In vitro Ageing of Dental Amalgams

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Introduction

Dental amalgam is the most commonly used of all restorative materials in current dental clinic. Nevertheless, the secondary caries has occurred the most frequently around the cavity restoration with amalgam.

Two major causes have been said (Fraunhofer, *et al.* 1975¹⁾) for inducing the failure of the amalgam restorations. One is the operator's unskillfulness such as inadequate cavity preparation or wrong manipulation of amalgam, and the other the defects of the materials themselves. Marginal fracture is one of the definite defects of amalgam causing subsequent secondary caries. Jørgensen (1965)²⁾ explained the mechanism of the marginal fracture by corrosion. Mahler and Terkla *et al.* (1970)³⁾, on the other hand, proposed to lower the creep of the amalgam in order to minimize the marginal fracture. Many brands of amalgams containing high amount of copper have been put on the market on the basis of Mahler's concept. American Dental Association (A.D.A.) specifies to determine the static creep of the amalgam for the specimen stored for seven days. It would be difficult to predict the true aspect of the marginal fracture of aged amalgam by such an early creep value. Effect of ageing as well as corrosive attack must be taken into consideration. Only a few studies were found about this matter (Phillips (1949)⁴⁾, Wilkinson and Haack (1958)⁵⁾, Ohtani (1970)⁶⁾, Jørgensen (1972)⁷⁾, Partel and Boyd (1979)⁸⁾).

In the present study, diametral tensile strength, Knoop hardness and static creep were determined after ageing up to six months to evaluate the effects of the environment, temperature and repeated small amount of compressive loading. All tests were performed for one conventional lathe cut, one conventional spherical, one admixed type of high-copper, and one single-phase type of high-copper amalgam.

Materials and methods

Four typical commercial amalgam systems were employed for this study. They are listed in Table 1. Mercury-alloy ratios and mixing times were chosen on manufacturer's recommendations. Six-tenth grams of alloy and the proper weight of mercury were used to make the specimen of 4 mm ϕ in accordance with A.D.A. specification No. 1.

The amalgam specimens were stored in air, distilled water, saline solution (0.9% NaCl) or artificial saliva at 37°C for some periods of time: one week, one month,

Table 1 Alloys selected for testing

Material	Manu.	Batch	Type	Form	Hg/Alloy
Luna Alloy	G-C	MY 16	conventional	lathe cut	1.67
Hi Atomic M	G-C	NM 5	conventional	spherical	0.75
Dispersalloy	J & J	19 JG	high Cu, admixed	lathe cut	1.00
Dialloy	G-C	JM 10	high Cu, single phase	spherical	0.82

three months or six months. Diametral tensile strength, static creep and Knoop hardness were examined for the specimens after each period of storage.

In order to find the effect of the temperature on these properties of amalgam, the specimens were immersed in artificial saliva at 4, 37, 60°C or alternatively 4 and 60°C cycled by one minute's interval for each period.

Moreover, the same tests were conducted for the specimens which had been subjected to repeated small amount of compressive loading. The loading machine was designed in the laboratory so that the repeated load could be applied on the specimen in the solution at 37°C by the rate of 3600 cycle/hr. The stress of 2.5 kg/cm² was adopted repeatedly to the specimen in the artificial saliva at 37°C for one hour per day from 24 hours after trituration.

Each five specimens were prepared for diametral tensile strength test and Knoop hardness test, and three specimens for creep test.

The diametral tensile strength was measured at the loading rate of 5 mm/min using universal testing machine (Tensilon, Toyo Boldwin LTD) at room temperature.

The Knoop hardness of the amalgam was measured using micro hardness tester (Micro Vickers, Shimadzu Seisakusho LTD, type M).

Twenty hour-creep value was measured in this study using multipurpose compressive loading tester (Seikisha LTD). A stress of 100 kg/cm² was applied to the specimen in air at 37°C for twenty hours.

Micro structure and fractured surface were observed by SEM (JEOL JSM 25) and a phase identification was conducted by energy dispersive spectrum type of X-ray micro-analyzer (KEVEX 5500).

Results

Results are summerized in Tables 2~13. Figures 1~4 show the changes of the diametral tensile strength, Knoop hardness, static creep by ageing in air(AIR), distilled water(DW), saline solution (SS) and artificial saliva(AS) at 37°C, respectively. Three amalgams except Dialloy exhibited a general tendency to decrease in diametral tensile strength from one week to one month. Knoop hardness and static creep showed significant difference among the storage environments at 37°C only for Luna Alloy, while no significant difference could be found in the examined properties for other amalgams as shown in Table 14.

