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Progress Report

ALLOYS OF GALLIUM HAVING POSSIBLE DENTAL USE

by

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Abstract

Plastic alloys which harden at room or mouth temperature were made by combining a liquid gallium-tin alloy with powdered alloys of nickel-copper, nickel-tin, silver-copper, palladium-tin and gold-tin. Alloys of monel-gallium-tin and beta-nickel-tin gallium had the most nearly satisfactory combination of physical properties for dental purposes. High setting expansions were obtained with combinations of the gallium-tin alloy with silver-copper, gold-tin or palladium-tin alloys. Mechanical dispersion hardening by the addition of chromium particles significantly increased the compressive strength of monel-gallium-tin alloys.

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1. INTRODUCTION

In previous investigations [1, 2] it was found that gallium could be combined with a number of powdered metals and alloys to form alloys or "cemented" materials which hardened at room temperature as do dental amalgams.

Physical properties of alloys made by combining a liquid of 89% gallium and 11% tin with powders of copper or of copper and tin showed promise for use as dental restorative materials. However, the corrosion resistance and biological passiveness of these alloys were not as good as desired.

The present report covers investigations of additional gallium alloys. Although no clinically satisfactory filling material has yet been developed, it has been necessary to defer the investigation temporarily. The results reported should serve as a guide to later research in this area.

2. MATERIALS AND METHODS

Gallium metal of 99.9+ per cent purity was used in the investigation described here. The gallium-tin eutectic alloy contained 89 per cent gallium and 11 per cent reagent grade tin. This alloy was prepared by immersing the proper amount of tin in liquid gallium at 37°C. The tin dissolved in 2 hours and the resulting liquid alloy was assumed to have reached equilibrium in 6 hours.

Some of the powdered metals and alloys used were obtained from commercial laboratories and supply houses. Others were obtained by alloying and comminuting in the Dental Research Section at the National Bureau of Standards. Only that portion of the metal or alloy powder that passed a No. 325 sieve of the U. S. Standard Sieve Series was used. All powders were boiled in distilled water for 10 minutes, washed and decanted twice with alcohol, once with ether, and dried on a steam bath. The procedure cleaned and dried the powders and also removed the fines.

The powders and liquids were proportioned by weighing. The solid gallium and the liquid gallium-tin eutectic alloy were placed in a Teflon cup for weighing. After weighing solid gallium liquefied by exposure in a 37°C air bath. The amount of liquid combined with the powders varied from 25 to 50 percent depending upon the metal or alloy powder used.

Hand trituration was done in a glass mortar fitted with a stainless steel pestle. A constant load of 3 pounds was applied to the pestle. Mechanical trituration was done with a mechanical amalgamator fitted with a Teflon capsule. Trituration of alloy combinations in which gallium was used was done at 37°C, while trituration of those using the gallium-tin eutectic alloy was done at 23°C.

The plastic alloys were packed in steel molds using a force of 8 to 10 pounds on a plugger having a face diameter of 2 mm. Pluggers of slightly smaller face diameter than the diameter of the molds were used to express excess liquid in some instances. Packing of the alloys containing liquid gallium was done at 37°C, while packing of those containing the gallium-tin eutectic alloy was done at 23°C.

Determinations of the dimensional change were made at 23°C using unrestricted specimens 10 mm long and 5 mm in diameter in a differential interferometer with a fiducial reading 15 minutes after trituration of the alloy was started. Baby Brinell hardness numbers were determined at 23°C for cylinders 3 mm long and 5mm in diameter that had been stored at 37°C prior to testing. Compressive strengths of cylinders 8 mm long and 4 mm in diameter, stored at 37°C prior to testing were determined at 23°C. The rate of loading the compressive strength specimens was 100 pounds per minute.

3. ALLOYING PROCEDURES AND RESULTS

Nickel-copper alloys. Alloys containing 90 percent nickel-10 percent copper, 80 percent nickel-20 percent copper, and 70 percent nickel-30 percent copper were prepared by induction melting and comminuting the ingots on a lathe. Commercial monel powder (68 percent nickel, 30 percent copper, 2 percent impurities -- mainly iron and manganese) was also used in this investigation.

