# Effect of ZrO<sub>2</sub> addition on the corrosion resistance of galliumbased restorative

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### Abstract

Specimens of a gallium-based dental alloy were prepared with different liquid parts (Ga, GaSn) and different  $ZrO_2$  addition particle sizes (nano and micro) and their effect on the corrosion resistance of the filling was explored. The solid part was admixed from a low copper alloy and metallic glass of silver copper eutectic (1/3rd Low Cu + 2/3rd Ag–Cu eutectic). The low copper alloy comprising 66 wt% Ag, 30 wt% Sn, 4 wt% Cu and Zn was added at a constant weight of 1.2 g per cast. The specimens were prepared according to ADA specification no. 1 and stored at  $37\pm1^{\circ}$ C. The corrosion test was carried out according to ASTM standard (G5 – 87) and at  $37\pm1^{\circ}$ C. Two types of electrochemical tests were made: Open Circuit Potential (OCP) – time measurements, and potentiodynamic polarization in artificial saliva at  $37\pm1^{\circ}$ C. The results obtained show that  $E_{corr}$  is shifted in the positive direction and the mean corrosion current densities decrease with  $ZrO_2$ , and with a change from Ga to GaSn.

*Keywords:* gallium restorative, corrosion,  $ZrO_2$ , potentiodynamic test, dental material, metallic glass, nano, artificial saliva.

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# **1. Introduction**

Dental restorative materials are used to replace lost tooth structure as a result of dental caries and tooth wear. Dental restorative materials are also used for cosmetic purposes [1]. In an attempt to eliminate mercury from direct metallic restorative materials, gallium, which is liquid when alloyed with Sn and In at ambient temperature, is regarded as a substitute [2]. This liquid can then be triturated with a silver-tin-copper alloy powder in the same fashion as dental amalgam [3]. The interest in Ga alloys as a substitute for amalgam has grown in the past years because of the hazard of environmental pollution from amalgam [4]. The use of Ga alloys as a dental filling material was proposed by Puttkamer back in 1928. Despite this, it was not until 1956 that such an alloy was created. However, very little interest in this amalgam that is different from silver was shown by dentists or patients [5]. In 1990, gallium alloy GF (Tokurike Honten, Tokyo, Japan) was introduced to the Japanese markets. By alloying Ga with In and Sn, a ternary eutectic alloy was done and the melting point was reduced down to 10°C. This liquid Ga alloy was triturated with a spherical powder alloy consisting of Ag, Sn, Cu, Pd, and Zn. However, this filling exhibited such marked surface roughness, discoloration and marginal breakdown that a new alloy system was soon introduced. [6, 7]. A non-palladium gallium-based filling alloy marketed as Galloy was presented in Australia. Also, a spherical high Cu alloy powder and a Ga alloy liquid were used. The maker stated a lower setting expansion and enhanced clinical performance as a result of changes in the formulation and recommended procedure [8, 9].

A study using mercury, indium nitrates and gallium, indium nitrate and gallium showed no cytotoxic effect on the mitochondrial activity of mouse fibroblasts. Another study on the effect of corrosion products in short term tests shows a lower cytotoxicity the gallium alloy compared to the amalgam. [10, 11]. The human pharmacology of Ga exhibits significant differences from that of mercury. Ga is not an ordinary constituent of body tissues though it could accumulate in bones that it's a predilection in minute amounts. Ga has a low vapor pressure and is not absorbed by the lungs, nor the skin. However, it is maintained in the lung alveoli [7].

This work aims to evaluate the effect of  $ZrO_2$  addition on the corrosion resistance of a gallium-based restorative.

#### 2. Experimental

#### 2.1. Preparation of liquid alloy for filling

Mercury is used for the preparation of amalgam filling, which is used as a base for comparison with the gallium base filling, in liquid state at room temperature. Mercury melts at -38.83 °C. Gallium that melts at 29.76 °C, *i.e.*, slightly above room temperature, is used to substitute mercury in ordinary dental amalgam. To lower the melting temperature of pure gallium, it was alloyed with tin. Liquid gallium alloys (Ga-Sn) are prepared by progressive addition of fine Sn powder to reach a melting temperature of 20.5 °C [12].