Table 2 Diametral Tensile Strength of Luna Alloy

(Kg/cm²)

	1 week	1 month	3 months	6 months
37°C in Air	344 (46.2)	282 (48.9)	387 (74.9)	307 (31.2)
37°C in Distilled Water	362 (96.6)	288 (64.8)	408 (50.3)	290 (118.3)
37°C in Saline Solution	370 (138.5)	386 (31.1)	375 (79.7)	370 (48.6)
37°C in Artificial Saliva	393 (114.8)	364 (103.7)	398 (75.4)	349 (96.6)
4↔60°C in Artificial Saliva	336 (47.9)	371 (125.6)	313 (46.6)	314 (60.8)
4°C in Artificial Saliva	329 (57.2)	315 (73.7)	349 (84.1)	476 (116.1)
60°C in Artificial Saliva	225 (28.0)	178 (14.2)	223 (33.6)	100 (15.2)
37°C with Loading*	334 (62.1)	322 (66.2)	288 (78.6)	274 (61.2)

* Loading repeatedly in artificial saliva
() SD

Table 3 Knoop Hardness Number of Luna Alloy

	1 week	1 month	3 months	6 months
37°C in Air	588 (121.6)	780 (80.4)	779 (102.0)	986 (169.4)
37°C in Distilled Water	827 (147.7)	619 (112.3)	791 (232.4)	789 (125.0)
37°C in Saline Solution	752 (106.1)	914 (160.5)	1,008 (178.2)	816 (63.9)
37°C in Artificial Saliva	656 (71.9)	583 (102.0)	779 (113.5)	797 (130.8)
4↔60°C in Artificial Saliva	789 (121.4)	612 (71.1)	765 (136.1)	936 (243.2)
4°C in Artificial Saliva	704 (69.1)	805 (184.8)	858 (125.6)	746 (226.8)
60°C in Artificial Saliva	715 (88.3)	692 (129.0)	334 (88.9)	779 (138.2)
37°C with Loading*	966 (312.7)	1,073 (57.7)	999 (81.7)	1,120 (63.7)

* Loading repeatedly in artificial saliva
() SD

Table 4 Creep Value of Luna Alloy

(%)

	1 week	1 month	3 months	6 months
37°C in Air	0.89 (0.120)	1.26 (0.356)	0.73 (0.184)	1.01 (0.310)
37°C in Distilled Water	2.67 (0.978)	1.69 (0.431)	1.46 (0.105)	3.03 (1.382)
37°C in Saline Solution	1.47 (0.116)	2.84 (2.326)	1.30 (0.213)	3.08 (0.978)
37°C in Artificial Saliva	1.18 (0.374)	1.26 (0.238)	3.15 (0.713)	1.99 (0.965)
4↔60°C in Artificial Saliva	0.97 (0.217)	1.40 (0.905)	1.45 (0.093)	1.90 (0.577)
4°C in Artificial Saliva	2.51 (0.370)	3.19 (0.351)	3.44 (1.738)	3.46 (2.794)
60°C in Artificial Saliva	1.70 (0.138)	1.75 (0.686)	0.81 (0.106)	0.74 (0.296)
37°C with Loading*	1.11 (0.185)	2.23 (0.430)	1.99 (0.138)	1.61 (0.113)

* Loading repeatedly in artificial saliva
() SD

Table 5 Diametral Tensile Strength of Hi Atomic M (Kg/cm²)

	1 week	1 month	3 months	6 months
37°C in Air	525 (117.5)	478 (71.4)	558 (22.8)	572 (103.5)
37°C in Distilled Water	417 (69.1)	469 (22.3)	442 (152.2)	555 (53.7)
37°C in Saline Solution	533 (99.7)	417 (76.3)	466 (87.2)	521 (136.6)
37°C in Artificial Saliva	492 (157.2)	426 (134.1)	531 (52.9)	463 (17.2)
4↔60°C in Artificial Saliva	441 (140.0)	382 (89.5)	553 (58.5)	476 (92.5)
4°C in Artificial Saliva	412 (87.8)	370 (65.7)	521 (44.7)	554 (48.1)
60°C in Artificial Saliva	568 (76.0)	544 (54.9)	512 (45.6)	495 (57.5)
37°C with Loading*	420 (102.7)	367 (65.8)	430 (104.7)	449 (106.7)