Commercial monel powder was combined with the gallium-tin eutectic alloy to form plastic alloys which hardened on setting at 23 and 27°C. The 7-day dimensional change of these alloys was approximately 7 microns per centimeter, however the 7-day compressive strength was only 24,000 psi. Cold working the particles prior to hand trituration with the gallium-tin eutectic alloy increased the hardness and compressive strength of the resulting alloy and also decreased the dimensional change slightly. Prior cold working of the particles had little effect on these properties when a mechanical amalgamator was used.

Mixes consisting of 40 to 50 percent gallium-tin eutectic alloy were made. Those with 50 percent gallium-tin eutectic alloy were too wet for easy handling. Hand trituration required 360 revolutions in 180 seconds with a force of 3 pounds. Use of a mechanical amalgamator provided with a Teflon capsule gave more uniform mixing with complete recovery of the mix from the capsule. The time required for trituration varied with the size of the mix with 60 to 70 seconds sufficient for most mixes.

Results of hardness tests on specimens made by hand and mechanical trituration, and for different powder-liquid ratios are presented in Table 1. For the same powder-liquid ratio, mechanically triturated specimens have higher hardness than hand triturated specimens. Increasing the amount of the gallium-tin eutectic alloy increased the setting expansion while longer trituration by hand or use of mechanical trituration reduced the setting expansion and also delayed it (Table 2). The effect of type of trituration and powder-liquid ratio on compressive strength and setting expansion is shown in Table 2. For a given powder-liquid ratio the type of trituration does not affect the compressive strength significantly.

Alloys prepared by combining nickel-copper alloys containing 80 and 90 percent nickel with the gallium-tin eutectic alloy required more trituration than the alloy containing 70 percent nickel. These alloys did not harden rapidly and had 24 hour compressive strengths of less than 9,000 psi. The 70 percent nickel-30 percent copper powder combined with the gallium-tin eutectic and developed a 24 hour compressive strength of 14,000 psi which was comparable to that developed by the commercial monel powder-gallium-tin alloys.

Within 12 days after compressive testing of the 55 percent (90 percent nickel-10 percent copper)-45 percent gallium-tin eutectic alloy, examination of the pieces of the broken specimens indicated that liquid metal droplets had liquated over most of the surface. Examination of all other nickel-copper-gallium-tin specimens did not reveal this phenomenon.

Nickel-copper-chromium alloy. The low setting expansion and relatively low compressive strength of the monel-gallium-tin alloy made this alloy particularly attractive for study of a method of mechanical dispersion hardening. The addition of hard metallic or nonmetallic particles of the proper shape, size, number, and distribution, which gallium wets but with which it does not alloy to the monel powder, could strengthen the alloy.

Chromium was selected for this purpose because of its hardness, lack of alloying action with gallium, and the chemical passivity. Proportions of up to 20 percent chromium powder which passed a No. 325 sieve were mixed with the monel powder. All chromium additions up to 20 percent gave an increase in the 1 hour compressive strength of the monel-gallium-tin (Table 3). The 10 percent chromium addition gave the maximum increase in compressive strength. Addition of 10 percent chromium produced an increase of approximately 30 percent in the strength of the alloy while the 7-day setting expansion was increased from 7 1/2 to 12 1/2 microns per centimeter (Table 4).

Addition of chromium particles to various nickel-gallium, nickel-tin-gallium, and nickel-silicon-gallium alloys decreased their strength when either the gallium-tin eutectic or pure gallium was used. The reason that chromium additions did not harden these alloys is not apparent but it is probably related to the amount of chromium, particle size and shape, and its distribution in the alloy rather than to any alloying action.

