The Copper concentration variation to physical properties of high copper amalgam alloy

Aminatun
Department of Physics Faculty of Mathematics and Physics Airlangga University
Surabaya - Indonesia

ABSTRACT

The function of copper (Cu) inside amalgam is to increase hardness and impact force and to decrease thermal expansion coefficient. In general, amalgam which is used in dentistry and available in the market is contain Cu 22%, while the maximum Cu concentration is 30%. It is necessary to determine the concentration Cu does generate the best physical properties to be used as dental restorative agent. Amalgam is made by mixing blended-metal Ag-Sn-Cu (with Cu concentration of 13%, 21%, 22%, and 29%) and Hg, stirred manually in a bowl for 15 minutes,leave it in temperature 27°C for 24 hours to become hardened. The result of X-Ray Diffractometer (XRD), analyzed by Rietveld method and Rietica program, shows amalgam with Cu 29% concentration for Cu_3Sn compound density is 31.790 sma/Å^3, for Ag_2Hg_3 compound is 41.733 sma/ Å^3, a Cu_3Sn relative weight percentage of 43.23%, Ag_2Hg_3 of 54.54%, Cu_7Hg_6 of 2.23% and hardness of Cu 29% is 90.700 ± 0.005 kgf/mm^2. These numbers are the highest values on Cu 29% concentrations compared to other copper concentration variants. Whereas amalgam thermal expansion coefficient on Cu 29% is (2.17 ± 0.91)10^{-3} mm/°C is the lowest value compared to other Cu concentration. The conclution is that adding Cu concentration into amalgam will increase density value, Cu_3Sn relative weight percentage, hardness level and will decrease amalgam thermal expansion coefficient. Amalgam 29% Cu concentration has better physical properties compared to amalgam Cu 22% concentration.

Key words: *amalgam, Cu, density, hardness level, thermal expansion coefficient*

Correspondence: Aminatun, c/o: Jurusan Fisika – FMIPA Universitas Airlangga. Jln. Mulyorejo, Sukolilo Surabaya 60115, Indonesia.

INTRODUCTION

Amalgam is an alloy of mercury (Hg), silver (Ag), tin (Sn), copper (Cu) and zync (Zn) metal compounds.[1] Based on the concentration of Cu in the alloy, amalgam is divided into two types, conventional and high copper amalgam alloy.[2] The conventional amalgam contains lower Cu concentration (0–6%) and high copper amalgam alloy contains higher Cu concentration (12% or more).[2,3] Based on the concentration of zync (Zn), amalgam is divided into 2 types i.e. the blended alloy type with 1% zync content and composition alloy with 0% zync content. Amalgam high copper alloy has contained more than 12% copper (Cu) concentration and 0% zync (Zn) concentration (no mixture of Zn inside amalgam).

The presence of Cu in amalgam will form Cu_3Sn compound replacing Sn_7Hg which has a corrosive nature and weakens amalgam's hardness. Cu inside amalgam can perform a reaction with Sn creating a compound of Cu_3Sn, so that the newly formed amalgam is not easily corroded and its marginal strength is better than the conventional amalgam (amalgam without Cu). Furthermore, Cu increases amalgam's hardness and its impact force and decreases amalgam thermal coefficient.[4] The more Cu inside amalgam, the more amalgam's impact force and hardness will be. Copper (Cu) inside amalgam is presented as part of Ag-Sn compound with definite concentration from dental factories or there is also another presentation as a separate particle to be added (add-mixed) according to one's desired concentration.

In practical use, amalgam in dentistry is amalgam with Ag-Sn-Cu elements formed by dental factories and the circulating amalgam in the market is the Cu 22% concentration. In high copper amalgam alloy, the permissible Cu concentration is between 12–30%. For that reason, this research applies constant concentration of Ag-Sn compound added with varying Cu concentration of 13%, 21%, and 29% with one hope to generate a better quality amalgam. This research expects to give information on what Cu concentration in amalgam which will produce better physical properties compared to amalgam in the market.

MATERIALS AND METHODS

This is an experimental laboratory research done in the Material Physical Laboratory of the Faculty of Mathematics and Physics of both Airlangga University and the Institute of Sepuluh November and also at the Research Center of the Institute of Sepuluh November. Material were used powder of Ag-Sn-Cu compound, Ag powder, Sn and Cu powders with 98% purity, thick paper, the softest sand paper, liquid Hg, aquadest, acetone and NaCl of 98% purity.

Utilized tools were a small-sized bowl for the Ag-Sn compound powder, amalgam stirrer, plastic cast fitting to sample, scissor, tray and plastic pipette, X-Ray Diffractometer (XRD), Microhardness Vickers Test Future Tech FM 7, and thermal expansion coefficient test tool.

