Fatigue and Tensile Strength of Dental Gallium Alloys after Artificial Saliva Immersion

Setyowati MEIANA and Hidekazu TAKAHASHI
Department of Dental Technology I, Faculty of Dentistry, Tokyo Medical and Dental University
1-5-45 Yushima, Bunkyo-ku, Tokyo 113-8549, Japan

Received July 15, 1998/Accepted September 9, 1998

Fatigue strength using the stair-case method and tensile strength of dental gallium alloys after artificial saliva immersion were measured for evaluating the effects of corrosive environment storage on the mechanical properties of the gallium alloys. The fatigue and the tensile strengths of both gallium alloys stored in artificial saliva were significantly decreased after 12-month storage, while those stored in air increased with storage period. The fracture surfaces of the specimens in artificial saliva showed not only metallic luster but also dark areas. In the dark area, the matrix might have dissolved during immersion. These results suggested that the concern over corrosion resistance of gallium alloys still remained.

Key words: Gallium alloy, Fatigue, Artificial saliva

INTRODUCTION

Dental amalgam has been the material of choice for posterior dental restoration for more than 150 years because of its easy manipulation, economical performance, and suitable mechanical properties\(^1\). However, the environmental problems caused by the mercury in amalgam waste arose. Several alternative materials have been suggested, such as selenium added amalgam\(^2\), silver filling material\(^3\), and dental gallium alloy\(^4,5\). In spite of that, at present, the only commercially available direct metal filling material other than amalgam is gallium alloy.

Many studies have proved that the gallium alloy has excellent physical and mechanical properties\(^5-9\), and is not more toxic than amalgam\(^10\). On the other hand, the alloy has also been reported to have a relatively low resistance to corrosion\(^11-13\). However, the effect of corrosive environment storage on the mechanical properties of the gallium alloy has not yet been clearly investigated.

Intra-orally functioning dental restorative materials are exposed to the application of repetitive stress, namely mastication, and a corrosive environment. The evaluation of fatigue strength is thus of great importance\(^14\). Several fatigue testing methods have been introduced; out of those, the stair-case method is an appropriate statistical test method to obtain an accurate fatigue strength and its standard deviation from a small number of specimens\(^15-17\). The stair-case method has been employed to obtain the fatigue strengths of several kinds of dental materials\(^14,18-22\) and bovine dentin\(^23\).
In this study, fatigue strength using the stair-case method and tensile strength of dental gallium alloys after artificial saliva immersion were measured and the effects of corrosive environment storage on the mechanical properties of the gallium alloy were evaluated.

MATERIALS AND METHODS

Gallium alloy and mixing condition
Two commercially available gallium alloys were employed in this study; one was Gallium alloy GFII (GFII, Tokuriki Honten, Tokyo, Japan), and the other was Galloy (GLY, Southern Dental Industries, Bayswater, Victoria, Australia). The chemical compositions supplied by their manufacturers are shown in Table 1.

The amount of commercially available pre-capulated GFII alloy was insufficient to prepare the specimen. Therefore, for the preparation of a GFII specimen, 1.000 g of powder alloy and 0.500 g of liquid alloy was weighed and packed into an amalgam capsule (VS-III Capsule, GC, Tokyo, Japan), without pestle. GLY was pre-capulated; each capsule contained 0.700 g of powder alloy and 0.343 g of liquid alloy. The amount of packed GLY alloy was insufficient to prepare the specimen. It was not possible to weigh this alloy, therefore, the size of the specimen was reduced. The alloys were mixed according to the manufacturers' recommendations; an amalgam mixer (Type D, Shofu, Kyoto, Japan) for 10 seconds and another amalgam mixer (Ultramat 2, SDI, Bayswater, Victoria, Australia) for 8 seconds were employed for GFII and GLY, respectively.