#### 2.2. Preparation of the solid alloys

An admixed alloy (1/3 Low Cu + 2/3 Ag–Cu eutectic) was made by mixing the low copper amalgam powder with silver copper eutectic. The elements of the solid alloy part (Ag, Cu, Sn and Zn) were melted together by an electrical furnace and the process was completed under inert argon gas atmosphere. The cast alloy was composed of 66 wt% Ag, 30 wt% Sn, 4 wt% Cu, as well as Zn that was added at a constant weight of 1.2 g per cast (the weight of each cast was 50 g). The casting operation was done in the following sequence. First of all, Ag was placed in a crucible in the electrical furnace till melting, then Cu was added gradually. The melted metals were left to be super-heated for ten minutes. Next, Zn was added to scavenge oxygen. An inert atmosphere was made immediately after the addition of

Zn by placing an argon gas tube into the crucible, after that Sn was added at once. At the last step, the melted alloy was poured into a heated steel mold.

The second part of the admixed alloy (silver copper eutectic) was made by the melt spinning technique as shown in Figure 1. The operation was done by melting silver, then adding copper particles piece by piece into the melt, which was then poured into a crucible with an orifice of 1 mm in diameter at a distance of 2 mm from a spinning copper wheel. The melt solidified as a ribbon of small thickness. The high speed of solidification prevents the formation of a long-range order, instead a short-range order is formed.



Figure 1. Schematic melt spinning technique.

### 2.3. Heat treatment

The mechanical properties and the corrosion resistance of metallic alloys depend strongly on the microstructural arrangement. The ingots obtained by casting show a dendritic structure. The correlation of the corrosion behavior and mechanical properties will be affected directly by the microstructure parameters. So, in order to achieve uniform distribution of elements and phases in the ingot and to relieve the stresses that formed during solidification, the ingot obtained by casting was heat treated at 400°C for four hours [13]. Heat treatment was performed in an inert atmosphere by using a special-shaped stainlesssteel container to enclose the inert gas.

### 2.4. Powder alloy preparation

Mechanical comminution was used to transform the prepared cast alloys and the ribbon of the melt spin alloy into a powder. This transformation was performed by milling with ceramic balls in a stainless-steel jar. The powders thus obtained are subsequently sieved through a 200 mesh sieve having an aperture of 73  $\mu$ m according to British standard 410 by a mechanical sieving device that was turned on for 10 minutes. Particles with two dimensions smaller than that of the sieve openings can go through the openings of the sieve as it is vibrated, whereas large particles remain in the sieve. The larger powder particles are remilled

to smaller size and sieved again until all the powder passes through the sieve. The sieving process guarantees that there are no foreign materials in the powdered alloys. The ADA specification no. 1 [14] defines that the total allowable number of foreign materials is five particles per ten grams of sieved powder. The average size of the particles was calculated by Bettersize 2000 laser particle size analyzer. The particles in the range between 5 and 25  $\mu$ m size were found to be present in the maximum amount. Figures 2 and 3 show the powder particles shapes. Finally, the powder was heat treated at 100°C to relieve the stresses formed during milling for three hours under a vacuum atmosphere according to C.P. Ju's procedure [15]. Figures 4 and 5 show the powder particles of the ceramic additives of micro and nano powders, respectively.

After such powder preparation, sieving and heat treatment, it is blended and mixed to enhance powder flow and reduce dusting and segregation of alloy powder and additions. This increases the density uniformity and alloy homogeneity.



Figure 2. The shapes of powder particles of the Ag–Cu eutectic obtained.



Figure 3. The shapes of powder particles of the low copper alloy.



Figure 4. The powder particles of the ZrO<sub>2</sub> micro powder ceramic additives.



Figure 5. The powder particles of the  $ZrO_2$  nano powder ceramic additives.

### 2.5. Amalgam specimen preparation

All specimens of dental amalgam and Gallium-based alloy filling were made according to the ADA specification no. 1 [14]. The amalgam samples were made of equal amounts of mercury and powdered alloy, 0.7 g of each, by trituration for 30 s by means of a Ling Chen mechanical amalgamator for the amalgams. For the gallium base restorations, the liquid part of the alloy was made by trituration with 0.7 g of the powder alloy in the same mechanical amalgamator for 20 s.