Sample was blended of 5 grams Ag-Sn-Cu powder in weight comparison 3:1:1, along with dental factory composition which is mixed with Hg liquid equal to the weight of Ag-Sn-Cu compound (1:1). Stirred manually in the bowl using amalgam stirrer for 15 minutes (until the sample homogenous) and leave for 24 hours in room temperature to harden, will produce sample with Cu concentration similar to the dental factory (22%).[3]

Five grams Ag-Sn powder of dental factory composition is added separately (add-mixed) with varying Cu concentration of 13%, 21%, and 29%. Then, it is stirred manually for ±15 minutes until homogenous and leave it to harden in room temperature (27 °C) for 24 hours.[3]

The four results of the above process (with Cu concentration of 13%, 21%, 22%, and 29%) were printed in plate forms, each with 3 different sizes i.e. 2 cm × 1.5 cm for measuring the level of hardness, 5 cm × 5 cm for measuring X-Ray Diffractometer, and 2 cm × 0.2 cm for measuring thermal expansion coefficient. The samples were pressed with the tip of stirrer to obtain samples in plate forms and a soft sand paper were used to smooth their surfaces. Afterwards, the four samples were characterized with XRD test, with level of hardness measurement and with thermal expansion coefficient.

XRD was used to obtain information pertaining to amalgam composing compound and impurity phases. Amalgam samples of 5 cm × 5 cm were put on XRD holder and X-Rayed. The diffraction results are recorded for 20 certain angles acquiring a curve of the correlation of X-Ray diffraction intensity towards 20 diffraction angles. The curve was analyzed qualitatively and quantitatively. Qualitative way is to determine the amalgam composing compound by comparing to Joint Committee on Powder Diffraction Standard data (JCPDS). Furthermore, to find out the density and the relative weight percentage of each element is done by Rietveld method and Rietica program.[5,6,7] The XRD test was performed on all four samples.

Measuring the level of hardness was used Micro Vickers Hardness (MVH) test tool with procedures as follows: the 2×1.5 cm^2 amalgam sample was pressed with a pyramidal shape diamond in 136° slanted angle. The penetration on sample surface leaves diagonal bundles which can be observed by MVH test tool as d_1,d_2, P values. VHN (Vickers Hardness Number or sample hardness level) can be calculated with formula

$$\text{VHN} = 1.854 \frac{P}{d^2} (\text{kgf/mm}^2).$$ [8]

Level of hardness test is performed on all four samples with similar procedure.

This is the procedure to measure thermal expansion coefficient: the 2×0.2 cm^2 amalgam sample is immersed in water, the water is heated until sample's temperature reaches 37° (T_1), then the amalgam is taken out and measured. The measurement at that time is the initial amalgam length (L_1). Afterwards, amalgam is re-immersed in water, the water is heated until sample's temperature reaches 60 °C (T_2), then amalgam is taken out and re-measured, that is the final length (L_2).[1,9]

Grounded on T_1,T_2, L_1, and L_2, the thermal expansion coefficient can be counted with formula:

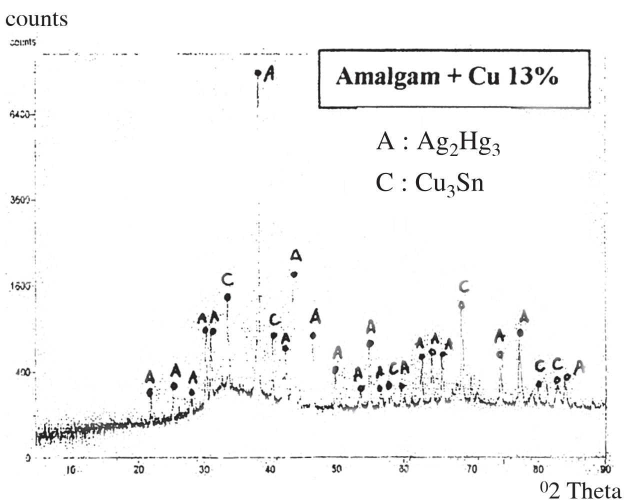
$$\alpha = \frac{\Delta L}{L_1 \Delta T}$$

The Thermal Expansion Coefficient test is performed to all four samples.

