SURFACE DEGRADATION OF GALLIUM-ALLOYS DURING TOOTH BRUSHING IN VITRO

Seok-Hyung Lee

Samsung Medical Center, College of Medicine, Sungkyunkwan University

When the exposure surface of restoration is brushed with various toothpaste in the mouth, wear or undesirable surface deposit of restoration can occur. Surface change of gallium alloys according to brushing and toothpaste may directly affect oral hygiene. The aim of this study was to evaluate the surface alterations of Gallium alloys during tooth brushing with different prophylactic agents. Two gallium-alloys and an amalgam as a control were investigated. Without and with brushing were applied with three kinds of prophylactic agents on the sample for 0, 1, 5, 10, 60 and 360 minutes. At each time interval, surface roughness was recorded by a profilometer and some pictures were taken by a SEM. All results were analyzed by the one-way ANOVA, followed by Tukey multiple comparisons and the simple linear regression analysis. The results indicate that gallium alloys are more susceptible to surface degradation during tooth brushing than amalgam with respect to the specific prophylactic agent used.

Key words: Gallium alloy, surface degradation, surface alteration, prophylactic agent

Ⅰ. INTRODUCTION

Direct filling materials have many advantages such as easy handling, low cost, fast treatment and so on. Dental amalgam as a direct filling material satisfied these conditions. Dental amalgam has provided valuable and comparatively inexpensive service to patients for nearly two centuries. Despite the contribution of dental amalgam for a long period of time, amalgam has a bad reputation due to some disadvantages such as released mercury, bad color, toxicity and so on. Therefore, new direct filling materials have been developed. Gallium alloy as a direct filling material is one of the developed restorative materials. Treatment procedure and color of gallium alloy are similar to those of amalgam. However, gallium alloy does not use mercury. A gallium-alloy has been marketed as a direct replacement for amalgam.

Some studies about gallium alloys reported that corrosion resistance of gallium alloy was inferior to that of high-copper amalgam[1]. Kaga et al[2] clinically found corrosion of gallium alloy restoration in primary teeth. Gallium alloy showed severe inflammatory response in the subcutaneous tissue of rats[3,4,5].

Clinical researchers detected notable discoloration, surface roughness and a partial destruction of marginal integrity in the gallium restoration[6,7,8,9,10].
Dilley et al[11] described the advantages of composite restoration as a direct restoration for amalgam which are long chair time and technical sensitivity.

Some clinical studies[8,12] have demonstrated that the Gallium Alloy GF Ⅱ was suitable for clinical use.
For suitable clinical use of gallium alloy, one of the most important properties is the ability to withstand wear. Undesirable surface deposits, rough surface and wear of gallium alloy may directly affect oral hygiene, secondary caries and pathological condition. This study

was conducted to determine how gallium alloys and amalgam are affected by tooth brushing with various toothpastes. Commercial electric brushing machine was used to simulate the wear procedure occurring in the mouth. The influence of brushing on gallium alloys and amalgam were evaluated with surface roughness analyzer (profilometer) and scanning electron microscope (SEM).

The aim of this investigation was to evaluate the surface changes of two gallium alloys and an amalgam during tooth brushing with different prophylactic agents.

Ⅱ. MATERIALS AND METHOD

The materials used in this study included a gallium alloy (Gallium Alloy GF II®, Tokuriki Honten Co., Japan), a gallium alloy (Galloy® SDI) and an amalgam (Amalcap Plus®, Vivadent) as a control.