Nickel-tin and nickel-tin-silicon alloys. Use of the gallium-tin eutectic alloy instead of liquid gallium for alloying with nickel powder resulted in alloys which hardened slowly and did not attain the high strength of nickel-gallium alloys. The setting expansion of these alloys was about 10 microns per centimeter in 7 days. The presence of tin apparently contributes to the sluggishness of the hardening reactions; however, the presence of tin in a binary nickel-tin alloy would hasten the reaction with the gallium-tin eutectic.

Similarities between the copper-tin and nickel-tin binary phase diagrams indicated that the beta-solid solution of tin in nickel which has a range from approximately 38-42 percent tin might combine with the gallium-tin eutectic. The 60 percent nickel-40 percent tin alloy may be represented by the stoichiometric relation Ni_3Sn. This particular alloy was chosen for study. Alloys of lower tin content in the alpha-solid solution range from 10 to 20 percent tin and can be age-hardened by the precipitation of Ni_3Sn from the alpha-solid solution. A composition 85 percent nickel-15 percent tin was chosen for heat treatment.

Both alloys were obtained by induction melting the proportioned high purity metals in a graphite crucible and allowing the melt to cool in the crucible. The alpha-solid solution alloy was solution treated for 1 hour at 815°C (1500°F), water quenched and aged 8 hours at 595°C (1100°F). This alloy was reduced to powder form by comminuting with a lathe. The brittle beta-nickel-tin alloy ingot was reduced to powder with a diamond mortar and a porcelain mortar and pestle.

Hand trituration of these alloys was difficult because the gallium-tin eutectic did not wet the particles as readily as it did the glass mortar, thus more of the liquid stuck to the mortar and made uniform mixing and removal of the plastic mass difficult. Mechanical trituration for 50 seconds with a mechanical amalgamator provided with a Teflon capsule produced a plastic mass which could be easily removed from the capsule. The combination of 60 percent powder with 40 percent liquid gave the best results for easy packing. Lower liquid contents produced dry crumbly masses while higher contents were too wet and sticky for proper packing. Excess liquid was expressed during packing.

The hardness of the 60 percent beta-nickel-tin-40 percent gallium-tin eutectic alloy increased from 70 Bhn after 24 hours to 98 Bhn at the end of 7 days. This alloy developed the highest 1 hour compressive strength of any of the gallium alloys investigated, but did not increase in strength after setting for 24 hours at 37°C. The 7-day setting expansion of this alloy was 3 microns per centimeter. Results of hardness tests, compressive strength tests and dimensional change measurements are given in Table 5.

The age-hardened 85 percent nickel-15 percent tin alloy, when combined with the gallium-tin eutectic, did not harden enough to attain a 3,000 psi compressive strength in 1 hour so no further testing was done on this combination.

In order to reduce the setting expansion of the beta-nickel-tin-gallium alloy, two methods of adding silicon were attempted. The first method consisted of incorporating the silicon in the alloy by adding 1.5 percent to the properly proportioned nickel and tin and melting the alloy in a graphite crucible. The resulting alloy was powdered in the same manner as the beta-nickel-tin alloy. When combined with the gallium-tin eutectic, the resulting alloy had a slightly lower compressive strength but the same setting expansion as the beta-nickel-tin combination (Table 5). The second method of addition of from 1 to 2 percent silicon powder to the beta-nickel-tin powder drastically reduced the strength of the gallium alloy.

Silver-copper alloys. Although both silver and copper have face-centered-cubic crystal structures, differences in their atomic radii and valence restrict the range of solid solutions formed. Two alloys of this binary system were selected for combining with the gallium-tin eutectic alloy, an alpha-solid solution alloy containing 7 percent copper and the eutectic composition alloy containing 28.2 percent copper. These alloys were obtained by induction melting high purity silver and copper in a graphite crucible, solution heat treating the ingots at 745°C (1375°F) for 1/2 hour and aging at 245°C (475°F) for 6 hours. Filings passing a No. 325 sieve were obtained from the heat treated ingots for combining with the gallium-tin eutectic alloy.