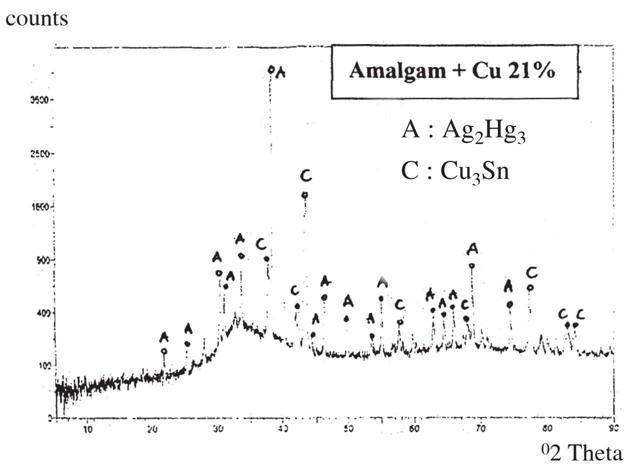
RESULT

X-Ray Diffractometer test result of the four samples is shown in Figure 1(a), (b), (c), and (d).

Based on XRD test result, two analyses can be conducted i.e. qualitative and quantitative analyses.



(a)



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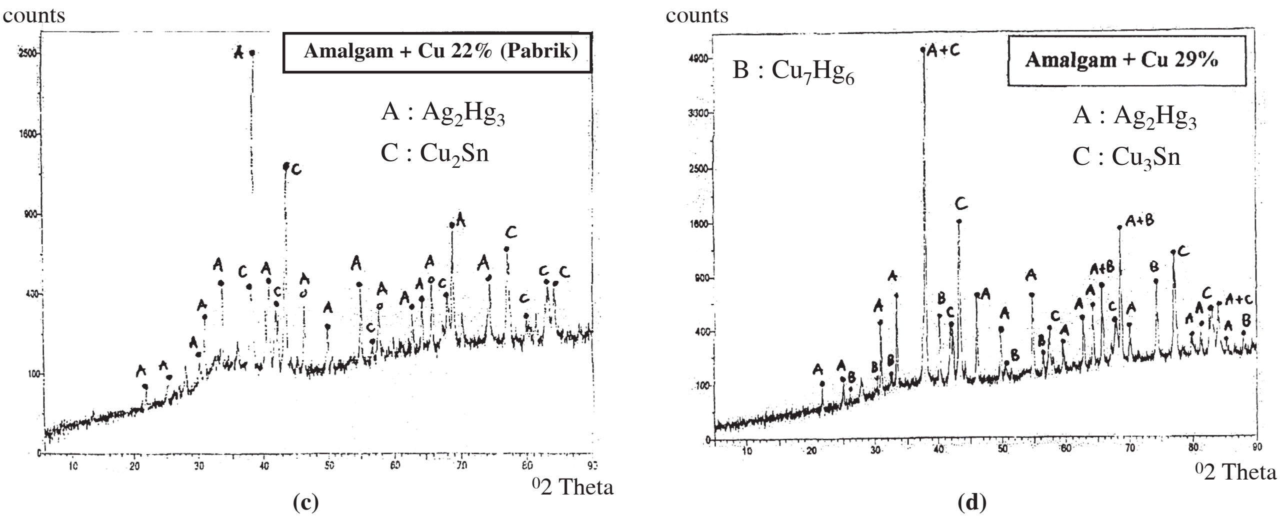

Figure 1. XRD spectrum of four samples. (a) XRD spectrum of amalgam Cu 13%; (b) XRD spectrum of amalgam Cu 21%; (c) XRD spectrum of amalgam Cu 22% (factory); (d) XRD spectrum of amalgam Cu 29%.

Qualitative analysis is done by search matching the spectrum of XRD test result with Joint Committee on Powder Diffraction Standard (JCPDS) data to find out the phases inside amalgam (identification phase). Quantitative analysis is meant to know the relative weight percentage of each phase inside amalgam and it is conducted with Rietveld analysis method. Rietveld method is an analysis method using search-match of calculated diffraction pattern (model data) and measured diffraction pattern (data from experiment's result).[10] One of the soft-wares of this method is Rietica program. Assissted by Rietica program and supported by International Crystallography Standard Database (ICSD) crystallographic data , one can calculate the relative weight percentage of each amalgam composing compound. The compounds composing amalgam are Cu_3Sn and Ag_2Hg_3. Special condition on amalgam Cu 29%, besides having Cu_3Sn and Ag_2Hg_3, it has another compound, i.e. Cu_7Hg_6 (Table 1 and Figure 2)

Based on crystallography data (ICSD), the structure of crystal Cu_3Sn is hexagonal with lattice parameter $a = b \neq c$; the structure of crystal Ag_2Hg_3 is cubical with

Table 1. Relative weight percentage of amalgam composing compound high copper type single composition alloy in Cu concentration variation