The 42 samples (∅ 8 mm) were made in the same condition from three kinds of materials (14 samples of each material). Three prophylactic agents (Elmex fluid, Elmex gelee and Meridol: Wybert GmbH, Lörrach, Germany) were used. They contained some kinds of fluorides. The Meridol has aminofluoride / tinfluoride of 1400 ppm. The Elmex fluid has aminofluoride of 13.26 g out of 100 g. The Elmex gel contains aminofluoride of 3.314 g and natriumfluoride of 2.210 g in 100g (Table 1). These prophylactic agents were diluted 1 : 10 with distilled water. Thus, seven abrasives (three prophylactic agents, diluted agents of the three prophylactic agents and distilled water) were prepared. The 42 samples were embedded in modeling resin and the exposure surface of the samples was polished after the setting of resin. The polishing was performed under running water from Sic - 100, 320, 600, 1200, 2500 until 4000 of sandpaper in the polishing machine (Jean Wirtz TG 200, Duesseldorf, Germany). Thereafter, the surface roughness of all samples was measured by a profilometer (S6P, Perthen, Hannover, Germany) and a SEM (Stereoscan 250, Cambridge, UK) before brushing or dental paste application. Every 14 samples from each material were divided into two groups. Seven samples of one group underwent brushing (Plaque control indicator brush head®, Braun AG, Frankfurt/Main, Germany) with the seven prophylactic agents, seven samples of the other group underwent only application of the seven prophylactic agents without brushing. The group that underwent brushing with the prophylactic agents and the group that only received application of the prophylactic agents were performed in time intervals of 0, 1, 5, 10, 60 and 360 minutes. After every application in time intervals, the roughness of the samples was measured by a profilometer and a SEM. Table 2 shows the composition of the Gallium alloy GF II.

Ⅲ. RESULTS

All 42 specimens were tested and the results were recorded. The mean values are described in Fig. 1. To analyze these data, the SPSS statistical analysis package was used (version 7.5, SPSS Inc., Chicago,

Table 1. Fluoride composition of the prophylactic agents (from manufacture's literature)

Prophylactic agents	Weight (g/100g)	Fluorides
Elmex gel	3.314 g	Aminofluoride
	2.210 g	Natriumfluoride
Elmex fluid	13.26 g	Aminofluoride
Meridol	1400 ppm	Aminofluoride/Tinfluoride

Table 2. The composition of the Gallium Alloy GF II. Powder and liquid ratio ; 1 : 0.5 ± 0.05 (from manufacturer's literature)

Powder	Weight (%)	Liquid	Weight (%)
Ag	60	Ga	65
Sn	25	In	18.95
Cu	13	Sn	16
Pd	2	Rest	0.05
Rest	0.3		

