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Young's modulus and mechanical damping of silver dental alloys

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The piezoelectric ultrasonic composite oscillator (PUCO) technique has been used at a frequency of 80 kHz to measure Young's modulus and mechanical damping in eight silver dental alloys. The time dependence for aging at 37° C and the temperature dependence of mechanical damping over the temperature range of 20 to 80° C were studied. Young's modulus (measured at 37° C) increased from around 17 GPa after 15 min and saturated near 70 GPa after 10^3 to 10^4 min. The mechanical damping increased by factors of 6 to 32 over the investigated temperature range, whereas Young's modulus decreased by 1.3 to 5%. Arrhenius plots of the data gave effective activation energies ranging from 0.35 to 3.1 eV. The results are interpreted in terms of various diffusion processes in the alloys and in terms of the microstructures.

1. Introduction

The phase changes and mechanical properties of Ag–Hg–Sn amalgams at and above body temperature are of obvious concern in dentistry. In particular, quantitative information on the changes in Young's modulus (E) of dental amalgams after compaction (condensing) is of fundamental importance. With standard tensile machines it is difficult to obtain reliable E values for such soft materials as dental amalgams just after their compaction. For this reason in this work the piezoelectric ultrasonic composite oscillator (PUCO) technique [1, 2] has been used at 80 kHz to measure E in dental amalgams at small strain amplitudes (ϵ_{11} typically about 10^{-7}) and hence also at low stresses (2 to 8 kPa), thus avoiding the possible complications of creep. The use of the PUCO technique has the added advantage that measurements of the mechanical damping of the specimen, Q_S^{-1}, can be made contemporaneously with the E measurements. With this technique both the E and Q_S^{-1} measurements could be made as functions of specimen aging time at 37° C and as continuous functions of temperature changed at a programmed rate. This paper reports the measurements of Young's modulus for eight dental amalgams for times (after compaction) as short as 15 min and up to 5.5 weeks, and measurements for four amalgams of the temperature dependence of mechanical damping for the range 20 to 80° C.

2. Experimental procedure

The Ag–Hg–Sn amalgams used in the experiments are listed in Table I. The mixing (trituration) of the amalgam components was carried out according to the standard procedures recommended by the manufacturers. Cylindrical test specimens (of approximate dimensions 3 mm diameter and 13 mm length) were compacted by an all-mechanical technique according to ADA Specification No. 1 [3], the only variation being an alteration in the amounts of alloy and mercury in order to produce a longer specimen. For the PUCO method experiments, with times after compaction, t, less than a few hours, the specimens were aged at room temperature; for $t \geqslant 4$ h the specimens were aged at 37° C.

The PUCO experimental arrangement consisted

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TABLE I Dental amalgams used in the investigation

Alloy	Manufacturer	Particle shape	Copper addition	Copper in alloy (%)	Batch number
New True Dentalloy (NTD)	S. S. White, Philadelphia, PA 19102, USA	Fine lathe cut			576720
20th Century (Caulk Micro)	L. D. Caulk, Milford, DE 19963, USA	Micro lathe cut			none
F400	Southern Dental Industries, Bayswater, Victoria 3153, Australia	Micro lathe cut			708281
G & C (Luna Atomic non-zinc)	G–C Chemical Manufacturing Co. Ltd, Tokyo, Japan	Spherical			HJ26
Shofu (Spherical)	Shofu Dental Manufacturing Co. Ltd, Kyoto, Japan	Spherical			31
Dispersalloy	Johnson & Johnson, East Windsor, NJ 08520, USA	Spherical/ lathe blend	Admix	12	5H085
Sybralloy	Kerr, Romulus, MI 48174, USA	Spherical	Ternary alloy	29	0205761023
Tytin	S. S. White, Philadelphia, PA 19102, USA	Spherical	Ternary alloy	12	017700

