

# INVESTIGATING THE PHYSICAL AND MECHANICAL PROPERTIES OF HIGH-COPPER AND SILVER DENTAL-FILLING AMALGAM ALLOYS

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**Abstract:** The aim of the present investigation is to study the physical and mechanical characteristics of dental-filling spherical high-copper and silver amalgams and to compare them with a common high-copper domestic uni-compositional amalgam. In this study, cylindrical specimens were mechanically condensed according to the ISO 1559:1986 Standard in order to measure the compressive strength, Vickers hardness, static creep and dimensional change on setting. Adding more silver to the amalgam increased its compressive strength, creep resistance and reduced mercury vapor. After 1, 24 and 168h of amalgamation and Modulus of elasticity of specimen S1, the mean hardness and compressive fracture strength were significantly lower than those of . No significant differences were identified for the two alloys in the creep and dimensional changes on setting. It can be concluded that as far as the mechanical properties or corrosion resistance is concerned, the amalgam should be comprised of at least one spherical alloy.

**Keywords:** Dental alloys; Powder metallurgy; Setting time; Heat treatment

## 1. INTRODUCTION

Although the Chinese knew the initial form of the dental amalgam in the 7<sup>th</sup> century and the medical book written by Su-Kung introduced it in 695 AD., it is not clear who first recognized the silver-tin-Hg alloy, produced as and called *amalgam* [1]. Dental amalgam was used in France for about 170 years to restore the dental material tissue and it was one of the most widely used dental restorative materials [2]. In spite of being a controversial issue within the recent century, no one can completely ignore the role of dental amalgams in the restorations conducted on the teeth. The multi-compositional dental alloy is made of some pure metals, which are produced industrially, and exists in the form of spheroid and pellet [1- 4]. The particles of this alloy are very suitable for being mixed with Hg in normal temperature in order to make dental amalgams [3]. The new mixture created through this process is flexible and formable and it could be compressed and put in the cavity made by the dentist. This restoration material has been used for more than one hundred years. However, the efforts to mitigate the physical and mechanical characteristics of this material have only been made in recent decades [5]. Although many tremendous achievements are made, the research

is continuing to improve the quality of the material and to identify the possible harmful effects of corrosion on human body [6, 7]. Before the end of 1970s, the use of traditional and dental amalgam with low amount of copper was prevalent. One of its constituents was Sn-Hg phase, named  $\gamma_2$  [8], which has the least strength and resistance. The efforts aiming at increasing these qualities in this amalgam lead to the deletion of the undesirable characteristics and increase of the amount of copper in this amalgam [9]. In fact, in these amalgams, more copper enters the alloy rather than silver while the amount of tin is kept constant. The existing copper in the initial alloy powder of copper and silver reacts with  $\gamma_2$  as soon as mixing [10]. In less than few hours, it reaches phase  $\epsilon$  and this deletes  $\gamma_2$ ; hence the resistance and strength of the amalgam increases. The deletion of phase  $\gamma_2$  starts immediately after creating the amalgam [11]. The popularity of the high-copper dental amalgams among dentists is due to its high compression strength, wear resistance, low cost, high corrosion resistance and long medical performance [12, 13].

## 2. EXPERIMENTAL

In the present study, the initial materials for

making the dental amalgam included tin, silver, copper with the chemical composition of 59%Ag, 13%Cu and 28%Sn, which is a dental filling amalgam and a uni-compositional alloy with high percentage of silver and copper.

Type DEGOSA Hg was used in the amalgam, which is a confirmed material in dentistry with the highest purity. The mixture of the elements was heated in a melting furnace under normal and controlled atmospheric circumstances. After 20 minutes, the elements melted and were ready for pouring. The temperature of the melting liquid was between 1200 and 1300°C. So, in order to create the proper sphere of alloy powder with the gas atomizing system, the temperature of the melted liquid was adjusted to around 780 to 850°C at the time of pouring. The powders were meshed based on the required sizes by a special wire mesh with the required graining. This amalgam alloy powder, with the required and intended graining, underwent the heat treatment in the atmosphere of the Argon gas in 145 °C. Different characteristics of the two dental amalgams, one made in laboratory and the other through domestic production which acted as the reference sample, are mentioned in Tables 1 & 2. Some of these characteristics include the ratio of the powder to Hg content, triturating and grinding time, graining type, chemical combination, shape of the particles and the utilized amalgamator which was supposed to follow the standards of the Iran National Standard, 4301.