* Loading repeatedly in artificial saliva

() SD

Table 6 Knoop Hardness Number of Hi Atomic M

	1 week	1 month	3 months	6 months
37°C in Air	1,076 (133.6)	1,011 (152.1)	933 (108.2)	982 (186.0)
37°C in Distilled Water	1,289 (304.1)	964 (129.7)	950 (40.3)	851 (309.0)
37°C in Saline Solution	1,132 (122.6)	940 (108.6)	935 (110.5)	1,080 (117.3)
37°C in Artificial Saliva	1,009 (157.9)	1,140 (106.5)	989 (257.5)	1,078 (133.7)
4↔60°C in Artificial Saliva	892 (120.0)	1,138 (232.7)	989 (64.9)	976 (93.5)
4°C in Artificial Saliva	918 (289.6)	1,113 (117.1)	933 (92.0)	821 (46.6)
60°C in Artificial Saliva	872 (93.8)	853 (31.3)	847 (82.8)	817 (55.0)
37°C with Loading*	782 (115.8)	1,060 (294.2)	1,146 (132.2)	1,220 (186.7)

* Loading repeatedly in artificial saliva

() SD

Table 7 Creep Value of Hi Atomic M (%)

	1 week	1 month	3 months	6 months
37°C in Air	1.16 (0.379)	1.12 (0.330)	0.64 (0.148)	1.06 (0.244)
37°C in Distilled Water	0.89 (0.275)	0.79 (0.238)	0.82 (0.139)	1.03 (0.191)
37°C in Saline Solution	0.92 (0.269)	1.55 (0.754)	0.85 (0.289)	1.57 (0.127)
37°C in Artificial Saliva	1.57 (0.102)	0.94 (0.045)	0.52 (0.170)	1.20 (0.231)
4↔60°C in Artificial Saliva	0.42 (0.257)	0.77 (0.222)	0.82 (0.005)	0.93 (0.611)
4°C in Artificial Saliva	1.43 (0.193)	1.46 (0.529)	1.43 (0.862)	0.70 (0.198)
60°C in Artificial Saliva	1.15 (0.424)	1.05 (0.159)	0.83 (0.196)	0.93 (0.726)
37°C with Loading*	0.36 (0.037)	0.41 (0.212)	0.78 (0.280)	0.47 (0.120)

* Loading repeatedly in artificial saliva

() SD

Table 8 Diametral Tensile Strength of Dispersalloy (Kg/cm²)

	1 week	1 month	3 months	6 months
37°C in Air	327 (83.9)	233 (43.7)	368 (141.4)	356 (140.3)
37°C in Distilled Water	287 (61.0)	264 (36.6)	331 (117.8)	390 (123.5)
37°C in Saline Solution	319 (76.9)	226 (18.1)	302 (46.3)	427 (68.2)
37°C in Artificial Saliva	279 (48.7)	255 (38.3)	262 (85.3)	353 (121.1)
4↔60°C in Artificial Saliva	257 (42.3)	309 (33.9)	347 (67.6)	336 (111.4)
4°C in Artificial Saliva	253 (49.7)	235 (28.4)	272 (51.8)	323 (95.3)
60°C in Artificial Saliva	373 (139.5)	334 (66.6)	331 (83.0)	455 (29.1)
37°C with Loading*	343 (51.9)	300 (97.1)	364 (101.1)	365 (81.4)

* Loading repeatedly in artificial saliva
() SD

Table 9 Knoop Hardness Number of Dispersalloy

	1 week	1 month	3 months	6 months
37°C in Air	1,353 (175.5)	1,103 (191.0)	947 (108.5)	1,324 (118.9)
37°C in Distilled Water	1,006 (246.0)	1,435 (120.9)	1,103 (186.4)	1,375 (181.3)
37°C in Saline Solution	1,199 (158.5)	1,282 (122.4)	1,092 (155.3)	1,312 (149.4)
37°C in Artificial Saliva	1,119 (191.7)	1,265 (127.6)	1,048 (205.9)	1,122 (196.4)
4↔60°C in Artificial Saliva	965 (285.6)	1,261 (84.8)	1,160 (158.4)	1,152 (296.7)
4°C in Artificial Saliva	1,164 (186.8)	1,085 (231.8)	1,091 (209.8)	1,036 (164.4)
60°C in Artificial Saliva	1,291 (167.5)	1,123 (89.0)	724 (126.2)	774 (95.7)
37°C with Loading*	1,105 (124.2)	1,252 (161.5)	1,123 (356.4)	1,116 (300.3)

