The Adhesion Mechanism of Dental Adhesive Resin to the Alloy — Adhesive Ability of Dental Adhesive Resin to the Cleaned Metal Surface Obtained by Hydrogen Gas Reduction Method —

Hiroki OHNO, Yoshima ARAKI, Kazuhiko ENDO and Isao KAWASHIMA

Department of Dental Materials Science, School of Dentistry, Higashi-Nippon-Gakuen University,
Ishikari-Tobetsu, Hokkaido, Japan

Received on December 15, 1988

Accepted on March 16, 1989

With the cleaned metal surface without passive film or an oxide layer, chromium, cobalt, and iron show excellent bonding strength, indicating values similar to 18-8 stainless steel. Therefore the existence of a passive film and oxide layer at the interface metal/resin is not essential for metal-resin bonding. The adhesive ability decreases in the order :
 $Cr \approx Co \approx Fe > Cu > Ag > Au \approx Ni > Pt > Pd$.

Key words : Adhesive resin, Adhesive ability, Cleaned metal surface

INTRODUCTION

Studies on adhesion between metals and a dental adhesive resin containing 4-META have shown that : the adhesive ability of resin to the as-polished surface of Co-Cr alloy, which is covered with a passive film, is superior to that of the alloy surface oxidized at high temperatures¹⁾. For passive films formed on the as-polished surface, the adhesive ability of the Ni-Cr alloy is inferior to that of the Co-Cr alloy²⁻⁴⁾. This shows that the adhesive ability of the resin is greatly affected by the surface state of the alloys.

The state of a metal surface varies by metal type and surface treatments. On base metals, different amounts and kinds of oxides form on the metal surface. On noble metals which do not form oxides, the metal surface adsorbs gas and water molecules to decrease surface energy, and the adsorbed species and amounts vary by the kind of metal. Since the oxides and adsorbed gas layers are between the adhesive and the metal substrate, it is critical to understand the roles of the adsorbed layer, oxides, and passive film on the adhesion.

In the present study, the adhesion of a dental adhesive resin to cleaned metal surfaces was investigated on nine pure metals and on 18-8 stainless steel. The cleaned metal surfaces were obtained by heating the metal specimens in flowing hydrogen gas. As the cleaned metal surfaces adsorb oxygen and water molecules when the surface is exposed to air, adhesion procedures were performed in a polyethylene chamber filled with ultra-high purity argon gas without oxygen, water or other contaminating species.

MATERIALS AND METHODS

Materials

The pure metals and the alloy studied were gold, platinum, palladium, silver, copper,

nickel, cobalt, iron, and chromium of a purity better than 99.99% and 18-8 stainless steel. The pure metal specimens (except for chromium) were made by soldering pure metal chips to 18-8 stainless steel rod for the tensile test as shown in Fig. 1. The chromium specimen was made by electro-plating chromium on a mild steel rod of the same size as the 18-8 stainless steel rod. Both the rod specimens and 18-8 stainless steel circular brock (Fig. 1) were metallographically polished to eliminate mechanical factors affecting the bonding strength.

The dental adhesive resin was 4-META/MMA-TBB resin*. The monomer and polymer of the adhesive resin were dried to eliminate trace amounts of water: the monomer was dehydrated by a drying agent, well-dried anhydrous magnesium sulfate. The polymer was dried in a drying furnace at 70°C for 60 min and then stored in a silica gel desiccator.

Hydrogen Gas Reduction Method

Figure 2 shows the apparatus for hydrogen gas reduction used to obtain the cleaned metal surface: the pipes were stainless steel except for the reduction tube which was made of silica glass. The silica glass tube was narrowed in several places to prevent movement of

Fig. 1 Tensile test piece for bonding strength measurements. The pure metal chip was soldered at the end of 18-8 stainless steel rod. The U-shaped piece was applied to the groove in the rod for the testing.