For these tests, completely mechanical instruments should be used. In the first section,

sufficient amount of each type of amalgam was prepared using stainless steel molds. To create the samples, each mold had a cylindrical container with the diameter and height of  $4.0 \pm 0.1$ mm and  $8.0 \pm 0.1$ mm, respectively. The homogeneous amalgamated amalgam was put on the hole of the mold. Then, using a special instrument with the diameter less than  $4.0 \pm 0.1$ mm, the amalgam was compressed into the mold. The pressure of the compression was  $14 \pm 1$ MPa. The compression of the amalgam was done immediately after grinding and softening the alloys and Hg in an enclosed capsule; then the extra Hg was gathered from the surface. The speed of the amalgamator was chosen to be 4000 RPM. All of the samples were prepared based on the ISO 1559 Standard and under the constant laboratory conditions (temperature of  $23 \pm 1^\circ\text{C}$  and humidity of 50-55 %). Three samples were prepared for measuring the samples' compression strength. These samples were stored in an incubator maintained at  $37 \pm 1^\circ\text{C}$ . The first measurement was done one hour after the amalgamation; the second was measured 24 hours after it and the last measurement was conducted after 168 hours. The measurement of compression strength was conducted by a SANTAM-SMT200 machine which had a computer system and exerted a pressure in the direction of the axis of the test with the speed of 0.5mm per minute. The schematic representation for measuring the compression strength is shown in Fig.1. In order

**Table 1.** The chemical composition and shape of the particles of Amalgam alloy.

Amalgam alloy	Chemical combination (Weight percent)			Shape of the particles
	Ag	Sn	Cu	
$C_1$	59	28	13	Sphere
$S_1$	43	31	26	Sphere



**Fig. 1.** Schematic diagram for compressive strength testing.



Fig. 2. Schematic diagram for creep testing.

to determine the dimensional changes of each specimen through the test, the specimen should not undergo a force exceeding 0.02 N. The first measurement was done 5 minutes after the amalgamation and the last measurement was done at the end of 24 hours. During the test, the samples were stored in an incubator maintained at  $37 \pm 1^\circ\text{C}$ . The dimensional changes were measured under the accuracy of 0.5mm and the result was calculated by dividing the change of the height by the height after 24 hours (with 0.01 approximations). In order to measure the creep, the prepared specimens were stored in an incubator maintained at  $37 \pm 1^\circ\text{C}$ . Before running the test, the area of the two sides of the specimen was grinded with Silicon ASTM 600 sand paper. In wet situations, it should be done in a vertical manner to the longitudinal axis of the specimen. The length of each specimen should be measured and then the pressure of  $36 \pm 2\text{MPa}$  should be exerted to each end of the specimen along with its vertical axis. This was done using an EIE51100 in a continuous manner for four hours and in the temperature of  $37 \pm 1^\circ\text{C}$ . The schematic representation for measuring the creep is shown in Fig. 2. The creep strains were calculated using the following equation:

$$\text{Creep} = (L_4 - L_1)/L_0$$

where  $(L_0)$  is the original length of the

specimens;  $(L_1)$  is the creep strain after 1h and  $(L_4)$  is the creep strain after 4h. All the compressive strength and creep value data were the average of ten tests and the amount of creep was calculated with an approximation of 0.1.

In order to measure the Vickers hardness, the required specimens were prepared and the samples were stored in an incubator for 24 and 168 hours at the temperature of  $37 \pm 1^\circ\text{C}$ . The measurement of the Vickers hardness was done using a micro-hardness tester N830020 MT. Three samples of each material were prepared for testing the micro-hardness. One end of each sample was first manually grinded by the sand paper No.320, then the process continued by sand papers No. 800, 1200, 2400 and 4000 using aqua lubricant. Finally, it was finished using  $0.3\mu\text{m } \alpha\text{-Al}_2\text{O}_3$ . 5 dents created on the polished surface of the specimen by an effective force of 100 g for 30 seconds. The resultant diametrical lengths of the effect point were determined and the Vickers hardness was read using the standard tables. In order to measure the hardening time of the specimen, amalgamation was conducted in plastic capsules under the above-mentioned conditions (Table 2). Then, the amalgamated amalgam mass was taken out of the capsule and compressed using the thumb and index fingers. This process continued until the mass was crushed. The length of the time for this action, from the beginning to the end, determines the hardness or softness of the amalgam. The hardening time was measured by chronometer. For measuring Hg release from the amalgam, the samples were immediately weighed by a scale of

Table 2. Some characteristics of dental amalgam alloys.

Dental amalgam	Ratio of the powder to Hg	Triturating and grinding time (Sec)	Amalgamator
$C_1$	1/0.8	12	Silamat
$S_1$	1/0.8	12	Silamat

0.0001 g accuracy (Mettler HK 160). The weight of the amalgamated samples was measured in 24 hours, 168 hours, 15 days, 30 days and 45 days, during which the temperature was kept between 36 and 38. The difference between the weight of the acquired samples and that of the initial samples showed the amount of Hg release. The microstructure and chemical analysis were studied using a Scanning Electron Microscope (model Camscan MV2300).