Fatigue and tensile test specimen preparation
Cylindrical specimens with stainless steel screw pins at both ends were used for the fatigue and tensile tests[18-19]. The stainless steel screw pins (M1.6 × 0.35, SUS304, Nitoh Seikoh, Tokyo, Japan) had a diameter and length of 1.6 mm and 10 mm, respectively; the pitch and the height of the screw thread were 0.2 mm and 0.45 mm, respectively.

A cylindrical brass mold, constructed of three parts, was used to prepare the specimen (Fig. 1). The central part of the mold was a hollow cylindrical brass with a polytetrafluoroethylene inner lining (Fig. 1-c). Each end of the hollow cylinder was covered with a brass lid (Fig. 1-b, d). A screw pin hole was drilled through the lid. The hollow cylindrical mold was placed on the top of the screwed lid, in which a
screw was previously positioned with 3 mm of its length projecting into the mold (Fig. 1-d). The freshly mixed gallium mass was condensed into the mold, and the other lid was positioned on the mold assembly. A second screw was screwed from the top, until 3 mm length of the screw was embedded in the specimen (Fig. 1-e, f). Within 2 minutes after the start of mixing, a load of 147 N parallel to the axis of the screws was applied on the assembled mold for 1 minute. One hour after the start of mixing, the specimens were removed from the mold. The diameter and the height of GFII specimens were 4 mm and 10 mm, respectively; while those of GLY specimens were 4 mm and 9 mm, respectively. The total number of specimen prepared was 190 for each gallium alloy.

**Storage conditions**

One half of the specimens prepared for each alloy were left in 250 ml containers at bench at 23±2°C (referred to hereafter as Air). The other half were stored in the containers filled with 150 ml artificial saliva and stored in an incubator (C-310 Advantec Incubator, Toyo Seisakusho, Chiba, Japan) set at 37±0.2°C, with circulating air bubbles to provide oxygen (referred to hereafter as Saliva). The artificial saliva used was one of the compositions suggested by ISO/TR 1027125); 0.400 g of NaCl, 0.400 g of KCl, 0.795 g of CaCl₂·2H₂O, 0.780 g of NaH₂PO₄·2H₂O, 0.005 g of Na₂S·2H₂O, and 1.000 g of urea dissolved into 1000 ml of distilled H₂O. Ten specimens were stored in each container and the artificial saliva was changed every 7 days to maintain a constant composition of the solution.

**Fatigue test**

Fatigue tests were conducted after the specimens had been stored for 1 week, 3 months, or 12 months in their respective storage conditions. The fatigue test was conducted using a digital servo-hydraulic testing machine (8501, Instron, Canton, MA,
USA) and fatigue testing software (MAX, Instron, Canton, MA, USA). The specimens were removed from their storage environments and mounted on the machine using special jigs for the fatigue test. The specimens were double bolted on each end to prevent any movement. The distance between the bolts and the ends of the specimens was 2 mm (Fig. 2-a). The fatigue test for the specimens stored in Air was conducted in air, while that for the specimens stored in Saliva was performed in a circulating water bath at 37±0.2°C (Fig. 2-b).

Fatigue strength and the standard deviations were obtained by means of the stair-case method15–17. Sinusoidal cyclic unipolar stress at a frequency of 5 Hz was applied 10⁶ times. The stress applied was tensile stress between a minimum of 0.93 MPa and a maximum of the desired stress. The initial test was performed with a maximum stress of 70% tensile strength for each storage condition. The stress increments were 0.5-5 MPa, determined in respect to the storage condition. The strength of each specimen was calculated based on the cross section area of the specimen after the area of the screw was omitted. The fatigue strength obtained from this method was the stress level at which 50% of the specimens were subject to fracture when tested for 10⁶ cycles. Fifteen specimens of each alloy were tested for each storage condition. The results were statistically analyzed by the t-test.