* Super-Bond C & B, SUN MEDICAL Co., Ltd., Kyoto, Japan

Fig. 2 Apparatus for hydrogen gas reduction : H₂ the hydrogen gas cylinder ; OX the U-shaped tube including oxygen removal agent, Oxyout ; DP the oil diffusion pump.

Table 1 Values of the Gibbs energy change and partial pressure ratio of H₂O to H₂ at different temperatures.

°C	K	$\Delta G_T(\text{cal})$	$(P_{\text{H}_2\text{O}}/P_{\text{H}_2})_{\text{eq}}$
800	1073	84,839	1.7×10^{-6}
900	1173	83,530	6.5×10^{-6}
1000	1273	82,270	2.0×10^{-5}

the specimens and to facilitate sealing of the specimen. Preparatory evacuation was done by an oil rotary pump and a diffusion pump up to 1×10^{-6} Torr. The stainless steel pipes and silica glass tube were baked by a gas burner under evacuation to eliminate oxygen and water molecules adsorbed on the inner surface of the pipes.

With deoxidizing oxides of metals having a strong chemical affinity for oxygen, ultra-high purity hydrogen gas is necessary because traces of water and oxygen molecules pollute the metal surface⁷⁾. For example, a stream of extremely dry hydrogen gas is necessary to reduce the Cr-oxide, Cr₂O₃, to metallic chromium by equation (1) : The partial pressure ratio of water to hydrogen is as in equation (2) in terms of the standard Gibbs energy change of reaction (1). Table 1 shows the values of the Gibbs energy change and the partial pressure ratio at 800°C, 900°C, and 1000°C.

$$\frac{1}{3} \Delta G_T^\circ = -4.574T \log\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{eq} \dots\dots\dots(2)$$

The reduction has to be carried out in flowing hydrogen, containing less than $6.5 \times 10^{-4}\%$ water at 900°C.

The hydrogen gas used to deoxidize the metal surface was ultra-high purity gas, purity better than 99.99999% ; oxygen below 0.2 ppm ; dew point -70°C (ca. 0.0003%). A U-shaped tube including an oxygen removal agent[†] was attached between the hydrogen gas cylinder and the silica glass reduction tube and maintained the oxygen content below 0.05 ppm. The metal specimen in the silica glass tube was heated by an electric furnace from the outside of the tube under a hydrogen gas flow of 100 ml/min. Deoxidation of the metal specimen for adhesion was confirmed visually by the color change of the oxidized chips of metal, oxidized by pre-heating in air and then placed in the silica glass tube with the metal specimen. Heating time was 5 min and the heating temperatures for the reduction were 900°C for the chromium, iron, cobalt, and 18-8 stainless steel, 700°C for the copper and nickel, and 500°C for the gold, platinum, palladium, and silver. The silica glass tube was evacuated to 1×10^{-6} Torr after the reduction treatment and then melted and cut by a gas burner at the narrow parts to enclose the deoxidized metal specimen.

Adhesion Procedures

Adhesion procedures were performed in a polyethylene chamber⁷⁾ with glove filled with ultra-high purity argon gas (purity 99.999% ; oxygen content below 0.2 ppm ; dew point below -70°C). The silica glass tube was broken to obtain the deoxidized metal specimen in the polyethylene chamber.

Before adhesion, the monomer must be in contact with oxygen to produce TBB peroxide immediately after the addition of TBB to the monomer. Therefore the monomer preparation was performed in a chamber with ultra-dried air (dew point below -60°C) and using a dried dish and spatula to avoid contamination with water vapor during mixing. After mixing for 40 sec, the monomer dish was immediately transferred to the polyethylene chamber where the argon gas pressure was raised so as not to introduce air. In the previous paper¹⁾, the adhesive resin layer was maintained at 50 μm by first placing the specimen in contact with the circular block and next removing it to apply the resin. In this study the thickness of the resin layer could not be kept constant, because touching the cleaned metal surface to the circular block would contaminate it with the water molecules adsorbed on the surface of the circular block.