Hand trituration of 70 revolutions in 30 seconds in a glass mortar produced a satisfactory plastic alloy for packing when 35 percent liquid was combined with the powder. These alloys packed easily and excess liquid was expressed during packing. The alpha-solid solution alloy combined with the gallium-tin eutectic alloy did not harden rapidly, while the eutectic alloy hardened rapidly. The setting expansion of the eutectic alloy combination was so rapid during the first hour after trituration that it was impossible to follow it accurately with the interferometer. After about 24 hours, the setting expansion leveled off at approximately 350 microns per centimeter. Compressive strengths and dimensional change of this alloy are given in Table 6.

Palladium-tin and gold-tin alloys. The intermetallic compounds AuSn and Pd_3Sn were prepared by induction melting of the correctly proportioned high purity metals in a graphite crucible. Both of these intermettalic compounds were brittle and were easily reduced to pass a No. 325 sieve through the use of a diamond mortar and a porcelain mortar and pestle.

Previous unpublished data of Smith and Caul indicated that these intermetallic compounds combined with the gallium-tin eutectic to produce alloys of high hardness and superior corrosion resistance to the copper-tin-gallium alloys. In order to further evaluate these alloys, specimens were prepared for dimensional change and compressive strength determinations. Hand trituration of 70 revolutions in 30 seconds under a 3-pound force produced a plastic mass which was easily removed from the glass mortar and packed easily. With the exception of some liquid sticking to the plugger, no liquid was expressed during packing. Although these alloys develop good strength and hardness (Table 7), their setting expansion of 124 u/cm in 24 hours is too high for their consideration in dental applications.

Previous attempts to blend various powdered alloys by mechanical mixing powders had resulted in poor specimens with apparently little cementing of the articles by limited alloying with gallium or the gallium-tin eutectic. Cementing of Pd_3Sn and AuSn powders with the gallium-tin eutectic was accomplished but the resulting strength of these combination alloys was less than that of alloys of either Pd_3Sn or AuSn with the gallium-tin eutectic (Table 8). A rough measurement of the 24 hour dimensional change, based on change in diameter of the compressive strength specimens, is also indicated in this table.

4. SUMMARY OF RESULTS

Two nickel base gallium-tin alloys, 60 percent beta-60 percent nickel-40 percent tin-40 percent gallium-tin eutectic alloy and 55 percent monel-45 percent gallium tin eutectic alloy, have some physical properties which indicate that these alloys could be considered for dental purposes. The beta-nickel-tin-gallium developed a 1 hour compressive strength of 10,700 psi and a 24 hour compressive strength of 30,200 psi. Although there was little increase in the compressive strength of this alloy after 24 hours, the hardness increased from 70 Brinell hardness number after 24 hours to 98 Brinell hardness number after 7 days. The 7-day setting expansion of this alloy was 33 microns per centimeter. Attempts to reduce the setting expansion by addition of silicon as an alloying constituent of the nickel-tin alloy and as a powdered addition to the powdered alloy were not successful. Alloys of 45 percent gallium-tin eutectic alloy with 55 percent monel or 55 percent (70 percent nickel-30 percent copper) did not develop strength rapidly, but their 7-day setting expansion of 4 to 7 1/2 microns per centimeter was the lowest of any of the gallium alloys which hardened to any extent. A 10 percent addition of powdered chromium to the powdered monel increased the compressive strength of this gallium alloy by approximately 30 percent. The chromium addition also increased the setting expansion of the alloy to 12 1/2 microns in 7 days. The strengthening action of the chromium results from its hardness and the distribution of the particles throughout the alloy rather than any alloying action.

The method of trituration and the liquid-powder ratio have some influence on the properties developed by these nickel base gallium-tin alloys. In hand trituration the gallium-tin eutectic alloy wets the surfaces of the particles, mortar and pestle and acts as a lubricant. This lubricating action allows the articles to slide over one another without enough surface contact to break up the oxide film on the surface of the particles. Mechanical trituration results in more uniform mixes and the impacting action in the capsule breaks up the surface oxides of the particles making the wetting action of the gallium more uniform. Increasing the liquid content of monel-gallium-tin alloys increased their hardness, but these alloys were wet and difficult to pack.