**Tensile test**

The tensile test was conducted after the specimens had been stored for 1 week, 1 month, 3 months, 6 months, or 12 months in their respective storage conditions. The tensile test was conducted using a universal testing machine (1123, Instron, Canton, MA, USA) with a crosshead speed of 0.2 mm/min. The specimens were removed from their storage environments and mounted in a similar manner to that described for the fatigue test. The tensile strength was calculated by dividing the stress at the moment of fracture by the sectioned area of the specimen, minus the area of the screw. Ten specimens of each alloy were tested for each storage condition. The results were statistically analyzed by One-way ANOVA and Scheffe's test. Relationships between the tensile strengths and the storage periods were evaluated using regression analysis.
SEM observation and surface element analysis
To determine changes in fracture surface appearance and their chemical composition, the fracture surfaces of the specimens after fatigue and tensile tests were observed using a scanning electron microscope (DS-130 C, Akashi Beam Technology, Tokyo, Japan) and analyzed using an energy dispersed X-Ray spectroscopy (EDX, Delta V, Kevex, Foster City, CA, USA) at 15 kV with a gun current of $5 \times 10^{-8}$ A.

RESULTS

Fig. 3 shows the specimens after 12-month storage in Air and Saliva. The surface of the specimens of both alloys stored in air did not show any apparent change and they maintained their metallic luster even after 12 months from preparation. On the other hand, those immersed in artificial saliva showed obvious changes after 1 week immersion. The specimens of both alloys stored in artificial saliva for 1 week were surrounded by white gelatinous clouds. The cloud became thicker with the longer immersion period, and white sedimentation started to precipitate on the specimen surface. The surface of the gallium alloys became dark in several spots. After immersion for 12 months, almost all parts of the gallium surface were dark, covered with white solid sedimentation and occasionally brown sedimentation. In addition, some translucent rod-form sedimentation was present on the gallium alloy and the screw.

Fig. 4 and 5 show the fatigue strengths and tensile strengths after Air and Saliva storage; error bars in the figures indicate standard deviations. The fatigue strength of GFII after 1 week storage in Air was 45.3 MPa; that of 3-month storage increased until 12-month storage, 50.8 MPa. The fatigue strength after 1 week storage in Saliva was 44.0 MPa, which was significantly lower than that after 1 week storage in Air ($p<0.05$). The fatigue strength of GFII did not change until 3 months, then it decreased significantly to 36.4 MPa after 12 months ($p<0.05$).

The fatigue strength of GLY after 1 week storage in Air was 38.1 MPa, which
244  FATIGUE AND TENSILE STRENGTH OF GALLIUM ALLOY

was lower than that of GFII after 1 week storage in Air. The fatigue strength of GLY significantly increased to 49.3 MPa after 3 months storage (p<0.05), and did not change until 12 months storage. The fatigue strength after 1 week storage in Saliva was 46.6 MPa. The fatigue strength of GLY was significantly higher compared to that stored for 1 week in Air (p<0.05). The fatigue strength of GLY continued to decrease to 40.2 MPa after 12 months storage in Saliva, which was higher than that of GFII after 12 months storage in Saliva. Standard deviations of both GFII and GLY became larger with longer immersion period.

Tensile strength of GFII after 1 week storage in Air was 61.3 MPa; that of 1 month storage significantly increased (p<0.05) but did not change until 12 months storage, which was 73.2 MPa. The strength after 1 week storage in Saliva was 70.7 MPa which was significantly higher than that after 1 week storage in Air (p<0.05). Tensile strength of GFII after 1 month storage in Saliva decreased, and continued to significantly decrease until 12 months, at which time it was 48.0 MPa (p<0.05). The estimated regression curves for the tensile strength of GFII in Air and Saliva were, \( Y=47.8+20.8 \log X-4.2 \left( \log X \right)^2 \), and \( Y=71.5+2.9 \log X-4.5 \left( \log X \right)^2 \), respectively; where \( Y \) was the strength in MPa and \( X \) was the storage period in days. The correlation coefficients of the tensile strength of GFII in Air and Saliva were 0.536 and 0.860, respectively, which were not significant.