of piezoelectric quartz drive (D) and gauge (G) crystals to excite longitudinal ultrasonic (80 kHz) resonant stress waves in the specimen (S) of appropriate resonant length. For the measurements at room temperature the three-component system (DGS) was used; for the experiments with specimen temperatures, T, in the range 20 to 80° C the four-component system (DGQS) was required; a fused quartz rod (Q) (3 mm x 3 mm in cross section and of length about 370 mm) tuned for 80 kHz resonance at 50° C acted as a spacer between the gauge crystal and the specimen. The components were joined together with Loctite glue. The resonant system was driven by a closed-loop oscillator which maintained a constant (preselected) gauge crystal voltage (V_g) and hence a constant maximum strain (or stress) amplitude in the specimen. During the experiments conducted at room temperature using the three-component DGS system, values of the drive crystal voltage, V_d, V_g and the resonant period, τ_{DGS}, of the system were measured. For the experiments at temperatures above room temperature the specimen, previously aged at 37° C for at least 1 week, and the entire oscillator were contained in a vacuum system maintained at 1 mPa. The specimen heating or cooling rate was about 20° Ch^{-1}. During these tests, values of V_d, V_g, τ_{DGQS} and T were measured continuously. Full details of the PUCO method are given elsewhere [1, 2, 4]. From the measured values of V_d, V_g, τ_{DGQ}, τ_{DGQS}, the masses $m(i)$ (where i is D, G, Q or S) and l_S (the specimen length) standard calculations [1, 2] yielded values of E and Q_S^{-1}.

3. Results

The reproducibility of the measurements of Young's modulus was tested using eight separate specimens of F400 amalgam aged for about 1 week. These eight E values gave a mean of 58.03 GPa with a standard deviation of only 0.70 GPa. Such reproducibility was considered quite adequate for the present study.

The measured values of Young's modulus as functions of aging time for the eight amalgams are listed in Table II and plotted in Fig. 1. The temperature dependences of the mechanical damping of the specimen, Q_S^{-1}, and Young's modulus are plotted for the four amalgams Tytin, NTD, G & C and Shofu in Figs 2 to 5. The Arrhenius plots for these amalgams are shown in Figs 6 to 9. The time dependence of Q_S^{-1} for Tytin, Dispersalloy, NTD and 20th Century is presented in Fig. 10 and that for Sybralloy, Shofu and G & C is presented in Fig. 11.

4. Discussion

While the values of Young's modulus measured here are at variance with those measured by conventional mechanical techniques utilizing slow rates of loading [5], they compare will with those obtained by comparable techniques [6]. The advantage of the PUCO technique is that the kinetics of the E measurements could be monitored.

TABLE II Measured values of Young's modulus E

Amalgam	Young's modulus, E (GPa)			
	Aged for $\lesssim$ 1h	Aged for 4h	Aged for 1 week	Aged for 3 to 5.5 week
Sybralloy	45	61	72	72
Tytin	49	67	70	69
G & C	35	52	64	63
Dispersalloy	40	43	62	63
Shofu	37	50	59, 61	61
F400	33, 40		58	62
NTD	29	48	60	62
20th Century	17, 22	52	60	60

As Fig. 1 indicates, the E against t curves for the eight amalgams tended to group together with a plateau value for t values greater than 10^3 min of between 60 and 72 GPa, although for short times there were significant differences in the E values. For Tytin the E values increased by 43% over the time range studied and this amalgam has the highest E values for $t < 10^3$ min. The E values for 20th Century increased by 253% and formed a sigmoidally shaped curve, having the lowest E values for $t < 1$ h. The amalgam with the highest E value for $t > 10^3$ min was Sybralloy, closely followed by Tytin. With F400 Young's modulus was still increasing at $t = 10^3$ min. For all the amalgams studied it can be seen that the maximum values of E were obtained for aging times above 10^4 min (1 week).

The temperature dependences of mechanical damping and Young's modulus shown in Fig. 2 indicate that for Tytin the Q_S^{-1} values increased by a factor of 19 as the temperature was raised from 20 to 80° C and the E values decreased by 3%. There was a rapid increase in Q_S^{-1} at 65 to 70° C which was probably connected with the reported $\gamma_1 \rightarrow \beta_1$ phase transformation in these alloys [7]. The E–T curve showed a corresponding change in slope. The damping data points for cooling fell on the same Q_S^{-1}–T curve while the E values for cooling showed a slight hysteresis. This small hysteresis probably reflected the thermal inertia of the specimen–furnace system. The highest value of mechanical damping reached was 2×10^{-2}. This is a high value compared to those for common metals (except Pb) and alloys (which are typically between 10^{-3} and 10^{-4}). Thus the amalgam is very efficient at damping out vibrations at temperatures around 65 to 80° C.