The ADA provided some standard dimensions for the specimens of 1:2 (4 mm diameter and 8 mm height). The amalgamated material was evacuated on the top cavity of the die. Then it was packed by hand into a Teflon mould with amalgam condenser of 3 mm diameter condensing point. After that, the mold has the anticipated dimensions, setting on a flat surface, and a compressive stress of 14  $MN/m^2$  was applied according to the ADA specification no. 1 [14]. After ejection, the specimen was transferred into an environment maintained at a constant temperature of  $37\pm1^{\circ}$ C.

### 2.6. Microstructure observation

The first specimen was reserved from the low copper alloy after casting another specimen from the same alloy after heat treatment was completed in order to make sure that the heat treatment was satisfactory. Seven specimens were selected for SEM examination of the microstructure and for identifying each phase in the microstructure by the EDS-equipped SEM. A specimen of each alloy was taken and cold mounted using a polyester resin. Standard metallographic procedures were followed. Wet grinding was done on successively finer grades of emery papers (220, 360, 400, 600, 800, 1000, 1200, 1500, 2000, 2500). Polishing was done manually on diamond paste. The specimens were washed completely with water, dried in a hot air blast, and kept for the minimum time possible before etching. A chemical etchant (30 vol% nitric acid) was used to etch the polished specimens [13]. Then the latter were inspected by optical microscopy at 400x magnification. Scanning electron micrography was made using a SEM (TESCAN, Vega III/Czech Republic), Netherlands. The amalgam surface was analyzed quantitatively and qualitatively for the distribution of elements.

#### 2.7 Corrosion test

#### 2.7.1. Electrolytic solution

Artificial saliva (Fusayama solution) with the composition presented in Table 1 [16], which closely resembles the mineral composition of natural saliva, was used as the electrolyte in this study. The solution pH was 6 at 37°C. The constituents of the electrolyte were dissolved in distilled water using a magnetic stirrer.

Compound	g/l	
NaCl	0.4	
KCl	0.4	
CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.906	
NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	0.69	
Na <sub>2</sub> S·9H <sub>2</sub> O	0.005	
Urea	1	

**Table 1.** The composition of artificial saliva used [16].

#### 2.7.2. Open circuit potential (OCP) test

The open circuit potential (OCP) test was made by immersing the working and reference electrode into the electrolyte solution and measuring the potential by a voltmeter connected between the reference electrode and the working electrode. The specimen was the working electrode, standard calomel electrode (SCE) was the reference electrode, and a solution of artificial saliva in 400 ml capacity glass electrolytic cell was the electrolyte. The experimental arrangement for the measurement of open circuit potential is shown in Figure 6. The schematic drawing describes the experimental situation. For each individual specimen, the test continued for about three hours of measuring the open circuit potential  $E_{OC}$ . The first record was taken immediately after immersion, then the voltage was monitored for the entire test period at a five minute interval.



**Figure 6.** A schematic drawing of the experimental setup for open circute potential measurment.

#### 2.7.3. Potentiodynamic polarization test

A three-electrode cell containing the artificial saliva electrolyte used in the experiment was employed to perform the potentiodynamic polarization electrochemical test. A platinum counter electrode and a SCE reference electrode were used, and a specimen served as the working electrode, as set by the American Society for Testing and Materials (ASTM) [17]. Figure 7 shows a schematic diagram of the potentiodynamic polarization cell.



Figure 7. Schematic diagram of the potentiostatic polarization cell.

Polarization experiments were performed using a DY2300 Potentiostat (USA). The potentiodynamic polarization curves were plotted and the corrosion current density ( $I_{corr}$ ) and corrosion potential were calculated from Tafel plots using the anodic and cathodic branches. The test was done by scanning the potential at a scanning rate of 0.4 mV/s from the starting potential of 250 mV beneath the open circuit potential and the scan was continued up to 250 mV over the open circuit potential. The corrosion rate was calculated using the following equation [18]:

Corrosion rate (mpy) = 
$$\frac{0.13i_{\text{corr}}(\text{E.W.})}{A \cdot \rho}$$

where:

E.W. = equivalent weight (g/eq.);  $A = \text{area (cm}^2);$   $\rho = \text{density (g/cm}^3);$  0.13 = metric time conversion factor; $I_{\text{corr}} = \text{current (}\mu\text{A}\text{)}.$ 

# 3. Results and Discussion

# 3.1. Microstructure observation of amalgam alloys

The image in Figure 8 shows the cast alloys before and after homogenization heat treatment. Part (a) refers to the as-cast microstructure while part (b) refers to the microstructure after homogenization heat treatment. The first part of the microstructure shows the characteristics microstructure of the as-cast alloy that contained dendrites and small grains rapidly cooled from the melt, while the second part shows the microstructure after homogenization heat treatment in which the grains are larger and more uniformly distributed than in the as-cast alloy. The chemical gradients in the dendritically cored structure shown was reduced to an

acceptable level by homogenization heat treatment. These structures consist mainly of two regions: matrix in the lighter region and dark regions. These regions represent Ag<sub>4</sub>Sn in the lighter region and a grain boundary in the dark regions.



**Figure 8.** The microstructure of the low copper alloy (a); as cast structure (b) after homogenization heat treatment.

### 3.2. Microstructure observation of the filling alloys

The microstructure of the set filling alloys consists primarily of unreacted particles surrounded by a matrix of the reaction products because the amount of the liquid part used to amalgamate with the alloy particles is smaller than that required to complete the reaction and dissolve all alloy particles. The filling alloys constituents are bonded together by the matrix.

The microstructure of the gallium-based filling  $Ag_{0.72}Ga_{0.28}$  consists of the matrix of light gray color and the darker areas which are the unreacted particles and the ceramics additions. There are also some voids in the matrix when viewed in the microscope. The voids appear as black, out of focus areas.

SEM equipped with an EDS was used. The results are shown in Figures 9–14. At least five regions were selected for EDS. The first region includes the dark gray regions. In all the alloys, this region contains silver, tin and copper alloying elements, in addition to oxygen and a minor amount of zinc. The oxygen was found to form  $ZnO_2$  with zinc as determined from the EDS result. Based on this result, these regions are definitely the unreacted particles. The second region is also dark gray with smaller particle size. The highest element content is silver and copper, this is also the unreacted Ag–Cu admixed part of the powder alloy. The third region is light gray. It belongs to the matrix in the microstructure and contains all the alloying elements of the filling alloy. The black out of focus areas in the microstructure are not phases: they are formed during the forming due to the lack of condensation.

The fifth region is the reaction layer formed on the surface of the powder. Figure 15 shows a closer image of the reaction layer formed by the low copper part of the admixed alloy powder. The same image shows that there is no reaction layer on some particles. These particles without a reaction layer consist of the Ag–Cu eutectic. The reason that there is no reaction layer is attributed to their low activity compared to the low copper alloy part. This is beneficial for the properties because it reduces the amount of the liquid needed to form the paste on amalgamation and reduces the amount of the matrix which is weaker than the unreacted and is identical to the finding by other researchers [19].

This is true for all the tested alloys. For dental amalgam the matrix contains mercury rather than gallium and as shown there is no reaction layer, which is in agreement with other researcher findings [20].

For the first Ga-based alloy that formed at 1:1 liquid to powder ratio it is obvious that the unreacted particles are widely spaced as compared to other alloys. This is because of the high liquid amount that forms larger amounts of the matrix.



Figure 9. SEM image of the dental amalgam.



Figure 10. SEM micrograph for the 1:1 Ga.



Figure 11. SEM micrograph of Ga without addition.



Figure 12. SEM micrograph of Ga 0.5 ZrO<sub>2</sub> Micro.



Figure 13. SEM micrograph of Ga 3 ZrO<sub>2</sub> Micro.



Figure 14. SEM micrograph of Ga 0.5 ZrO<sub>2</sub> Nano.



Figure 15. SEM micrograph of Ga 3 ZrO<sub>2</sub> Micro.

#### 3.3. Electrochemical tests

### 3.3.1. Open Circuit Potential (OCP) – Time Measurements

The OCP *versus* time was measured for the selected filling alloys with respect to SCE in the electrolyte of synthetic saliva at  $37\pm1^{\circ}$ C that simulated the human body temperature. Figures 15–19 show the plots of the corrosion potential of the filling alloys *versus* time. The test time period for all alloys goes up to 180 minutes. The readings were taken every 5 minutes throughout the test period. The mean values of the OCP were recorded using two specimens for each filling alloy.