Tensile strength of GLY after 1 week storage in Air was 50.7 MPa, which was lower than that of GFII. The tensile strength was increased until 12 months storage, 66.6 MPa. The tensile strength after 1 week storage in Saliva was 56.8 MPa which was higher than that after 1 week storage in Air; however, the tensile strength of GLY after 1 week storage in Saliva was lower compared to that of GFII after 1 week storage in Saliva. The tensile strength of GLY after 1 month storage in Saliva increased, however, that after 12 months storage, 47.7 MPa, significantly decreased (p<0.05). The rate of tensile strength decrease of GLY was small, therefore, the value after 12 months storage in Saliva was similar to that of GFII. The estimated regression curves for the tensile strength of GLY in Air and Saliva were \( Y=35.4+22.4 \log X-4.2 \left( \log X \right)^2 \), and \( Y=36.0+34.1 \log X-11.5 \left( \log X \right)^2 \), respectively; the correlation coefficients of the tensile strength of GLY in Air and Saliva were 0.921 and 0.977 (p<0.01), respectively.

The ratios of fatigue to tensile strength of GFII in Air for 1 week, 3 months, and 12 months were 0.739, 0.774, and 0.676, respectively; those of fatigue to tensile strength of GFII in Saliva for 1 week, 3 months, and 12 months were 0.622, 0.777, and 0.758, respectively. The ratio of fatigue to tensile strength of GLY in Air for 1 week, 3 months, and 12 months were 0.752, 0.794, and 0.768, respectively; those of fatigue to tensile strength of GLY in Saliva for 1 week, 3 months, and 12 months were 0.822, 0.746, and 0.843, respectively.

The fractures in the fatigue and tensile test occurred mostly at the screw end; 374 out of 380 specimens. Almost all fracture origins were estimated at the end of the screw along the first screw thread. The fracture surface of specimens of both alloys stored in Air showed a metallic luster even after 12 months storage; however, those
Fig. 4 Change in fatigue and tensile strength of GFII in Air and in Saliva.  
a: in Air, b: in Saliva.

Fig. 5 Change in fatigue and tensile strength of GLY in Air and in Saliva.  
a: in Air, b: in Saliva.

specimens stored in artificial saliva had dark areas on their fracture surface (Fig. 6). The dark areas of fracture surface became larger with longer immersion period.

The fracture surface showed two obviously different patterns; the fracture pattern in the metallic luster area was relatively regular and smooth, while that in the dark area was relatively irregular. Similar images were observed on both GFII and GLY fracture surfaces, regardless of fatigue or tensile test conducted.

SEM observation of fracture surfaces revealed that there were no obvious differences between fracture surfaces after the fatigue test and those after the tensile test; however, different fracture patterns were recognized between the metallic luster area and the dark area, and between the two gallium alloys. The fracture surface of GFII in the metallic luster area was considered to be the core-reaction zone interface or the
matrix-reaction zone interface (Fig. 7a); nevertheless, in a few cases, fractures of the core could also be observed. The fracture surfaces of GFII's dark area were mostly in the matrix, and the unfractured core was covered by a layer of fractured matrix (Fig. 7b). On the other hand, a lot of core fractures were observed on the fracture surface of GLY’s metallic luster area, which was similar to fractures of dental amalgam (Fig. 8a); however, in a few cases, unfractured cores without reaction zone were also observed. The fracture surface of GLY’s dark area showed a fragmented matrix and irregularly fractured cores, therefore, it was difficult to distinguish the fractured core from the surrounding matrix (Fig. 8b).

Observation by EDX of the fracture surfaces of both immersed alloy specimens revealed the presence of chemical components of the gallium alloys. However, neither the elements from the screw nor the artificial saliva were detected on the fracture
DISCUSSION

The direct tensile test using screw pins has been used for evaluating fatigue and tensile strength of brittle dental materials\(^{19-20}\). The screw inside the specimens directly contacted the gallium alloys, creating a possibility for the occurrence of a local electrode potential cell; this was considered to have accelerated the corrosion process. These situations might cause the corrosion-fatigue phenomena. However, the direct contact of gallium alloy to stainless steel might be regularly encountered in the oral cavity in the application of gallium alloy because dental amalgam is used as a core build up material combined with a prefabricated stainless steel post\(^{26}\).