Evaluation of Adhesive Ability

The bonded specimens were stored at 37°C in a dry chamber for 24 hr after the adhesion procedure. Before testing, the specimens were thermocycled 20 times, 1 min in a water bath at 40°C followed by 1 min in liquid nitrogen (-196°C).

The tensile test for the bonding strength measurement was performed on a testing machine[§] with a cross-head speed of 2 mm/min, after inserting a U-shaped piece in the groove of the stainless steel rod (Fig. 1) and placing the test piece in the jig for the tensile test.

Thermal stress induced by thermal cycles reach maximum at the periphery and zero at

[†] Oxyout, Ohsaka Sanso Co., Ltd., Ohsaka, Japan

[§] Auto-Graph IS-5000, Shimadzu Co., Kyoto, Japan

the center of adhesion⁸⁾. When chemical bonding between the metal surface and the adhesive resin is weak, cracks at the resin/metal interface propagate from the periphery to a point where the thermal stress balances with the adhesive force. The relationship between the bonding strength (kgf/cm^2), Y , and the area fraction (interface failure ratio, %), X , of the interface failure at the periphery of the adhesion is represented by equation (3) :

$$Y = -6X + 435 \quad \dots\dots\dots(3)$$

On the basis of this relation, the bonding strength can also be obtained by measuring the interface failure ratio. The values obtained by equation (3) are close to the mean value obtained by measuring many specimens, and this offers an advantage in obtaining the mean value of the bonding strength of a small number of specimens as in the present study. The following discussion regards the adhesion both with the bonding strength obtained by this method and that measured in the tensile tests.

RESULTS AND DISCUSSION

Trace amounts of hydrogen gas remain on the metal surface though the hydrogen gas was evacuated to 10^{-6} Torr after the reduction procedure. Copper, gold, and silver do not adsorb hydrogen gas, however, chromium, iron, nickel, cobalt, platinum, and palladium do⁵⁾. The cleanliness of the metal surface was not evaluated in this study. The study examined the adhesive ability of the adhesive resin to the metal surfaces without passive and oxide films, and did not evaluate the effect of adsorbed hydrogen gas in the metal surface.

Figure 3 shows the measured bonding strengths with the failure types after the thermal

Fig. 3 Measured bonding strengths with the failure types after thermal cycles: The notation ● shows a failure in the resin (cohesive failure); ◐ a cohesive failure and interface failure on the alloy surface at the periphery; ○ total interface failure.

Table 2 Averages of the measured and calculated bonding strengths with interface failure ratios.

Metals	Bonding Strength (measured) (kgf/cm ²)	Interface Failure Ratio (%)	Bonding Strength (calculated) (kgf/cm ²)
18-8 Stainless Steel	397	0	435
Cr	365	0	435
Co	340	0	435
Fe	404	0	435
Cu	414	2	423
Ag	324	5	403
Au	299	7	357
Ni	315	25	285
Pt	171	49	141
Pd	60	86	0

cycles. The interface failure at the metal/resin appears in the case of poor adhesive ability. On platinum and palladium, bonding strength zero, total interface failure, shows separation during the thermal cycles.

There is a wide scattering of bonding strengths with 18-8 stainless steel, chromium, iron, and cobalt and all show cohesive failure in the resin. The bonding strength is strongly affected by factors such as thickness of the resin layer, inclusion of air in the resin, and variations in the monomer-polymer ratio. However, the adhesive ability at the metal/resin interface is superior to the cohesion of the resin when the fracture is a cohesive failure, even though the bonding strength is low. Since the appearance of the fracture rather than the bonding strength reflects the characteristics of the metal surface, the type of failure is important in evaluating the adhesive ability.

Table 2 shows the averages of the measured bonding strength, interface failure ratio to the adhesion area, and the bonding strength calculated from the ratio based on equation (3). For the base metals, iron, chromium, and cobalt show excellent bonding strength, indicating values similar to 18-8 stainless steel. It has been shown that a passive film on chromium containing alloys is effective in obtaining good bonding strength with dental adhesive resin⁹⁾. However, the present study shows that excellent bonding strength was obtained on the cleaned surface without a passive film. Therefore the existence of a passive film and oxide layer at the alloy/resin interface is not essential for the alloy-resin bonding.