Combinations of the gallium-tin eutectic alloy with the silver-copper eutectic alloy, and intermetallic compounds of palladium-tin and gold-tin result in alloys which harden rapidly and attain compressive strengths of over 30,000 psi in 24 hours. The high setting expansion of over 125 microns per centimeter in 24 hours make these alloys unsuitable for dental purposes. These gallium alloys require 20 to 35 percent gallium-tin eutectic alloy and are easier to manipulate than base-metal gallium alloys.

5. CONCLUSIONS

1. The gallium-tin eutectic alloy combines with powdered alloys of nickel-copper, nickel-tin, silver-copper, palladium-tin, and gold-tin to form plastic alloys which harden at room or mouth temperatures.

2. Monel-gallium-tin and beta-nickel-tin-gallium alloys

have the best combination of physical properties for dental purposes.

3. Silver-copper, gold-tin and palladium-tin alloys combine with the gallium-tin eutectic alloy to form rapid setting alloys; however, their high setting expansions make them unsuitable for dental purposes.

4. The strengthening of the monel-gallium-tin alloy by the addition of chromium particles indicates that this mechanical dispersion hardening technique might be used to strengthen other gallium alloys.

5. Sluggish reaction of gallium with powders of solid solution alloys indicates that atomic radii and solubility are important in producing hard alloys.

6. The formation of fast hardening alloys by combining the gallium-tin eutectic alloy with intermetallic compounds containing tin and certain solid solutions containing copper indicates that the presence of copper or tin atoms hastens the setting reaction in these combinations.

6. REFERENCES

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Table 1

Effect of Method of Trituration and Powder-Liquid Ratio on the Baby Brinell Hardness of Monel-Gallium-Tin Alloys

Alloy Composition	Method of Trituration	Baby Brinell Hardness 1 day	7 days
60 Monel-40Ga-Sn E	Hand	53	68
55 Monel-45Ga-Sn E	Hand	60	93
50 Monel-50Ga-Sn E	Hand	70	105
60 Monel-40Ga-Sn E	Mechanical	70	87
55 Monel-45Ga-Sn E	Mechanical	60	98

Above values are the average of two readings.

Ga-Sn E = gallium-tin eutectic

Hand trituration: 3 minutes, 360 revolutions, 3 pounds force.

Mechanical trituration: 70 seconds in Teflon capsule.

Table 2

Compressive Strength and Dimensional Change of

Monel-Gallium-Tin Alloys

Alloy Composition	Method of Trituration	Time after start of Trituration 1 hour	1 day	7 days
		(compressive strength - psi)		
60 Monel-40 Ga-Sn E	Mechanical	5,100	13,200	24,000
55 Monel-45 Ga-Sn E	Hand	6,800	13,200	34,200
55 Monel-45 Ga-Sn E	Mechanical	5,400	17,500	35,000
		(dimensional change - u/cm)		
60 Monel-40 Ga-Sn E	Hand	1	5 1/2	6 1/2
60 Monel-40 Ga-Sn E	Mechanical	0	1/2	4
55 Monel-45 Ga-Sn E	Hand	1/2	1	7 1/2
55 Monel-45 Ga-Sn E	Mechanical	0	1/2	3 1/2

Compressive strength values are the average of at least 2 determinations.

Dimensional change values are individual values or an average of 2 determinations.

Ga-Sn E = gallium-tin eutectic alloy.

Hand trituration: 3 minutes, 360 revolutions, 3 pound force.

Mechanical trituration: 70 seconds in Teflon capsule.