### 3. RESULTS AND DISCUSSION

The acquired results from the compression strength tests at 1, 24 and 168h are shown in Table 3. According to the ADA manual No. 1, the lowest acceptable level for one-hour and 24-hour compression strengths is 80 and 300 mega Pascal, respectively. The results of the analysis reveal that, compared with the reference sample, the 1-hour compression strength increases by 16%, 24-hour compression strength by 8% and 168-hours compression strength by 11 %. Although the average compression strength increased by time in a non-linear form after 24 hours, this amount did not make any salient



Fig. 3. Total mercury released by vaporization during setting.

changes after one week or so. The acquired results from the measurement of the dimensional changes are presented in Table 3. In the No.1 ADA manual, the limited dimensional changes are to be determined by  $\pm 20 \mu\text{m/cm}$  or between  $-1.5$  and  $+2\%$ . After a short time, about 20 minutes after the amalgamation, there was an initial contraction in the amalgams which was due to solving Hg in the alloy particles. After this period, the expansion occurred, which was due to the formation of intermetallics. But, the final dimensional changes were negative. Another

Table 3. The mechanical and physical properties of the two dental amalgams,  $C_1$  and  $S_1$ .

Mechanical property	ISO specification	$S_1$	$C_1$
1 h Compressive strength (MPa)	Minimum 50	200	232
24 h Compressive strength (MPa)	Minimum 300(<15%)	467	504
168 h Compressive strength (MPa)	None	487	540
1 h Modulus of elasticity (GPa)	None	2.22	2.33
24 h Modulus of elasticity (GPa)	None	3.31	3.76
168 h Modulus of elasticity (GPa)	None	3.58	3.79
24 h Vickers hardness number	None	150	160
168 h Vickers hardness number	None	160	170
Static creep (%)	Maximum 3.00	0.26	0.13
Setting dimensional change (%)	-1.5 to +2.0	-0.06	-0.05
Setting time (min)	None	3.5	3.5



Fig.4. SEM micrographs and particle size distributions of  $C_1$  and  $S_1$  amalgam alloy powders.

point is the existence of more contraction in the laboratory sample  $C_1$  because of Hg's quick reaction with the alloy; hence the matrix phase was formed in the first hour. The results obtained from the creep test on the samples are shown in Table 3. Even after the amalgam became stiff and hard, its elasticity feature or permanent change in the shape was reflected under static loads. According to the ADA manual No. 1, the acceptable creep level in a dental amalgam should be at last 3%. Therefore, the laboratory sample  $C_1$  which had a less creeping degree and showed the maximum compression strength through 7 days demonstrates a better clinical performance in the loading with low speed. The results of the micro hardness done on the samples are shown in Table 3.

The 24-hour Vickers hardness after mixing, for the samples  $S_1$  and  $C_1$ , were 160 and 170 HV, respectively, which shows a significant difference. There was no significant change in the Vickers hardness after one week. The hardness will experience no change after 30 days.

The reason for the lower Vickers hardness of the  $S_1$  sample in comparison with the laboratory sample  $C_1$  can be attributed to its slower hardening reaction. This can be a reason for the lower compression strength and lower hardness in the beginning stages. The results obtained from measuring the samples' hardening time are shown in Table 3. As can be seen, the hardening time of the  $C_1$  is equal to that of  $S_1$ . One reason for the reduction of the hardening time in dental amalgams is the increase in the amount of silver and decrease in the amount of tin. In  $C_1$  alloy, because of more amount of silver in the alloy, the hardening time is expected to be shorter but, using the heat treatment on the alloy, the hardening time increased and the hardening time in this alloy was roughly as the same as that of  $S_1$  alloy. If more Hg is used for the amalgamation, the hardening time still will increase. The resulting diagram of the change measurement in the weight of the samples is shown in Fig. 3. In these samples, the weight changes are very subtle and the samples showed a minor Hg release. The

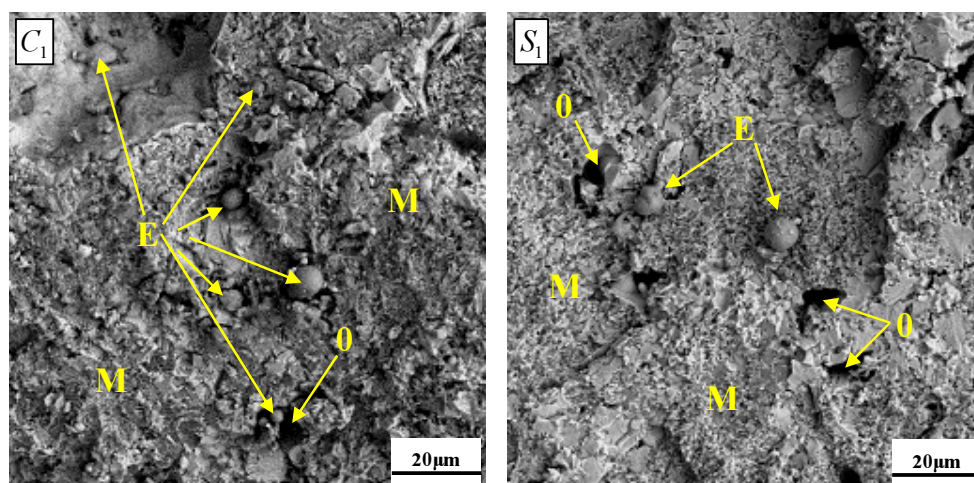
weight changes of the  $C_1$  sample are far less than those of the  $S_1$  sample in the measurement times. This, by itself, is a very positive advantage. In any case, if the recommendations put forward about the Hg hygienic situations are followed, body will show no harmful or incompatible reactions.