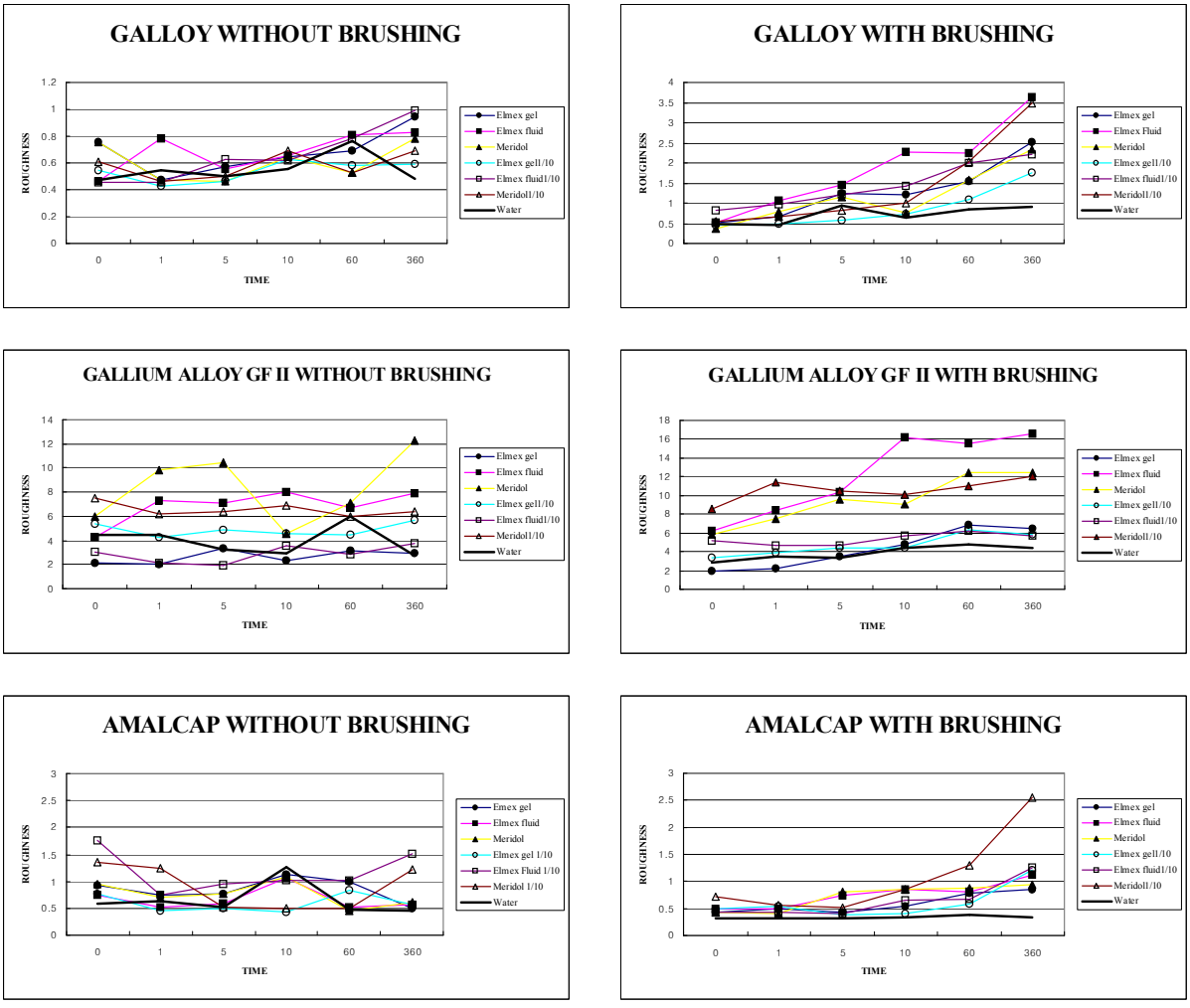


Fig. 1. Lines of mean roughness of 42 specimens divided by 6 groups

Ill, USA). Correlation coefficient and simple regression analysis were conducted to determine the relationship between surface roughness and time interval, and one way ANOVA, followed by Tukey multiplecomparisons were also used to compare between alloys and prophylactic agents.

Table 3. Correlation coefficient and regression equation of materials according to brushing

Material	Brushing	Correlation coefficient	F value	Regression equation
Amalcap	O	0.25981	0.0000*	Y = 0.13x + 0.48
	X	0.05307	0.4016	Y =-0.03x + 0.90
Galloy	O	0.31507	0.0000*	Y = 0.35x + 0.03
	X	0.22522	0.0003*	Y = 0.04x + 0.47
Gallium GF II	O	0.62732	0.0000*	Y = 0.9x + 4.06
	X	0.07453	0.2384	Y = 0.16x + 4.59

*: Significant relationship between time interval and surface roughness ($p < 0.001$)

1. Relationship between time interval and roughness of materials according to brushing

Correlation coefficient and simple regression analysis were performed to determine the relationship between time interval and roughness of materials according to brushing. Table 3 shows the statistical results of six tested groups. The surface roughness of the three materials (Amalcap, Galloy and Gallium GF II) increased significantly according to brushing ($p < 0.001$).

Surface roughness of the amalgam and the Gallium Alloy GF II did not significantly increase in the groups without brushing. But the Galloy showed significant increment of surface roughness without brushing ($p < 0.001$). Thus, the Galloy showed significant increment of surface roughness according to the increment of time intervals when both brushing and without brushing were applied. The correlation between time intervals and surface roughness in the Gallium Alloy GF II group with brushing is 0.63, indicating that it is the most positive and strongest among the six groups tested in this study. The Gallium Alloy GF II showed the highest intercepts (4.06 and 4.59). This means the surface of the Gallium Alloy GF II is rougher than that of the Galloy and the Amalcap.