Figure 15. The OCP–Time plot of amalgam and filling without additions.



Figure 16. The OCP–Time plot of filling with Ga liquid part and ZrO<sub>2</sub> micro addition.



Figure 17. The OCP–Time plot of filling with GaSn liquid part and ZrO<sub>2</sub> micro addition.



Figure 18. The OCP–Time plot of filling with Ga liquid part and ZrO<sub>2</sub> nano addition.



Figure 19. The OCP-Time plot of filling with GaSn liquid part and nano addition.

From the plots of the OCP with time it is noted that during the first minutes of the test, the corrosion potential increases at the greatest speed in this period in every case study. The initial increase normally looks to be due to the formation and thickening of the oxide film on the metal surface, enhancing its corrosion protection ability. Afterwards, the OCP increase rate tends to slow down because of the increase of the film on the metal surface. After this the potential tends to be stabilized and it remains almost stable in time. This is due to an equilibrium between dissolution and deposition.

It is obvious from Figure 15 that addition of tin to the liquid alloy stabilizes the potential with time because it increases the stability of the oxide film on the metallic surface, which in turn increases the corrosion resistance (increases nobility). Addition of  $ZrO_2$  increases the nobility of the filling as noted Table 2. Increasing the  $ZrO_2$  amount affects the potential and the stability of the protective layer.

	-		
Alloy	Liquid alloy	Additive type	Mean E <sub>ocp</sub> , mV
1	Hg	_	-427
2	Ga	_	-564
3	GaSn	_	-296
4	Ga	0.5 % Micro	-577
5	GaSn	0.5% Micro	-360
6	Ga	1% Micro	-575
7	GaSn	1% Micro	-278
8	Ga	2% Micro	-517
9	GaSn	2% Micro	-313
10	Ga	3% Micro	-631
11	GaSn	3% Micro	-557
12	Ga	0.5% nano	-270
13	GaSn	0.5% Nano	-364
14	Ga	1% Nano	-345
15	GaSn	1% Nano	-333
16	Ga	2% Nano	-448
17	GaSn	2% Nano	-515
18	Ga	3% Nano	-491
19	GaSn	3% Nano	-474

Table 2.	Open	circuit	potential.
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#### 3.3.2. Potentiodynamic Polarization

The polarization curves are shown in Figures 20–24 and data from these curves (the related corrosion current densities, corrosion potentials and the calculated corrosion rate) are summarized in Table 3.

Alloy	Liquid alloy	Additive type	Mean Ecorr, (mV)	<i>I</i> corr·10 <sup>-6</sup> , A	Corrosion rate (mpy)
1	Hg	—	-428	0.467	0.045338
2	Ga	_	-241	0.8896	0.178987
3	GaSn	_	-467	0.7834	0.153541
4	Ga	0.5 %Micro	-439	0.762	0.153314

**Table 3.** Corrosion potential ( $E_{corr}$ ), corrosion current ( $I_{corr}$ ) and corrosion rate.

Alloy	Liquid alloy	Additive type	Mean E <sub>corr</sub> , (mV)	<i>I</i> <sub>corr</sub> ·10 <sup>-6</sup> , A	Corrosion rate (mpy)
5	GaSn	0.5% Micro	-200	0.5787	0.113421
6	Ga	1% Micro	-436	0.5896	0.119164
7	GaSn	1% Micro	-311	0.5866	0.115496
8	Ga	2% Micro	-253	0.5674	0.115193
9	GaSn	2% Micro	-247	0.547	0.10821
10	Ga	3% Micro	-552	0.681	0.138876
11	GaSn	3% Micro	-321	0.7698	0.152948
12	Ga	0.5% nano	-204	0.6124	0.123214
13	GaSn	0.5% Nano	-351	0.5807	0.113813
14	Ga	1% Nano	-224	0.5466	0.110473
15	GaSn	1% Nano	-404	0.5689	0.112011
16	Ga	2% Nano	-405	0.5313	0.110391
17	GaSn	2% Nano	-399	0.535	0.105817
18	Ga	3% Nano	-419	0.6456	0.131657
19	GaSn	3% Nano	-422	0.5808	0.115376

The polarization test starts with cathodic polarization where the current density decreases with increasing potential. As the potential reaches  $E_{\text{corr}}$ , active anodic dissolution begins where the current density increases with increasing potential due to the dissolution of the alloys.