Table 3

Effect of Chromium Additions to Monel Powder on the One-Hour Compressive Strength of Monel-Gallium-Tin Alloys (55 percent powder - 45 percent gallium-tin eutectic)

Chromium addition	1 hour Compressive strength
wt %	psi
0	5,400
5	6,800
10	7,800
15	6,700
20	6,400

All values are results of individual determinations.
Mechanical trituration: 60 seconds in a Teflon capsule.

Table 4

Compressive Strength and Dimensional Change of a Monel-Chromium-Gallium-Tin Alloy [55 percent (90 percent monel-10 percent chromium)-45 percent gallium-tin eutectic]

Time after start of trituration	Compressive strength	Dimensional change
	psi	u/cm
1 hour	8,000	0
1 day	20,300	1 1/2
7 days	44,100	12 1/2

Above values are the average of 2 determinations.

Mechanical trituration: 60 seconds in a Teflon capsule.

Table 5

Hardness, Compressive Strength, and Dimensional Change of Beta-Nickel-Tin-Gallium and Beta-Nickel-Tin-Silicon-Gallium Alloys

Alloy Composition	Time after start of trituration 1 hour	1 day	7 days
	(Baby Brinell Hardness -Bhn)		
60 Ni_3 Sn-40Ga-Sn E	---	70	98
60 (98.5 Ni_3Sn-1.5Si)-40 Ga-Sn E	---	65	95
	(compressive strength - psi)		
60 Ni_3 Sn-40 Ga-Sn E	10,700	30,200	32,000
60 (98.5 Ni_3Sn-1.5 Si-40 Ga-Sn E	9,800	23,000	31,500
	(dimensional change - μ/cm)		
60 Ni_3 Sn-40 Ga-Sn E	1	17	33
60 (98.5 Ni_3Sn-1.5 Si)-40 Ga-Sn E	5	16	31

Above values for 60 Ni_3 Sn-40 Ga-Sn E alloys are the average of 2 determinations. Those for 60 (98.5 Ni_3 Sn-1.5Si)-40 Ga-Sn are individual results.

Ni_3Sn is the beta-nickel-tin alloy.

Ga-Sn E is the gallium-tin eutectic alloy.

Mechanical trituration: 50 seconds in a Teflon capsule.

Table 6

Compressive Strength and Dimensional Change of 65 percent Silver-Copper Eutectic (71.8 percent Ag, 28.2 percent Cu) - 35 percent Gallium-Tin Eutectic

Time after start of Trituration	Compressive Strength (psi)	Dimensional Change (μ/cm)
1 hour	9,300	175
1 day	31,800	347
7 days	41,000	351

Above values are results of 2 determinations.

Hand trituration: 70 revolutions in 30 seconds,
3 pound force.

Table 7

Compressive Strength and Dimensional Change of Palladium-Gallium-Tin and Gold-Gallium-Tin Alloys

Alloy Composition	Time after start of trituration 1 hour	1 day	7 days
	(Compressive strength - psi)		
70 Pd_3Sn - 30 Ga-Sn E	9,900	34,500	39,000
70 AuSn - 30 Ga-Sn E	10,000	33,200	37,900
	(Dimensional change - u/cm)		
70 Pd_3Sn - 30 Ga-Sn E	39	123	161
70 AuSn - 30 Ga-Sn E	37	124	136

Above values are the averages of 2 determinations or individual results.

Ga-Sn E is the gallium-tin eutectic alloy.

Hand Trituration: 70 revolutions in 30 seconds,

3 pound force.

Table 8

One Day Compressive Strength and Dimensional Change of Pd_3Sn and AuSn "cemented" with Gallium-Tin-Eutectic (70 percent powder, 30 percent gallium-tin-eutectic)

Composition of powder Pd_3Sn	AuSn	Compressive Strength 1 day	Dimensional Change * 1 day
wt %	wt %	psi	%
0	100	33,200	2.50
25	75	29,200	2.75
50	50	24,400	3.75
75	25	25,100	3.50
100	0	34,500	2.50

All values are individual results.

* Dimensional change measured as percentage increase in diameter.

Hand trituration: 70 revolutions in 30 seconds, 3 pound force.