaluate the results statistically when the comparison was made group wise and subgroup wise. It is a non-parametric test.

The formula used to carry out the test was

$$H=\frac{12}{N(N+1)}\left[\frac{R_1^2}{n_1}+\frac{R_2^2}{n_2}+\frac{R_3^2}{n_3}+\frac{R_4^2}{n_4}\right]-3(N+1)$$

R_1, R_2, R_3 and R_4 are the sum of the ranks of each group.

N= Total number

n_1, n_2, n_3 and n_4 are the sample numbers in each group.

Mann-Whitney 'U' test was done to compare the results statistically each group wise and sub-group wise. The formula used was:

$$Z=\frac{U\text{-}E(U)}{\sigma_U}$$

$$U1=n_1n_2+\frac{n_1(n_1+1)}{2}\text{-}R_2$$

$$U2=n_1n_2+\frac{n_1(n_1+1)}{2}\text{-}R_2$$

$$E(U)=\frac{n_1n_2}{2},\sigma_U=\sqrt{\frac{n_1n_2(n_1+n_2+1)}{12}}$$

Where, U = minute (U_1, U2)

n_1, n_2, n_3 and n_4 are the sample numbers in each group.

Table 1: Grouping and sub grouping of specimen

GROUPS TEMPERATURE	SUBGROUPS 3mins	SUBGROUPS 4mins	SUBGROUPS 5mins	SUBGROUPS 6mins
A 920˚C	A^1	A^2	A^3	A^4
B 950˚C	B^1	B^2	B^3	B^4
C 980˚C	C^1	C^2	C^3	C^4
D 1010˚C	D^1	D^2	D^3	D^4

Table 2: The Shear Bond Strength of Porcelain Fused to Metal Couple for each specimen.

A	A1 Max-Load N 304.656 215.703 158.828 252.203 335.078	A2 Max-Load N 392.750 149.781 185.531 113.968 256.078	A3 Max-Load N 296.281 285.187 302.031 284.546 228.937	A4 Max-Load N 321.625 279.796 340.750 242.968 315.515
B	B1 Max-Load N 249.671 207.734 389.234 308.546 395.375	B2 Max-Load N 119.562 242.234 222.703 63.1718 196.312	B3 Max-Load N 259.406 385.718 410.062 161.062 423.921	B4 Max-Load N 293.562 284.703 374.843 276.421 314.281
C	C1`Max-Load N 373.421 399.140 318.015 391.250 423.296	C2 Max-Load N 316.156 321.062 275.875 517.406 400.671	C3 Max-Load N **408.187** **443.796** **475.437** **370.625** **375.437**	C4 Max-Load N 279.078 262.640 314.390 199.453 276.328
D	D1`Max-Load N 201.812 225.468 344.859 511.062 236.703	D2 Max-Load N 326.640 246.312 277.078 262.359 311.656	D3 Max-Load N 186.234 270.171 291.906 266.171 317.609	D4 Max-Load N 317.156 281.515 276.500 286.843 255.718`

Table 3: The level of fracture as seen in the SEM study

Group (Temperature in˚C)	Sub-Group (Time in mins)	No of samples with cohesive failure within porcelain	No of samples with partial delamination of porcelain from metal
A(920˚C)	A_1 3	2	3
	A_2 4	1	4
	A_3 5	4	1
	A_4 6	4	1
B(950˚C)	B_1 3	3	2
	B_2 4	0	5
	B_3 5	3	2
	B_4 6	5	0
C(980˚C)	C_1 3	5	0
	C_2 4	5	0
	C_3 5	5	0
	C_4 6	3	2
D(1010˚C)	D_1 3	2	3
	D_2 4	2	3
	D_3 5	2	3
	D_4 6	4	1