* Loading repeatedly in artificial saliva
() SD

Table 10 Creep Value of Dispersalloy (%)

	1 week	1 month	3 months	6 months
37°C in Air	0.46 (0.293)	1.03 (0.358)	0.21 (0.028)	0.56 (0.213)
37°C in Distilled Water	1.49 (0.527)	0.50 (0.235)	0.49 (0.131)	0.36 (0.143)
37°C in Saline Solution	0.79 (0.170)	0.70 (0.175)	0.35 (0.131)	0.94 (0.207)
37°C in Artificial Saliva	1.46 (1.009)	0.75 (0.368)	0.83 (0.408)	0.38 (0.020)
4↔60°C in Artificial Saliva	0.87 (0.317)	0.41 (0.201)	0.88 (0.495)	0.33 (0.188)
4°C in Artificial Saliva	1.33 (0.073)	1.10 (0.788)	0.70 (0.135)	1.32 (0.138)
60°C in Artificial Saliva	1.38 (0.828)	0.51 (0.134)	0.28 (0.150)	0.58 (0.261)
37°C with Loading*	0.21 (0.071)	0.26 (0.252)	0.29 (0.154)	0.28 (0.120)

* Loading repeatedly in artificial saliva
() SD

Table 11 Diametral Tensile Strength of Dialloy (Kg/cm²)

	1 week	1 month	3 months	6 months
37°C in Air	263 (19.0)	395 (99.7)	331 (26.8)	326 (60.6)
37°C in Distilled Water	302 (64.8)	410 (95.4)	311 (86.1)	454 (111.3)
37°C in Saline Solution	353 (81.9)	316 (104.5)	490 (104.9)	396 (73.8)
37°C in Artificial Saliva	328 (49.7)	334 (93.8)	431 (107.0)	395 (83.8)
4↔60°C in Artificial Saliva	306 (91.5)	343 (130.7)	313 (82.4)	407 (110.0)
4°C in Artificial Saliva	388 (60.2)	276 (114.6)	326 (94.2)	370 (115.3)
60°C in Artificial Saliva	326 (77.3)	223 (56.9)	399 (81.1)	497 (60.3)
37°C with Loading*	332 (64.0)	256 (56.8)	428 (46.0)	502 (73.6)

* Loading repeatedly in artificial saliva

() SD

Table 12 Knoop Hardness Number of Dialloy

	1 week	1 month	3 months	6 months
37°C in Air	875 (209.0)	2,033 (551.7)	1,713 (834.6)	1,880 (505.6)
37°C in Distilled Water	1,485 (252.0)	1,581 (338.6)	1,267 (317.8)	1,379 (342.1)
37°C in Saline Solution	1,644 (253.4)	1,470 (332.9)	1,212 (99.8)	1,574 (356.3)
37°C in Artificial Saliva	1,398 (188.4)	1,322 (193.1)	1,211 (207.8)	1,713 (392.3)
4↔60°C in Artificial Saliva	1,598 (203.3)	1,322 (317.2)	1,195 (259.4)	1,357 (607.5)
4°C in Artificial Saliva	1,217 (163.9)	1,247 (359.2)	1,193 (193.2)	1,165 (340.8)
60°C in Artificial Saliva	1,640 (250.9)	1,389 (241.5)	1,123 (287.3)	1,298 (220.5)
37°C with Loading*	1,198 (297.4)	1,410 (204.8)	1,122 (384.4)	1,367 (311.2)

* Loading repeatedly in artificial saliva

() SD

Table 13 Creep Value of Dialloy (%)

	1 week	1 month	3 months	6 months
37°C in Air	0.92 (0.677)	0.73 (0.489)	0.17 (0.020)	0.28 (0.244)
37°C in Distilled Water	0.47 (0.153)	0.26 (0.122)	0.08 (0.079)	1.00 (0.285)
37°C in Saline Solution	0.82 (0.222)	0.65 (0.591)	0.03 (0.013)	0.23 (0.169)
37°C in Artificial Saliva	1.13 (0.308)	0.43 (0.198)	0.13 (0.110)	0.23 (0.251)
4↔60°C in Artificial Saliva	0.42 (0.806)	0.21 (0.052)	0.08 (0.112)	0.09 (0.066)
4°C in Artificial Saliva	1.16 (0.246)	0.71 (0.169)	0.32 (0.100)	0.23 (0.067)
60°C in Artificial Saliva	0.77 (0.870)	0.32 (0.127)	0.24 (0.058)	0.31 (0.065)
37°C with Loading*	0.14 (0.087)	0.07 (0.065)	0.18 (0.120)	0.05 (0.001)