Adhesion with nickel exhibits the poorest adhesive ability of the base metals as all failures were interface failures at the periphery of the adhesion. Of the precious metals, the adhesive ability for palladium and platinum was inferior to silver and gold.

The adhesive ability of the 4-META/MMA-TBB resin to the cleaned surfaces obtained

by the hydrogen gas reduction method decreases in the following order on the base of both the measured bonding strength and that calculated from the interface fracture ratio : $\text{Cr} \approx \text{Co} \approx \text{Fe} > \text{Cu} > \text{Ag} > \text{Au} \approx \text{Ni} > \text{Pt} > \text{Pd}$. Platinum and palladium have the poorest adhesive ability. The best adhesive ability is with chromium, cobalt, and iron, that with 18-8 stainless steel corresponds to chromium.

Mogi has reported¹⁰⁾ no adhesive ability of pure gold with 4-META/MMA-TBB resin. The bonding strengths to Cr, Ni, and Co were in order $\text{Cr} > \text{Ni} \gg \text{Co}$, different from the present study. Mogi has investigated the adhesive ability of pure metal surfaces exposed to air after metallographic polishing. Since small amounts of water molecules adsorbed on the alloy surface cause deterioration of the adhesive ability between the resin and alloy⁷⁾, the differences may be a result of characteristic differences in the adsorption ability of water molecules and other gas molecules on the metals and/or on the chemical affinity of oxygen to the metals.

CONCLUSION

The adhesive ability of resin (4-META/MMA-TBB) to cleaned metal surfaces without adsorbed, oxide, or passive film was investigated to explain both the role of passive or oxide films on the adhesion mechanism and the relation between the kind of metal and the adhesive ability. The cleaned metal surface was obtained by the hydrogen gas reduction method.

Excellent adhesive ability was obtained on chromium, cobalt, iron, and 18-8 stainless steel, showing that a passive or oxide film on the metals does not play an essential role in the adhesion. Nickel shows the poorest adhesive ability of the base metals investigated in this study. The adhesive ability of platinum and palladium is not as good as gold. The adhesive ability decreases in the order : $\text{Cr} \approx \text{Co} \approx \text{Fe} > \text{Cu} > \text{Ag} > \text{Au} \approx \text{Ni} > \text{Pt} > \text{Pd}$.

REFERENCES

- 1) Ohno, H., Araki, Y. and Sagara, M. : The adhesion mechanism of dental adhesive resin to the alloy — Relationship between Co-Cr alloy surface structure analyzed by ESCA and bonding strength of adhesive resin —, *Dent Mater J* 5(1) : 46-65, 1986.
- 2) Tanaka, T., Fujiyama, E., Shimizu, H. and Atsuta, M. : Study on surface treatment of non-precious alloys for adhesion bridge, *J Japan Prosthodont Soc* 27(4) : 706-712, 1983. (in Japanese)
- 3) Takeyama, M., Kashibuchi, S., Nakabayashi, N. and Masuhara, E. : Studies on dental self-curing resins, (Part 17) Adhesion of PMMA with bovine enamel or dental alloys, *J Japan Soc Dent Appar Mat* 19(47) : 179-185, 1978. (in Japanese)
- 4) Ohno, H., Araki, Y., Endo, K., Kawashima, I., Yamane, Y. and Sagara, M. : Adhesive ability of a dental adhesive resin (4-META/MMA-TBB) to as-polished, HNO_3 treated, and oxidized surfaces of the Ni-Cr alloy, *Higashi Nippon Dent J* 6(2) : 1-12, 1987.
- 5) Ohno, H., Araki, Y., Sagara, M. and Yamane, Y. : The adhesion mechanism of dental adhesive resin to the alloy — Experimental evidence of the deterioration of bonding ability due to adsorbed water on the oxide layer —, *Dent Mater J* 5(2) : 211-216, 1986.
- 6) Onchi, K. : Chemistry of metal surface, *Japan Institute of Metals*, Sendai, 1971, pp. 12-15 (in Japanese)
- 7) Keii, Y. : Adsorption, *Kyoritu Syuppan Ltd.*, Tokyo, 1965, pp. 11-61. (in Japanese)
- 8) Kubaschewski, O. and Alcock, C. B. : Metallurgical thermochemistry (5th ed.), *Pergamon Press Ltd.*, Oxford, 1979, p. 25.
- 9) Tanaka, T., Nagata, K., Nakabayashi, N. and Masuhara, E. : Application of 4-META on adhesive