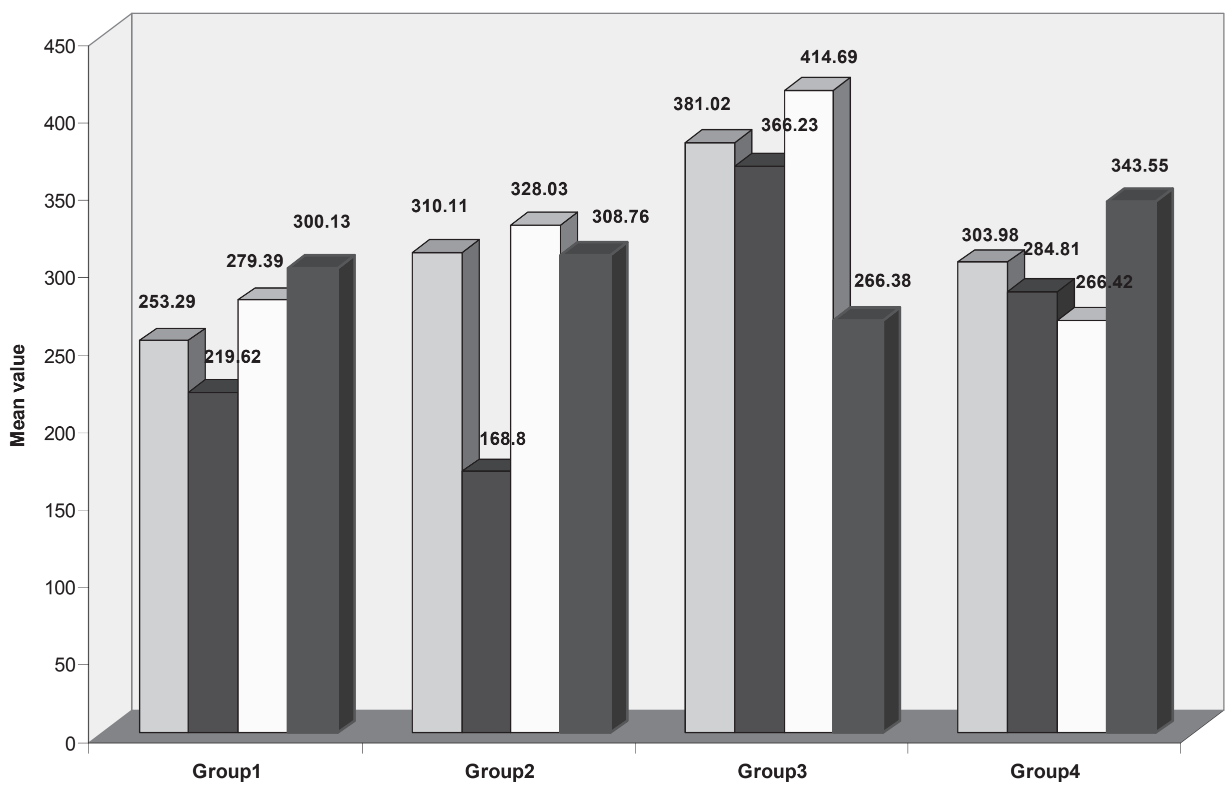

Fig. 1: Comparison of Maximum Load among four groups

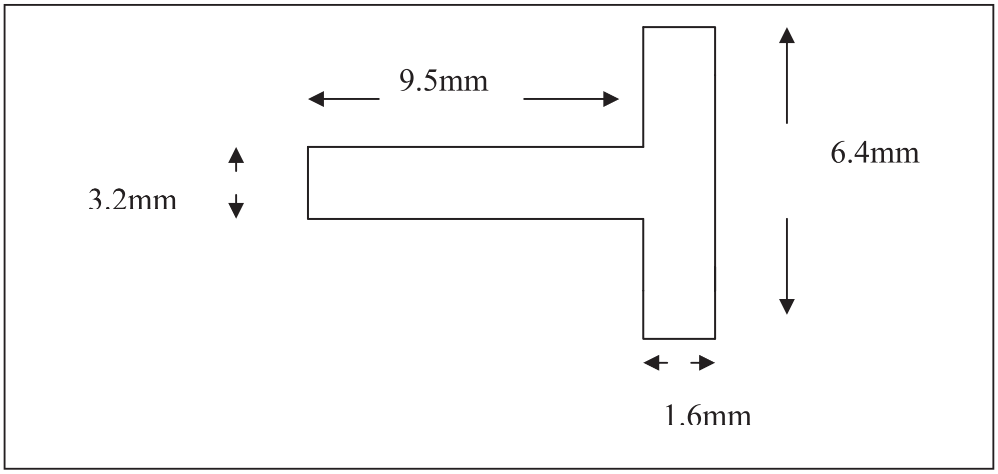

Fig. 2: Diagrammatic representation of the porcelain fused to metal couple

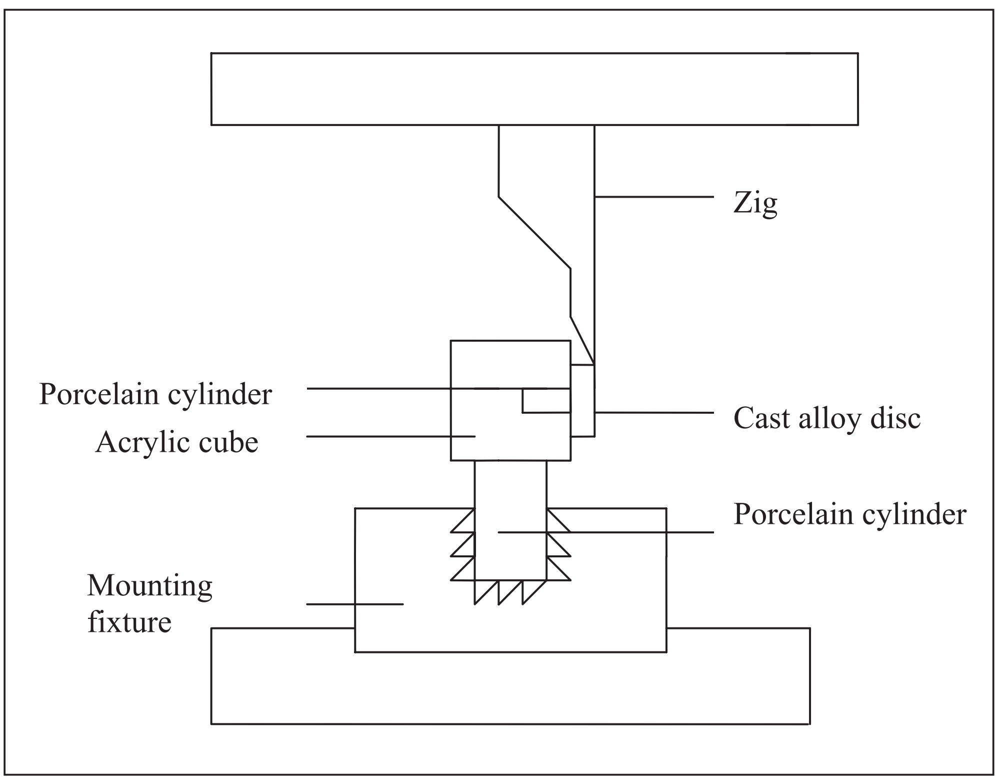

Fig. 3: Diagrammatic representation of the application of shear load on porcelain-metal couple

Discussion

The longevity of metal ceramic restoration relies on the formation of a strong bond between metal and ceramic, which can withstand forces common in the mouth.