* Loading repeatedly in artificial saliva

() SD

Table 14 Analysis of Variance

		Luna Alloy			Hi Atomic M			Dispersalloy			Dialloy		
		DS	KH	SC	DS	KH	SC	DS	KH	SC	DS	KH	SC
I	Time	n	hs	n	n	n	n	hs	hs	s	hs	s	hs
	Environment	n	hs	hs	n	n	n	n	n	n	n	n	n
	T×E	n	hs	hs	n	n	n	n	s	n	n	hs	hs
II	Time	n	hs	n	hs	hs	n	hs	hs	hs	hs	s	hs
	Temperature	hs	hs	hs	s	hs	n	hs	s	s	n	n	hs
	T×T	n	hs	n	s	n	n	n	s	n	n	n	n
III	Time	n	n	hs	n	n	n	n	n	n	hs	n	hs
	Loading	s	hs	n	n	n	hs	s	n	hs	n	n	hs
	T×L	n	n	s	n	n	s	n	n	n	n	n	hs

I : Ageing in different environments at 37°C

II : Ageing at different temperatures in artificial saliva

III : Ageing with or without repeated loading in artificial saliva at 37°C

DS : Diametral tensile strength

KH : Knoop hardness number

SC : Static creep value

Dispersalloy increased in diametral tensile strength highly significantly with time after one month. Dialloy also exhibited significantly higher strength after three months than one week. In Luna Alloy and Hi Atomic M, however, there were no significant difference in strength with the lapse of time. Statistical analysis revealed that the ageing of the amalgam affected the hardness, but no agreement could be seen between the changes of the hardness and strength. The effect of ageing on the creep value was found quite different between conventional amalgams and high-copper ones. Creep of Dispersalloy and Dialloy decreased significantly with time, while there was no statistical difference in creep by ageing from one week to six months in Luna Alloy and Hi Atomic M. Corrosive solutions including distilled water markedly increased the static creep of only Luna Alloy, indicating highly significant difference from air.

Results for the storage in artificial saliva at various temperatures were plotted on Figures 5~8 in order to check the effect of the ageing temperature on the properties of the amalgam. Although clear effect of the temperature was seen in all amalgams tested, conventional amalgams and high-copper amalgams exhibited their distinctive features from each other in relation to the ageing temperature. In general the higher the ageing temperature, the lower the diametral tensile strength for conventional amalgams, and *vice versa* for high-copper amalgams. Moreover, Luna Alloy and Hi Atomic M were still increasing in diametral tensile strength after three months storage at 4°C, while it began to slightly decrease at other storage temperatures. Eventually, rapid deterioration was observed for Luna Alloy stored at 60°C. In conventional amalgams

stored at this temperature much smaller size of residual alloy particles, bigger gamma-1 and more amount of gamma-2 phases were recognized than at lower temperatures (Figures 13~15). Figures 16 and 17 show the SEM images of Dispersalloy and Dialloy. In the specimens stored at 60°C for six months, Ag-Sn alloy particles in Dispersalloy and Ag-Cu-Sn core in Dialloy almost disappeared, and much gamma-1 phase and Cu, Sn-rich layer were recognized. Static creep was also affected by the ageing temperature, and lower ageing temperature generally yielded higher creep. This tendency was marked for Luna Alloy. On the contrary, lower Knoop hardness was obtained with increase of the temperature.

The effect of cyclic immersion of the specimen between the artificial saliva of 4 and 60°C was analogous to that of the immersion in the same solution of 37°C.

Figures 9~12 demonstrate the effect of the repeated loading on the specimen. The diametral tensile strength decreased in conventional amalgams while it increased in high-copper amalgams. Marked effect of the repeated stress did not appear on the

Fig 1 Changes in diametral tensile strength, Knoop hardness and static creep with time for Luna Alloy aged in different environments at 37°C.

Fig 2 Changes in diametral tensile strength, Knoop hardness and static creep with time for Hi Atomic M aged in different environments at 37°C.

hardness. Creep value, on the other hand, dropped considerably in all amalgams tested. Especially in the case of the high-copper amalgams this value became quite low from one week to six months.