2. Relationship between time interval and roughness of materials according to prophylactic agents

Correlation coefficient and simple regression analysis were performed to determine the relationship

Table 4. Correlation coefficient and regression equation of materials according to brushing

Material	Dilution	Correlation coefficient	F value	Regression equation
Elmex gel	X	0.26302	0.0001*	Y = 0.28x + 0.76
	1/10	0.12084	0.0764	Y = 0.16x + 1.48
Elmex fluid	X	0.18663	0.0059*	Y = 0.58x + 1.80
	1/10	0.13277	0.0513	Y = 0.16x + 1.48
Meridol	X	0.14080	0.0387*	Y = 0.38x + 2.25
	1/10	0.07067	0.3011	Y = 0.18x + 2.88
Water	X	0.03129	0.6474	Y = 0.04x + 1.64

*: Significant relationship between time interval and surface roughness ($p < 0.05$)

Table 5. Homogenous groups of the Mean surface roughness

Materials	Water	Elmex G	Elmex G 1/10	Elmex F 1/10	Meridol	Meridol 1/10	Elmex F
Galloy	0.5514	0.6794	0.5392	0.6556*	0.6072	0.5803	0.6836
Amalcap B	1.0036	0.7783	0.8022	0.8864*	1.1800	1.0778*	0.7497*
Amalcap	0.6533	0.8386	0.5872	1.1633	0.7583	0.8947	0.6700
Galloy B	0.7094	1.2836*	0.8472*	1.4464*	1.1603*	1.4203*	1.8672*
Gallium GF II	3.9606	2.6539	4.8694	2.8717	8.3683	6.5508	6.8744
Gallium GF II B	3.8703	4.2736*	4.7069	5.3414	9.4664*	10.5842	12.2236*

B: Brushing, G : gel, F : fluid,

*: Significant relationship between surface roughness and time interval ($p < 0.001$)

vertical and lateral bar : homogenous group

between time interval and roughness of materials according to the prophylactic agents. Table 4 shows the statistical results of the seven tested groups. Surface roughness of the three materials (Amalcap, Galloy and Gallium Alloy GF II) significantly increased when original prophylactic agents were applied to the materials ($p < 0.05$). Surface roughness of the materials did not significantly increase according to the time interval when diluted prophylactic agents and distilled water were applied.

3. Surface roughness and wear according to alloys and prophylactic agents

One way ANOVA and Tukey multiple comparisons were performed to analyze the results.

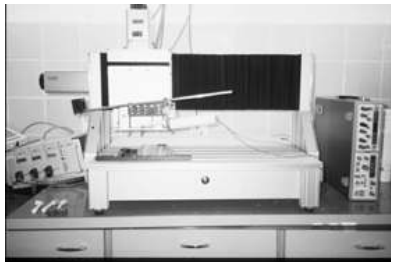
Table 5 shows the mean surface roughness of materials tested in this study. The surface roughness of the Gallium Alloy GF II showed significant difference compared to those of the Amalcap and the Galloy ($p < 0.001$). The Gallium Alloy GF II has a rougher surface than the Amalcap and the Galloy. The surface roughness of the Galloy with brushing, the Gallium Alloy GF II without brushing and the Gallium Alloy GF II with brushing were significantly different according to the prophylactic agents ($p < 0.001$).

SEM pictures shows difference of the material surfaces before and after brushing. The difference of surface roughness between the Gallium Alloy GF II and the Amalcap / the Galloy can be easily identified.

The Gallium Alloy GF II shows many defects such



Fig. 2a.
Prophylactic agents (Elmex Gel, Elmex Fluid, Meridol, Elmex Gel 1/10, Elmex Fluid 1/10, Meridol 1/10) and the tested samples.



2b.
Custom made brushing machine



2c.
Profilometer (S6P, Perthen, Hannover, Germany)

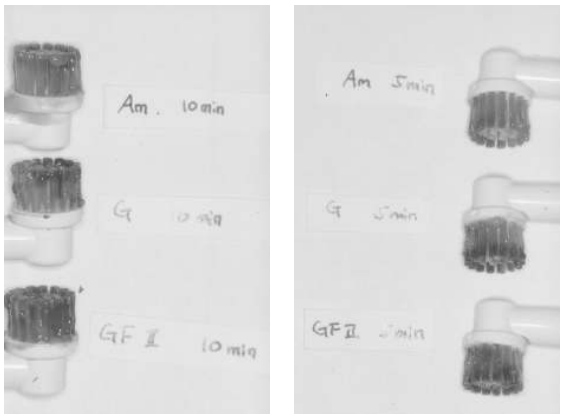


Fig. 3. Color change of Meridol after 5 and 10 minutes of brushing on the three alloys.