The objective of the present study was to determine the effect of variation in temperature and duration of oxidation on the bond strength of porcelain to Co-Cr alloy. Subjecting the Co-Cr alloy to oxidation heat treatment at high temperature for a longer duration of time may produce thick oxide layer which may affect its bond with porcelain. Oxidation firing done at high temperatures may produce excessive thickness of oxide layer whereas firing done at low temperatures may produce too thin oxide layer which may cause weak bond. The level of fracture between porcelain and Co-Cr alloy determines the type of failure. If the fracture occurs in porcelain, it is the type of cohesive failure which means to say that the bond was good.[3, 6] Whereas, if the fracture occurs in the oxide layer, it means that it is adhesive type of failure and that the bond is weak. [3, 6] We can correlate the level of fracture to the variation in temperature and duration of oxidation heat treatment and find out the optimum temperature and duration of oxidation heat treatment at which the bond can withstand maximum load.

In this study, a total number of eighty metal discs were subjected to oxidation heat treatment at the temperatures 920˚C, 950˚C, 980˚C and 1010˚C for the duration of 3 minutes, 4minutes, 5 minutes and 6 minutes. Porcelain firing was carried out carefully on the oxidized metal discs following the manufacturers' instructions. The results of the present study showed that the samples fired at 980˚C for 5 minutes showed the maximum bond strength of 414.69640N. The samples fired at 980˚C showed significantly better bond strength when fired for the duration of 3 minutes, 4 minutes and 5 minutes. The Mean of the bond strength obtained when subjected to oxidation firing for the duration of 3, 4, and 5 minutes were 381.02440 N, 366.23400 N and 414.69640 N respectively. However when it was fired for duration of 6 minutes, the maximum load that it could withstand was much less (266.37780 N). The study also revealed that the samples fired at 950˚C by varying duration showed the bond strength that were comparable to the samples fired at 980˚C. These results were of significance according to the statistical analysis. K. Asgar and Z.Giday in their study have shown that the bond strength were about 279.2 N (34.9 MPa) for push and 335.2 N (41.9 MPa) for pull shear tests.[19] Meyer JM et al, had shown in their research that the tensile strength of the metal-ceramic bond should exceed 224N (28 MPa) to have cohesive failure at the interface.[20] Johnston WM and O'Brien have said that measurement of shear strength of dental porcelain allows a similar prediliction for the minimum interfacial shear strength required for cohesive shear failure through the ceramic[21]. Earlier studies have shown that cohesive failure within the porcelain occurred at 120 N to 312 N (15 to 39 MPa), whereas bond strengths measured in shear ranged from 440 N to 824 N (55 to 103 MPa)[3].

In our study, the bond strength obtained by firing the samples at 920˚C and 1010˚C were relatively lower when compared to the samples fired at 950˚C and 980˚C. The statistical analysis showed that the results were less significant when the samples were fired at 920˚C and 1010˚C for the duration of 3, 4, 5 and 6 minutes.

The oxide layer between the metal and ceramic should have an optimum thickness for a strong metal-ceramic bond.[3] Sub minimal or excessive oxide formation at the ceramo-metal interface produces a weaker bond.[8] If an oxide layer is lacking or is of insufficient thickness to prevent complete dissolution by the fusing porcelain, the porcelain comes into direct contact with the alloy surface and the adherence is poor. Thick oxide layers are less coherent than thin oxide layers.[22] Particular care is required with the base metal casting alloys to avoid excessively thick oxide layers. However, if the oxide layer was absent, a much weaker Van Der Waals bond was produced.[14] It has been shown that in titanium and Ti-6Al-4V the 750˚C oxidation treatments produced oxide films too thin to be visualized in the SEM, whereas the 1000˚C oxidation treatments produced oxide films approximately 1 micron thick. In that study, the oxide adherence of the specimens oxidized at 750˚C was good, but those oxidized at 1000˚C exhibited significantly lower oxide adherence.[2]