The morphology and distribution of the particle sizes of  $C_1$  and  $S_1$  amalgams are shown in Fig. 4. Both of the atomized particles of the combination of Ag-Cu-Sn of  $C_1$  and  $S_1$  alloys are spherical in shape and are kept in equal atomized conditions. The average size of the atomized  $S_1$  alloy ( $19\mu\text{m}$ ) was bigger than that of  $C_1$  alloy ( $11\mu\text{m}$ ), which was possibly due to the higher melting point of the metal of  $S_1$  alloy which created higher viscosity in the metal. All of the atomized particles are usually used for making the amalgam alloy with the exception of some particles bigger than 75 microns. These cases are very rare and are crushed using a ball mill. Although the ratio of the powders to existing Hg for the amalgamation is always in the range of 0.8 to 0.86, a little more Hg will be needed while the pellet matrix alloys are used for the mixing process. This is possibly due to the bigger area of the irregular pellet particles. As the picture shows, the irregular particles of  $S_1$  alloy are more than those of  $C_1$  alloy.

The shape of the particles is an important

factor in determining the optimum ratio of powder to Hg content. The more regular and spherical are the particles, the lower ratio could be applied and the less Hg could be used. As explained before, the amalgamation process happens faster in  $C_1$  alloy, which is because both tinier and more spherical particles react with Hg and create  $\gamma_1$  phase or matrix faster; thus the amalgamation process completes faster. The mechanical compression of the amalgam's alloys during the operation decreases the tendency of the amalgam to stick to the dental instruments. In the beginning and after softening and grinding, the amalgams of the prepared samples were not very soft and fine during the compression. Also, they were hardened in 3 minutes after the softening process finished, which is not very fast. This interval allows the dentists to have enough time for repairing the damaged tooth. These changes are not observed in the Gallium-based alloys. In fact, this type of alloy gets hardened and crushable very fast after the softening process finishes. Also, this type of alloys is a little formable. The reduction in plasticity and difficulty during the compression and the possibility of joining the internal holes in the  $C_1$  and  $S_1$  amalgam alloys are not observed.

So there would be no reduction in the resistance and strength of the sample. As is shown in Fig. 5, there are only a few internal



**Fig. 5.** SEM micrographs of the fractured surface of  $C_1$  and  $S_1$  amalgam specimens prepared by: mechanical condensation and fractured under compression. The embedding matrix (M) contains porosity (O) amongst the unreacted cores of the powder particles (E).

holes in the samples, joining of which would be quite unlikely. The experimental sample is stronger and more resistant than the S1 sample, which is due to the existence of more untreated particles in the experimental sample and the smallness of the particles. The pressure exerted through mechanical compression was 14MPa which is more than manual compression; therefore, the mechanically compressed samples are more compact and compressed and there would be just a little internal porosity in these specimens.

#### 4. CONCLUSIONS

The obtained results from the present study could be summarized as follows:

1. The conducted heat treatment on the samples led to the release of created tensions in the powder particles during the production process, increase of the size of the grains, reduction in the speed of the reaction between the powder and Hg, sterilizing the powder of the amalgam alloy and mitigating and improving the shelf life of the production.
2. The final compression strength gained after 7 days is the maximum in the experimental alloy and the difference between the strength in other alloys is fairly small.
3. There is no considerable dimensional change between C<sub>1</sub> and S<sub>1</sub> samples.
4. The C<sub>1</sub> sample amalgam, which shows less creeping and more compression strength than others, demonstrates a better clinical performance while pouring slowly.
5. The obtained results from the weight changes in the samples show that the changes in the weight are very small and the samples showed a minor Hg release.
6. It is observed that the C<sub>1</sub> sample is stronger than the S<sub>1</sub> sample, which is due to the existence of more untreated particles and the C<sub>1</sub> sample's smaller sizes.
7. Compared with the S1 alloy, the small and sphere-like particles of C<sub>1</sub> alloy reacts faster with Hg; so α1 phase is made faster. Consequently, the amalgamation process happens faster in C<sub>1</sub> sample.

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