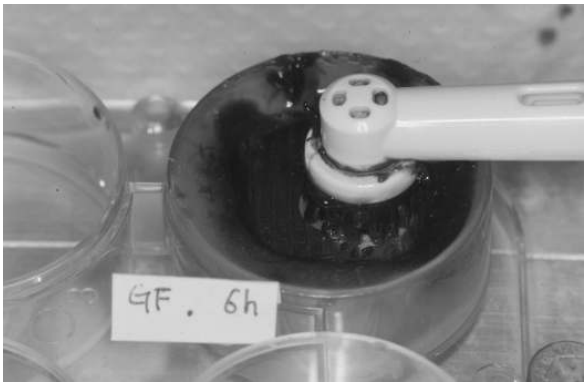


Fig. 4. Color change of Meridol after 6 hours of brushing on the Gallium alloy GFII alloy.

as air porous. The surface continuity of the Galloy is similar to that of the Amalcap. The gallium alloys showed severe abraded surfaces compared to the amalgam in the SEM pictures after brushing. During brushing with the Meridol, the gallium alloys showed many undesirable deposits compared to the amalgam (Fig. 3). The surfaces of the Galloy and the Gallium Alloy GF II were affected by the Elmex fluid, but the Amalcap showed no changes against the application of the Elmex fluid. It is assumed that the gallium alloy chemically counteract with the specific prophylactic agent.

IV. DISCUSSION

1. Wearing down of tested alloys according to brushing with prophylactic agents

Three tested alloys showed significant increment of surface roughness according to the increment of time interval when brushing was applied to the specimens ($p < 0.001$). This means that brushing with prophylactic agents wore off the three alloys (the Amalcap, the Galloy and the Gallium Alloy GF II). These three alloys showed undesirable deposits when brushing was applied with Meridol (Fig. 3). This is one of the methods to improve the wearing down of alloys when brushing is applied with the prophylactic agents. The Gallium Alloy GF II has the most undesirable deposit and the roughest surface. The surface of the Galloy significantly increased with brushing and without brushing. This means that gallium alloys are more susceptible to surface degradation compared with amalgam.

2. Role of prophylactic agents against wearing down of alloys

When the original prophylactic agents were applied on the alloys, the three alloys showed significant increment of surface roughness according to the increment of time interval ($p < 0.05$). The three diluted prophylactic agents and distilled water did not significantly affect the wearing down of alloys. This is assumed to be due to the weakening of a chemical action and mechanical action due to the 1/10 diluted prophylactic agents. The color of Meridol changed during brushing in the three alloys and the darkest color appeared on the Gallium Alloy GF II. This, which is produced by silica, looks unfavorable, and an abrasive composition of the Meridol is responsible for the discoloration of Meridol. The Elmex fluid which contains high consistency aminofluoride (13.20 g / 100g), affected surface roughness of the Gallium Alloy GF II and the Galloy. It is likely that the surface of

gallium alloys was changed by concentrated fluoride. The SEM pictures of the gallium alloys present these surface changes (Fig. 2). Amalgam surface showed no changes against the Elmex fluid. Thus, we may conclude that the gallium alloys have unsuitable surface roughness and unsuitable resistance against wear as a permanent direct filling material.

V. CONCLUSION

1. The tested alloys (the Amalcap, the Galloy and the Gallium Alloy GF II) showed a significant relationship between surface roughness and time with respect to the undiluted dental paste ($P < 0.05$).
2. The tested alloys showed a significant relationship between surface roughness and time during brushing ($P < 0.001$).
3. The Galloy showed significant increment of surface roughness according to the increment of time interval when both brushing and without brushing were applied.
4. The Gallium Alloy GF II showed the roughest surface at the 0.05 level.
5. The gallium alloys were more susceptible to surface degradation during brushing than amalgams with respect to the specific prophylactic agent used ($P < 0.01$).
6. The surface roughness of the Galloy with brushing, the Gallium Alloy GF II without brushing and the Gallium Alloy GF II with brushing was significantly different according to the prophylactic agents ($p < 0.001$).
7. The Galloy and the Gallium Alloy GF II were affected by the Elmex fluid, but the Amalcap showed no changes against the application of the Elmex fluid.
8. The gallium alloys showed severe abraded surfaces compared to the amalgam on SEM pictures.

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