Discussion

It has been said that the amalgams may still be increasing slightly in strength over six months' period. Especially, in this experiment, the high-copper type amalgams, Dispersalloy and Dialloy, increased in diametral tensile strength significantly with the lapse of time at 37°C. In the conventional type amalgams, Luna Alloy and Hi Atomic M, however, there was no statistically significant difference in the strength with time although the latter showed a slight increase of the strength up to six months. The amalgam itself may be strengthened by ageing as demonstrated by Phillips (1973)⁴⁾ but the resultant strength will depend on its insusceptibility to the structural change by corrosion. From the fact that Dispersalloy and Dialloy showed the strength

Fig 3 Changes in diametral tensile strength, Knoop hardness and static creep with time for Dispersalloy aged in different environments at 37°C.

Fig 4 Changes in diametral tensile strength, Knoop hardness and static creep with time for Dialloy aged in different environments at 37°C.

increasing with time, strength of the high-copper amalgams might be considered less sensitive to corrosion. Diametral tensile strength generally decreased in one month for these amalgams except Dialloy. This phenomenon can be seen in other works⁴⁾ although any attention has not been paid on it. It may be due to some change in the structure of the amalgam, but it was not proved in this study. Only Dialloy showed a steady increase in strength even at this stage, indicating that its setting may be faster and such a drop of the strength may have occurred at an earlier stage. The specimens were stored in air, distilled water, artificial saliva or saline solution at 37°C. Any of these storage environments did not significantly affect the strength of the amalgams. In spite of being corrosive against the amalgam, the artificial saliva and saline solution might not severely affect the strength for six months. However, they are likely to have greater or less effect on the creep value. It should be noticed that the creep

Fig 5 Changes in diametral tensile strength, Knoop hardness and static creep with time for Luna Alloy aged at different temperatures (4°C, 37°C, 60°C, and alternatively 4 and 60°C) in artificial saliva.

Fig 6 Changes in diametral tensile strength, Knoop hardness and static creep with time for Hi Atomic M aged at different temperatures (4°C, 37°C, 60°C, and alternatively 4 and 60°C) in artificial saliva.

value of the conventional lathe cut type Luna Alloy markedly increased by storing in distilled water, saline solution and artificial saliva.

When the specimens were kept in the artificial saliva at various temperatures between 4 and 60°C, notable differences were found by the temperature change between conventional amalgams and high-copper ones. The temperature dependence may be attributed to the possible difference in the structure of amalgam caused by the reaction rate difference at each temperature. In the conventional amalgams, the diametral tensile strength kept increasing for the specimen stored at 4°C, while it began to decrease slightly for the specimen stored at other temperatures, after three months storage. It is well accepted that the structure having more residual alloy particles and the less gamma-2 phase will make the amalgam stronger. Storage at 4°C would probably retard the reaction, making the alloy react only very slowly with mercury for appreciably long period. The specimen kept at 60°C has much smaller residual alloy

Fig 7 Changes in diametral tensile strength, Knoop hardness and static creep with time for Dispersalloy aged at different temperatures (4°C, 37°C, 60°C, and alternatively 4 and 60°C) in artificial saliva.

Fig 8 Changes in diametral tensile strength, Knoop hardness and static creep with time for Dialloy aged at different temperatures (4°C, 37°C, 60°C, and alternatively 4 and 60°C) in artificial saliva.

particles and more gamma-2 phase than those kept at other temperatures (Figures 13 and 14). Such structure may be considered to have been resulted from the further reaction of the residual alloy particles with residual mercury at higher temperature during ageing. In the case of the high-copper amalgams, the temperature affected the strength reversely to the conventional ones. Namely, the specimens stored at 60°C exhibited the highest diametral tensile strength after six months, and those at 4°C the lowest. Dispersalloy and Dialloy are both high-copper containing amalgams but their microscopic structures are quite different from each other. Ag-Sn alloy particles react with mercury to form mainly gamma-1 phase, Cu-Sn phase, and so-called reaction ring of Cu-Sn inside the Ag-Cu eutectic dispersant in Dispersalloy. In Dialloy, on the other hand, the phase containing much Cu and Sn is found in the original alloy particle, surrounding the unreacted Ag-Cu-Sn core. Those Cu-Sn phases are regarded as the hardest in the set amalgam. There can be seen no or very few gamma-2 phase in both amalgams. Scanning electron microscopic observation revealed that Ag-Sn alloy particles

Fig 9 Changes in diametral tensile strength, Knoop hardness and static creep with time for Luna Alloy aged with or without repeated loading at 37°C in artificial saliva.