Ni_2O and Cr_2O_3 were predominant after oxidation at high temperature 1000˚C.[5, 3, 6, 23] Excessive oxidation results in a non-adherent oxide layer and a poor metal ceramic bond. In non-precious alloys, metal oxides such as NiO and Cr_2O_3 or more complex forms such as TiO- Cr_2O_3 may play a prominent role in controlling ceramic-metal adherence[2]. At high temperature, Cr_2O_3 can form quite thick layers and will produce a weak layer of a dark green oxide.[5, 3, 6] The strength of the bond between dental porcelain and base metal alloys containing chromium and nickel is adversely influenced by the formation of chromium and nickel oxide[3,4,6,15,24]. McLean and Sced in their study suggested that potassium oxide, sodium oxide and stannous oxide in the porcelain are reduced by chromium in the alloy, and that chromium oxide and also nickel oxide diffuses in to porcelain. The modified porcelain then has a reduced coefficient of thermal expansion and a state of residual stress results at the interface, which weakens the adherence[15]. Excessive oxidation of the metal may diminish bond strength by interposing a layer of oxide so thick that fracture may proceed easily through it. In addition, the thermal expansion of oxide may be substantially different from the metal and its matching porcelain. As a result, differential stresses are generated upon heating & cooling that lead to interfacial fracture. The linear coefficients of thermal expansion for the metal and ceramic must closely match to achieve a strong interfacial bond. The slightly higher co-efficient for the metal causes the ceramic to be in a beneficial state of residual compressive stress at room temperature. Porcelain is much stronger in compression than tension, and residual tensile stress in the porcelain must be avoided to prevent fracture of the restoration[3].

The delaminated samples were then examined through scanning electron microscope to find out the level of fracture.

The SEM micrograph of the fractured specimen fired at 980˚C and 950˚C showed the cohesive type of failure in porcelain with a large portion of porcelain retained on to the surface of the metal. Cohesive type of failure suggests better bond between the metal and porcelain than adhesive type of failure wherein the fracture occurs either in the oxide layer or at oxide porcelain interface or at metal oxide interface. According to O'Brien, Cohesive Plateau Theory suggests that oxide adherence strength in excess of the cohesive strength of dental porcelain would be adequate for porcelain bonding.[3, 6]

The SEM micrograph of the fractured specimen samples fired at 1010˚C showed a type of adhesive failure in which porcelain is completely or partially delaminated from the metal surface. This may be the interfacial fracture at Metal-Metal oxide interface or Metal Oxide-Metal Oxide interface. Metal-Metal oxide interfacial fracture is seen due to over production of chromium and nickel oxide at the interface. Metal Oxide-Metal Oxide interfacial fracture is seen due to over-production of oxide causing sandwich effect between metal and porcelain. [3, 6]

Similarly the samples fired at 920˚C also showed weaker bond strength. The SEM Micrograph showed interfacial fracture wherein there was a slight amount of porcelain retained on the metal surface. This may be Metal-Porcelain type of interfacial fracture wherein it is generally seen that the metal surface is totally depleted of oxide prior to baking the porcelain or no oxides are available. [3, 6] Poor metal oxide adherence on Co-Cr and Ni-Cr alloys can lead to oxide 'wrinkling' and create a poor porcelain bond as a result of delamination of the metal oxide and porcelain from the underlying metal.[25]

Conclusion

The conclusion arrived at from the study may be enumerated as follows:

1. Samples subjected to oxidation heat treatment at 980˚C and 950˚C showed significantly good shear bond strength between porcelain to metal.
2. Samples subjected to oxidation firing for the duration of 4 and 5 minutes showed significant high bond strength than the samples fired for the duration of 3 and 6 minutes.
3. Maximum shear bond strength between porcelain to metal was observed when the samples were subjected to oxidation firing at 980˚C for the duration of 5 minutes.
4. Samples subjected to oxidation heat treatment at 980˚C for 3minutes, 4 minutes and 5 minutes showed cohesive failure within porcelain.

From this invitro study, cohesive failure within porcelain suggests sufficient bond between porcelain and metal. Often clinical interpretation of individual properties is difficult. It is usually a combination of properties that determine clinical performance.

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