No.	Cu concentration (%)	Relative Weight (%)		
		Cu_3Sn	Ag_2Hg_3	Cu_7Hg_6
1.	13	7.74	92.26	-
2.	21	40.52	59.48	-
3.	Factory (22%)	42.91	57.09	-
4.	29	43.23	54.54	2.23

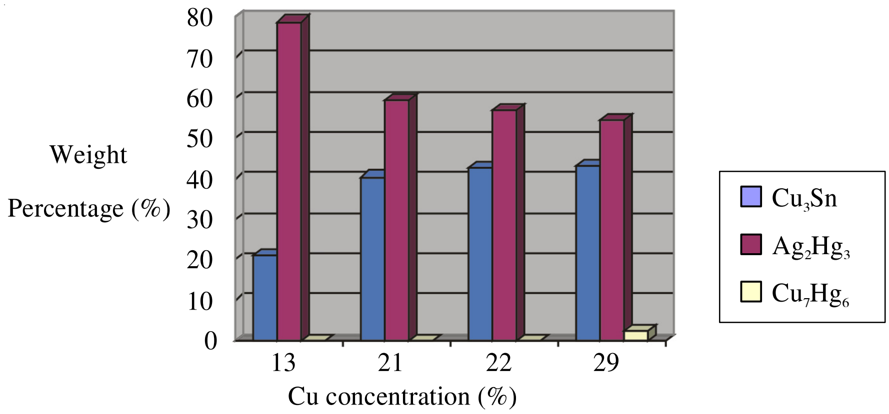

Figure 2. Graph of amalgam composing compound relative weight percentage on Cu concentration.

Table 2. Lattice parameter for high copper amalgam alloy with Cu concentration variation

No.	Cu concentration (%)	Latice Parameter		
		Cu_3Sn (Å)	Ag_2Hg_3(Å)	Cu_7Hg_6 (Å)
1.	13	a = b = 7.1 ; c = 8.4	a = b = c = 9.9	-
2.	21	a = b = 7.3 ; c = 7.8	a = b = c = 9.9	-
3.	Factory (22%)	a = b = 7.3 ; c = 7.8	a = b = c = 10.0	-
4.	29	a = b = 5.3 ; c = 5.8	a = b = c = 6.9	a = b = 5.3 ; c = 5.1

Table 3. Density and volume size of composing high copper amalgam alloy in Cu concentration variation

No.	Cu concentrate 9%0	Density (sma/ Å^3)		Volume size (Å^3)	
		Cu_3Sn	Ag_2Hg_3	Cu_3Sn	Ag_2Hg_3
1.	13	9.074	14.235	369.3	999.990
2.	21	11.876	14.335	365.9	999.999
3.	Factory (22%)	12.455	14.641	364.9	998.8
4.	29	31.792	41.733	143.3	341.0

lattice parameter a = b = c; and the structure of crystal Cu_7Hg_6 is trigonal with lattice parameter a = b ≠ c. The value of each lattice parameter can be seen in Table 2.

Based on the output result of Rietveld analysis method, the density of each sample can be found (Table 3). Grounded on table 3, a diagram of each density of amalgam composing compound in Cu concentration variation, can be made (Figure 3).

Adding Cu concentration will decrease amalgam volume size and increase the density value. This is in accordance with the theory: density is in reverse proportion with its volume size. Amalgam Cu 29% concentration has the smallest volume size so that it has the highest density of each composing compound.

The measuring result of amalgam high copper type single composition alloy sample thermal towards varying Cu concentrations with an initial temperature of 37 ºC and final temperature 60% is presented in table 4.

The result of level of hardness test using Vickers Hardness is presented in table 5.

The addition of Cu concentration has elevated amalgam level of hardness. Amalgam high copper type single composition alloy with Cu 29% concentration possesses the highest level of hardness, i.e. 90.70 ± 0.05 kgf/mm².

DISCUSSION

As seen in table 1 and figure 2, amalgam relative weight percentage, particularly Cu_3Sn, has continually increased

Table 4. Thermal expansion coefficient of amalgam high copper type single composition alloy in Cu concentration variation

No.	Cu concentration (%)	Thermal Expansion Coeffisient (°C)
1.	13	[(3.48 ± 0.17) 10^{-3}]
2.	21	[(3.04 ± 0.13) 10^{-3}]
3.	Factory (22)	[(2.61 ± 0.16) 10^{-3}]
4.	29	[(2.17 ± 0.91) 10^{-3}]