Fig 10 Changes in diametral tensile strength, Knoop hardness and static creep with time for Hi Atomic M aged with or without repeated loading at 37°C in artificial saliva.

in Dispersalloy and Ag-Cu-Sn cores in Dialloy had almost disappeared, and the Cu, Sn-rich layer had become thicker in both amalgams after six months' storage in artificial saliva at 60°C (Figures 16 and 17). It is considered that the residual alloy particle, Ag-Cu particle and Cu-Sn phase are responsible for the strength of these amalgams. Above all, the presence of the Cu-Sn phase seems to be the most effective to strengthen the amalgam. As shown in the present results, the strength increased with increase of the Cu-Sn phase resulting from further reaction during storage at 60°C, although residual alloy particles almost disappeared.

This tendency is quite parallel with the fact that the creep value became lower for the specimen stored at higher temperature. In general, low creep value is accompanied by high hardness value. However, the specimen stored at 60°C exhibited the lowest hardness. The diminution of the residual alloy particles will probably decrease the overall hardness of the amalgam in spite of partial growth of hard Cu-Sn layer, indicating that the strength of the amalgam is not always coordinated with the hardness

Fig 11 Changes in diametral tensile strength, Knoop hardness and static creep with time for Dispersalloy aged with or without repeated loading at 37°C in artificial saliva.

Fig 12 Changes in diametral tensile strength, Knoop hardness and static creep with time for Dialloy aged with or without repeated loading at 37°C in artificial saliva.

(Ooki, *et al.* 1979⁹⁾). The effect of cyclic immersion of the specimen alternatively into the solution of 4 and 60°C was not so marked. It was about the same as that of storing in the solution of 37°C.

When repeated small amount of compressive stress was applied to the specimen, its effect on the properties of the amalgam appeared quite different between conventional and high-copper amalgams. Apparent deterioration was recognized by the repeated stress for Luna Alloy and Hi Atomic M, while the strength still increased up to six months for Dispersalloy and Dialloy. Hardness increased by the repeated stress only for the conventional amalgams. Creep value dropped considerably by the application of the repeated stress in both types of amalgams. Such decreased creep value and increased hardness value in the conventional amalgam might be analogous to the typical aspect

Fig 13 Scanning electron micrographs of polished surface of Luna Alloy aged in artificial saliva at 37°C for one week (left) and at 60°C for six months (right). $\times 1,000$
A: Ag-Sn phase B: Ag-Hg phase C: Sn-Hg phase

Fig 14 Scanning electron micrographs of polished surface of Hi Atomic M aged in artificial saliva at 37°C for one week (left) and at 60°C for six months (right). $\times 1,000$
A: Ag-Sn phase B: Ag-Hg phase C: Sn-Hg phase

of fatigue process. The application of a repeated stress seems to have two different effects on the amalgam: the first is to make the specimen fatigue, and the second is to accelerate appreciably the reaction of the residual alloy particles with the residual mercury. The former might be evidenced by the considerable drop of the creep value. The latter can be realised by the fact that the SEM image of stress repeated samples and high temperature samples resemble each other quite well (Figure 17). It would be considered as a result of the interaction of these two effects that the decrease of the strength was found for Luna Alloy and Hi Atomic M as well as the increase for Dispersalloy and Dialloy. This may suggest that the high-copper amalgam will be strengthened by the action of the masticatory stress in some period after being filled, while the conventional one weakened.

Fig 15 Scanning electron micrographs of polished surface of Hi Atomic M aged in artificial saliva at 37°C (left) and 60°C (right) for six months. $\times 1,000$
A; Ag-Sn phase B; Ag-Hg phase C; Sn-Hg phase

Fig 16 Scanning electron micrographs of polished surface of Dispersalloy aged in artificial saliva at 37°C for one week (left) and at 60°C for six months (right). $\times 1,000$
A; Ag-Sn phase B; Ag-Hg phase C; Sn-Hg phase

Fig 17 Scanning electron micrographs of polished surface of Dialloy aged in artificial saliva at 37°C for one week (upper left), at 60°C for six months (upper) and at 37°C for six months with repeated loading (left). $\times 1,000$
A; Ag-Cu-Sn core B; Cu-Sn phase