Figure 20 shows the potentiodynamic polarization curve for the filling without addition and the dental amalgam. The corrosion current densities ( $I_{corr}$ ) obtained for these alloys are (0.467, 0.8896, 0.7834 · 10<sup>-6</sup> A) for dental amalgam, Ga based liquid filling and GaSn based liquid filling, respectively. It is noted that the lower current density was for dental amalgam followed with GaSn liquid based filling then for Ga based filling hence the corrosion rates are lower for dental amalgam followed with GaSn liquid based filling than for Ga based filling.

Figure 21 shows the potentiodynamic polarization curve for Ga filling with micro  $ZrO_2$  addition. The additions are (0.5, 1, 2, 3) wt%. The corrosion current densities ( $I_{corr}$ ) obtained for these alloys are (0.762, 0.5896, 0.5674, 0.681 · 10<sup>-6</sup> A) respectively. The ( $I_{corr}$ ) first increases as  $ZrO_2$  addition increases up to 2% then decreased for the 3%  $ZrO_2$  addition. This is the same for corrosion rate as shown in Table 4.

Figure 22 illustrates the potentiodynamic polarization curve for GaSn filling with micro  $ZrO_2$  addition of (0.5, 1, 2, 3) wt%. The corrosion current densities ( $I_{corr}$ ) obtained for these alloys are (0.5787, 0.5866, 0.547, 0.7698  $\cdot 10^{-6}$  A), respectively. The corrosion

rates follow the same trend as for the Ga based liquid filling. First it increases up to 2% then drops down.

Figures 23 and 24 show the potentiodynamic polarization curves for Ga and GaSn filling, respectively, with nano  $ZrO_2$  addition of (0.5, 1, 2, 3) wt%. The corrosion current densities ( $I_{corr}$ ) obtained for these alloys are (0.6124, 0.5466, 0.5313, 0.6456 · 10<sup>-6</sup> A) for Ga based liquid fillings and the corrosion current density of the GaSn based filling are (0.5807, 0.5689, 0.535, 0.5808 · 10<sup>-6</sup> A). All this follows the same trend as for the filling with micro sized ZrO<sub>2</sub> addition.

The results presented in Table 3 show that the corrosion behavior of the studied filling alloys varied with the composition of the filling alloys. The results showed that the alloys with Ga liquid part have higher corrosion rates than with GaSn liquid part. Addition of ceramic powder reduces the mean corrosion current densities of the filling, hence, it increases the corrosion resistance for all addition types then dropped for 3% ceramic addition.



Figure 20. The potentiodynamic polarization curve for filling without addition.



Figure 21. The potentiodynamic polarization curve for Ga filling with micro ZrO<sub>2</sub> addition.



Figure 22. The potentiodynamic polarization curve for GaSn filling with micro ZrO<sub>2</sub> addition.



Figure 23. The potentiodynamic polarization curve for Ga filling with nano ZrO<sub>2</sub> addition.



Figure 24. The potentiodynamic polarization curve for GaSn filling with nano ZrO<sub>2</sub> addition.

# 4. Conclusions

- 1. The addition of tin to the liquid alloy stabilizes the potential with time because it increases the stability of the oxide film on the metallic surface, which in turn increases the corrosion resistance.
- 2. The addition of  $ZrO_2$  increases the nobility of the filling. Increasing the  $ZrO_2$  amount affects the potential and stability of the protective layer. According to the composition of the filling alloys, the results showed that the alloys with Ga liquid part have higher corrosion rates than with GaSn liquid part.
- 3. The addition of ceramic powder reduces the mean corrosion current densities of the filling, hence, it increases the corrosion resistance for all addition types then drops down for 3% ceramic addition.
- 4. The corrosion rate of gallium is higher than that of the amalgam. The addition of  $ZrO_2$  also decreases the corrosion rate by 31% at 2%  $ZrO_2$  nano.

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