The presence of water does affect the strength of materials, moreover, the presence of chlorine ion is known to be more aggressive on a metallic surface. However, a minimal amount of chlorine ion was reported to depress the corrosion rate of gallium within 28 days immersion\(^{12}\). Therefore, the specimens were immersed for 12 months to evaluate the corrosion behavior of the gallium alloy.

The fatigue and the tensile strengths of both gallium alloys stored in Air showed a tendency to increase, while those stored in Saliva showed a tendency to decrease, especially after 3-month storage. The setting reaction of gallium alloy was considered more rapid than that of a dental amalgam\(^{10}\); however, the compressive strength and hardness of GLY were reported to increase after more than 7 days\(^9\). Therefore, the continuous setting reaction of gallium alloy might have caused the increase in the fatigue and tensile strengths after 12 months storage in Air. On the other hand, the fatigue and tensile strengths of gallium alloys decreased after 3-month storage in Saliva. The effect of corrosion might be greater than the effect of the setting reaction, and as a result the strength decreased with longer immersion.

The observation of the fracture surface did not show a distinct difference between
specimens after the fatigue test and those after the tensile test. It was difficult to identify the typical signs of fatigue such as striation\(^\text{37}\), because the gallium alloy consisted of a cored structure.

Dark areas were found on the surface of Saliva immersed specimens after both fatigue and tensile tests. These were larger in accordance with increased immersion period. Fig. 9 shows the surface of a specimen after 12 months storage in Saliva, of which the upper half was removed by clamping longitudinally along the screw axis. Observation of this fracture surface revealed a dark area, similar to those observed on fracture surfaces after the fatigue and tensile tests. Other specimens were cut longitudinally along the screw axis, polished and observed by a metallographic microscope (AX 70, Olympus, Tokyo, Japan) (Fig. 10). Fig. 11 indicates the region where the dark area might exist, at 200 times original magnification. The matrix in the dark area of GFII disappeared and the core outline was clearly seen; the matrix
might have dissolved during immersion in Saliva or the polishing procedure. The same observation of the GLY surface showed the presence of both matrix and core, even in the dark area. These findings suggested that the matrix degeneration caused the formation of dark areas and reduction of mechanical properties of gallium alloys. However, the element composition of the dark area by EDX analysis did not show a notable difference from that of the metallic luster area. Moreover, the dissolution of Ga, Sn, and In from gallium alloy into NaCl and saline solution has been reported\(^{13}\); all these elements are components of the matrix of set gallium alloy. This also supported the suspicion of the matrix corrosion.

Similar dark areas of gallium alloy have been reported in vitro\(^{13}\) as well as in vivo\(^{9}\). These dark areas were not strong and could be easily removed, revealing a new metallic luster surface; therefore, the dark area has been suggested not to be a problem\(^{9}\). However, if the dark area is assumed to be caused by a weakening of the matrix, then the removal of restoration parts might lead to the failure of the restoration in the long run.

There was no obvious corrosion evidence around the screw, which was considered to have accelerated the corrosion process. This slow corrosion rate in the area around the screws was assumed to be caused by a lack of oxygen. Therefore, the decrease in fatigue and tensile strengths after 12-month Saliva immersion was considered to be the result of the growing weak dark area of the peripheral structure.

By SEM examination, core fractures of GLY were more commonly observed than those of GFII. According to a report on the dynamic hardness of GFII\(^{28}\), the hardness of the matrix is significantly lower than the hardness of the core; therefore, fractures in GFII’s metallic luster area might occur at interfaces between the core and reaction zone or between the matrix and reaction zone. The tin content in the GLY powder was greater than that in the GFII powder, therefore the core structure of GLY was considered to be closer to the intermetallic compound (Ag\(_3\)Sn). With respect to a Ag-Sn-Cu alloy, the alloy becomes harder and more brittle as the composition of Ag to Sn becomes closer to the intermetallic ratio\(^{29}\). Therefore, the core of GLY could not show plastic deformation and fractured. Concerning the dark area fracture, the decrease of the matrix strength caused internal fracture of the matrix.