As mentioned above, almost opposite effects of the storage condition were found on the diametral tensile strength between the conventional and the high-copper amalgams. Creep value also showed different tendency with time between the two types. Luna Alloy and Hi Atomic M exhibited no significant differences in creep in relation to the storage period within six months except for the specimens subjected to the repeated stress. Relatively wide variation could be seen in the creep value for these amalgams. Especially it was marked for Luna Alloy. This means that creep behavior itself would be affected not systematically by the environments for the conventional amalgams. In the high-copper amalgams, on the other hand, creep value was found to drop by ageing. It should be noticed that the value decreased markedly with time after one week, and also that it dropped appreciably even at one week by repeated compressive loading during storage. Static creep after one week storage has usually been examined and discussed in association with the occurrence of the marginal fracture of amalgam. The fracture should occur more easily and frequently in the amalgam having higher creep value (Mahler and Terkla, *et al.* 1970)³⁾. If the relation between them is the case, the decreasing creep with time and repeated compressive loading, as shown in this study, seems to be much convenient for preventing marginal fracture in service.

Summary

Conventional and high-copper amalgams exhibited fairly distinctive features from each other by ageing. Diametral tensile strength increased with time in high-copper amalgams, while it did not significantly change with time in conventional amalgams for six months. Both of the amalgams were not affected by storing solutions used so far as they were kept at 37°C. As the ageing temperature was elevated up to 60°C in artificial saliva, the strength decreased in conventional amalgams and increased in high-copper amalgams. Especially marked deterioration was observed for Luna Alloy. Repeated small amount of compressive loading during ageing decreased the diametral tensile strength of conventional amalgams, showing approximately the same effect as the elevated ageing temperature. Luna Alloy seemed to have been suffered from severe attack of the corrosive solutions, resulting in higher static creep, although the strength was not significantly changed. The creep of Hi Atomic M was not severely affected by ageing. High-copper amalgams, on the contrary, showed considerably lower static creep by ageing, and the tendency was accelerated by the high temperature solution and the compressive loading during ageing. Knoop hardness was also affected by ageing in both amalgams, but clear relation was not obtained with the changes of diametral tensile strength and static creep.

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歯科用アマルガムの経時変化 (*in vitro*)

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アマルガムは今日の歯科臨床において最も使用されている修復材料の1つである反面、2次ウ蝕の発生率が非常に高い材料でもある。その原因については、術者に基づくものと材料自体によるものがあると言われている。そこで著者は6カ月間にわたり、種々の環境下における各種物性の挙動を測定し、アマルガムにおよぼす環境の影響を検討した。

実験にはLuna Alloy (従来型, 削片状), Hi Atomic M (従来型, 球状), Dispersalloy (高銅型, 分散型), Dialloy (高銅型, 単一型) を使用した。試料の保存環境は 37°C 大気, 蒸溜水, 生理食塩水, 4°C, 37°C, 60°C の人工唾液, 4°C と 60°C の人工唾液中でのサーマルサイクリングとした。またくりかえし荷重の影響を調べるために 37°C 人工唾液中で 2.5kg/cm² のくりかえし圧縮荷重を加えた。試料作成後1週間, 1カ月, 3カ月, 6カ月にダイアメトル引張り強さ, ヌープ硬さ, 静的クリープの各試験をおこなった。

その結果, 高銅型は従来型とは異なった傾向を示した。すなわち, ダイアメトル法での引張り試験では, 6カ月間にわたり高銅型アマルガムの強さが増加したのに対し, 従来型アマルガムでは有意な変化が認められな

かった。また温度を 37°C に保つ限り, 両アマルガムも共に溶液の影響間に差はなかった。また人工唾液の温度が高いほど従来型アマルガムでは強さが減少するのに対し, 高銅型アマルガムでは逆に強さが増加した。なかでも, Luna Alloy を 60°C に保存した場合の強さの低下は著しかった。また保存中試料にくりかえし圧縮荷重を与えた場合, 強さの変化は 60°C で保管した場合と同じ傾向を示した。保存中にくりかえし荷重を加えた試料は 60°C に保存した場合と同様の組織変化を起していることから, くりかえし荷重はアマルガムを疲労させる効果と同時に, 残留未反応合金と残留水銀との反応を促進する効果をもつものと考えられる。

クリープ値も従来型と高銅型とでは異なる傾向が認められた。従来型アマルガムにおいては, クリープ値は経時的にわずかな変動を示すにすぎないか, あるいは増加の傾向がみられた。これに対し高銅型では, 時間経過, 高温, くりかえし荷重の各影響によりクリープ値の低下が認められた。

ヌープ硬さにも保存条件により多少の影響が見られたが, 引張り強さやクリープ値の変化とは相関関係が認められなかった。