opaque resin (Part 2) Improvement of adhesive stability, *J Japan Soc Dent Appar Mat* **20** (52): 221-227, 1979, (in Japanese)

- 10) Mogi, T.: Studies on adhesion of methacrylic resin to cobalt-chromium alloy for denture base — Effects of 4-metacryloxyethyl trimellitate anhydride monomer —, *J Japan Prosthodont Soc* **23**(4): 660-676, 1979. (in Japanese)

本号掲載論文の和文抄録

接着性レジンと合金の接着機構の解明に関する研究 —— 水素ガス還元法で得た金属清浄化表面に対する接着性レジンの接着性 ——

大野弘機, 荒木吉馬, 遠藤一彦, 川島 功

東日本学園大学歯学部歯科理工学講座

接着性レジン (4-META/MMA-TBB) と合金の接着機構における合金表面の酸化膜, 不動態被膜の役割を解明するために, さらに, これらの被膜の存在しない金属そのものに対する接着性レジンの接着性を調べるために, 水素ガス還元法で得た金属の清浄化表面に対する接着性を検討した。

その結果, 酸化膜や不動態被膜が存在しなくても接着性レジンに金属に接着し, これらの被膜は両者の接着機構に本質的な役割を果たすものではないことが明らかになった。引張試験で求めた接着強さにおいて, 卑金属で

は, 優れた接着性は Cr, Co, Fe で得られ, 破断面はすべての試験片でレジン内での凝集破壊を呈していた。Ni は卑金属中で接着性が一番劣っており, 破断面は接着部の周辺で界面破壊を, 中心部で凝集破壊を示した。貴金属では Ag と Au が比較的良好な接着性を示すが, Pt と Pd は熱サイクル中に全面に界面破壊を起す場合があり, 実験に使用した金属中で一番接着性が悪かった。金属の種類による接着性は次の順で悪くなった。

$\text{Cr} \approx \text{Co} \approx \text{Fe} > \text{Cu} > \text{Ag} > \text{Au} \approx \text{Ni} > \text{Pt} > \text{Pd}$

歯科用陶材中の残留応力と冷却速度との関係

浅岡憲三*, John A. Tesk**

*徳島大学歯学部歯科理工学講座

**Dental and Medical Materials, National Institute of Standards and Technology

陶材焼成時の冷却過程をコンピュータ・シミュレーションにより解析し, 陶材中に残留応力が発生するメカニズムを明かにした。即ち, 温度依存の弾性係数, 熱膨張係数, 粘性係数と冷却速度依存のガラス転移温度, 材料内温度分布を考慮したプログラムを作製し, 材料内の応力, ひずみの経時的変化を粘弾性問題として計算した。シミュレーションの結果は風冷強化ガラスに対する実験結果と良く一致した。そして, 陶材中の残留応力, σ , が

板厚, $2t$, と冷却速度, q , の関数として次式で表されることが示され, 市販焼付用陶材に対して定数を求めた。

$\sigma = k t^n Q^n$ ここで, k , n は定数, $Q = q/q_0$, q_0 は参照冷却速度。風冷強化により陶材が強化されるために必要な陶材の物理的性質をシミュレーションの結果から議論した。金属焼付陶材補綴物中の残留応力の計算に, ここで用いた方法が適用できることが示唆された。