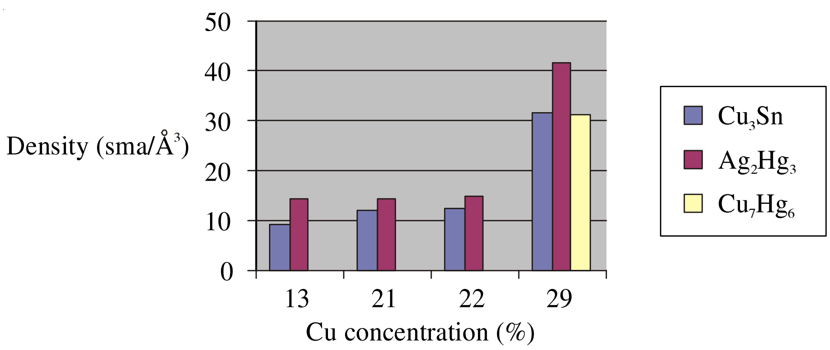

Figure 3. Graph of the correlation between each density of amalgam composing compound towards Cu concentration.

Table 5. Level of hardness of high copper amalgam type single composition alloy in Cu concentration variation

No.	Cu concentration (%)	Level of Hardness (kgf/mm^2)
1.	13	(60.30 ± 0.05)
2.	21	(66.90 ± 0.05)
3.	Factory (22)	(82.70 ± 0.05)
4.	29	(90.70 ± 0.05)

along with the addition of Cu concentration. The extent of relative weight percentage of each compound is closely related with mixing and stirring phase, although in amalgam Cu 29% occurs Cu_7Hg_6 (2.23%), it still does not decrease Cu_3Sn relative weight percentage. The occurrence of impurity factor is assumedly due to non-optimum mixing and stirring process producing non-homogenous sample. The copper is supposedly bonding with Sn instead of Hg. Based on table 3 and figure 3, there is an increase of amalgam density caused by the increase of Cu concentration after Cu is being added into AgSn + Hg. The reason of this occurrence is the granule of amalgam composing particles are not the same size, where any Cu and Ag-Sn-Hg particles are mutually complementing during the mixing and stirring phase. Ag_2Hg_3 compound density is higher than Cu_3Sn compound, so that the micro structure of Ag_2Hg_3 is more dense than Cu_3Sn. Thus, the most dense micro structure of the sample is amalgam with 29% Cu concentration. Mercury (Hg) is a neurotoxic agent. On one of previous researches, the amount of ejected Hg from amalgam which caused negative effect on cognitive (especially on children) was observed. Numerous new studies published in the weekly news of the American Medical Association have stated the safety assurance for amalgam use as dental filling.[11]

Based on the measurement of thermal expansion coefficient (Table 4) one can see that more concentration of Cu will result in the lower value of thermal expansion coefficient. Accordingly, the Cu concentration has a significant impact on thermal expansion coefficient. This physical property is related to the density of amalgam composing compound. If the amalgam becomes more dense, the amalgam composing compound inter-atom bond, also becomes stronger that makes thermal expansion coefficient decreases.

High thermal expansion coefficient in amalgam will cause amalgam to be easily cracked, thus the smaller thermal expansion coefficient, the better amalgam quality is to be used as a restorative agent.[12] Based on thermal expansion coefficient in this research, the best quality sample for dental restorative is Cu with 29% concentration.

The density of amalgam composing compound becomes bigger corresponding to more added Cu. Amalgam with 29% Cu has more solid micro-structures giving impact on amalgam to yield a higher level of hardness. It is deducted that amalgam with Cu 29% is the most durable to receive permanent pressure i.e. mastication load.

Based on physical properties analyses i.e. density, weight percentage, level of hardness and thermal expansion coefficient which are already done, the added Cu in amalgam had increased relative weight percentage of amalgam composing compound, density and level of hardness. Whereas adding Cu percentage can cause a smaller thermal expansion coefficient. This condition fits the physical properties of Cu i.e. that adding Cu concentration into amalgam will increase hardness leveland amalgam strength, and will decrease amalgam thermal expansion coefficient.[12]

Amalgam with the best physical properties in this research is amalgam with 29% Cu concentration, so that this type can be considered as restorative agent which is inexpensive, durable to bear the mastication load and has a small thermal expansion coefficient.

The conclution of this research that adding Cu concentration into amalgam will increase amalgam density value, Cu_3Sn relative weight percentage, hardness level and will decrease amalgam thermal expansion coefficient. Amalgam Cu 29% concentration has better physical properties compared to amalgam produced by factories (Cu 22%), fits to be used as dental restorative agent. It is necessary to do further studies to complete the basis of amalgam quality determination by observing corrosive durability and impact force.

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