The fatigue strengths of GFII and GLY after 12-month storage in Saliva were larger than that of the previous gallium alloy and amalgam after 1 week storage in Air and water at 37±0.2°C\(^{19}\); the tensile strength of GFII after 12 months storage in Saliva was larger than that of the previous gallium alloy and amalgam after 1 week storage in Air\(^{10}\). Moreover, the fatigue and tensile strengths of gallium alloys after 12-month artificial saliva immersion were larger than those of an MFR type composite resin after 12-month water immersion, however were smaller than those of a hybrid type posterior composite resin\(^{21}\). These results suggested a benefit of gallium alloy application for posterior restoration. However, the decrease rates of the strengths of composite resins were reported to be linear\(^{21}\), while those of gallium alloys in this study were supposed to be exponential. Therefore, an accelerated rate of a strength decrease with immersion period suggested a problem with the corrosion
resistance of dental gallium alloy. The cause of the corrosion of the gallium alloy was considered to be the weakness of the matrix. Improvement of alloy composition for a better corrosion resistance were required. GLY is recommended to be sealed by resin sealant for protection against moisture contamination during setting. This procedure might have resulted in greater fatigue and tensile strengths.

The ratios of fatigue strength to tensile strength of brittle materials (gallium alloy\(^\text{19}\) and amalgam\(^\text{19}\)) are reported to be 0.684-0.873; those of dental materials showing small plastic deformation (composite resins\(^\text{21}\) and bovine dentin\(^\text{24}\)) are 0.487-0.726; those of casting alloys as cast (Ag alloy\(^\text{20}\), Ag-Pd-Cu-Au alloy\(^\text{22}\) and Type 4 gold alloy\(^\text{23}\)) are 0.325-0.546. The ratios of fatigue strength to tensile strength in this study were 0.622-0.843 which was consistent with previous reports. It might be possible to classify the dental materials with respect to the fatigue to tensile strength ratio. Generally, different testing condition results in different strength values. Therefore, we propose to gather the fatigue strength and tensile strength of various dental materials under the same conditions in an effort to derive the fatigue strength from the tensile strength of a material.

CONCLUSION

Screw type tensile test specimens of two gallium alloys were prepared and stored in air at 23±2°C or immersed in artificial saliva at 37±0.2°C for 12 months. The fatigue test using the stair-case method and tensile test were performed and fracture surfaces were observed for evaluating the effects of corrosive environment immersion on the mechanical properties of gallium alloys.

The fatigue and the tensile strengths of both gallium alloys stored in air increased with storage period, while those stored in artificial saliva were significantly decreased after 12 months storage. The fracture surfaces of the specimen in air showed a metallic luster even after 12 months storage, however, those in artificial saliva showed not only a metallic luster but also dark areas. In the dark areas, the matrix might have dissolved during immersion. A corrosive environment such as saliva immersion was considered to reduce the mechanical properties of gallium alloys because of degeneration of the matrix.

Improvement of alloy composition for better matrix corrosion resistance was suggested.

ACKNOWLEDGMENTS

The authors would like to express our deepest appreciation to Professor Fumio Nishimura of Department of Dental Technology I at Tokyo Medical and Dental University for his invaluable guidance and help throughout this research. We would also like to express our appreciation to Dr. Hideo Nakamura, Dr. Kazuo Motomura, Mr. Naohiko Iwasaki and Dr. Tohru Ohtani of the same department for helping the preparation of the manuscript.
We would like to extend our gratitude to Tokuriki Honten, Japan for providing the material and Southern Dental Industries, Australia through Eiko, Japan for providing the material and equipment for this research.

REFERENCE