With NTD the shape of the Q_S^{-1}–T curve, shown in Fig. 3, is similar to that observed for Tytin. The increase in mechanical damping with temperature this time was a factor of 32, with a slight hysteresis evident near 70 to 80° C. Again there was a steep rise (for heating) or fall (for cooling) in Q_S^{-1} near 70° C. The maximum Q_S^{-1} value

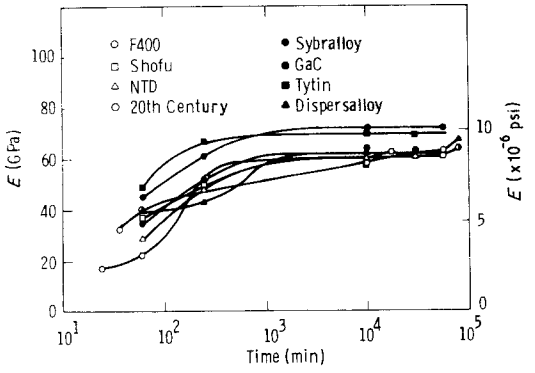

Figure 1 Measured values of Young's modulus, E, as a function of aging time at 37° C ($t \geq 4$ h) for eight dental amalgams.

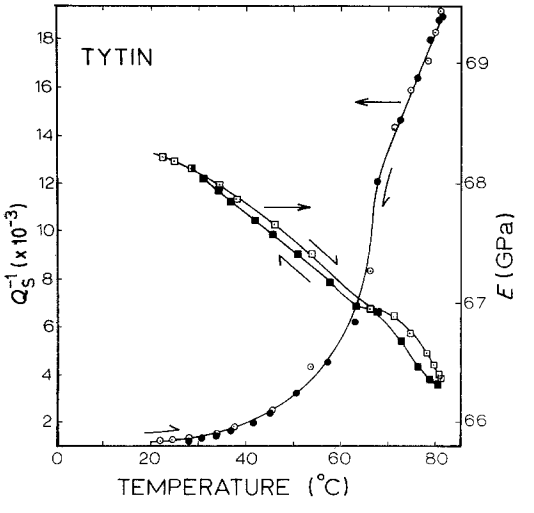

Figure 2 Temperature dependence of mechanical damping, Q_S^{-1} (round symbols), and Young's modulus, E (square symbols), for Tytin.

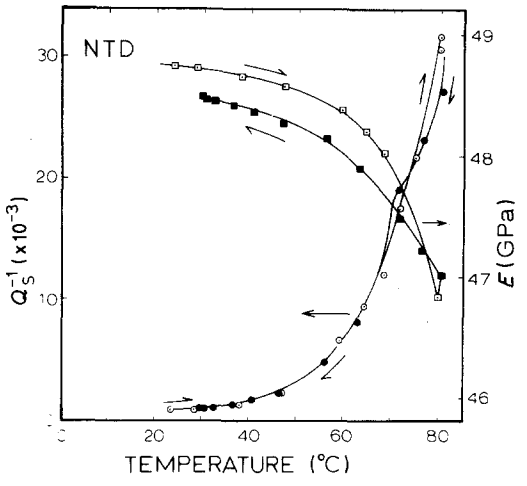

Figure 3 Temperature dependence of mechanical damping, Q_S^{-1} (round symbols), and Young's modulus, E (square symbols), for NTD.

was about 3×10^{-2}. Young's modulus decreased by 4% over the same temperature range and the $E-T$ curves for heating and cooling were not identical, even allowing for hysteresis effects of the specimen–furnace system.

The heating/cooling data for G & C, given in Fig. 4, showed that the $Q_S^{-1}-T$ and $E-T$ curves were not reversible, i.e., the heating and cooling curves were not identical. The increase in Q_S^{-1} with temperature was a factor of 15, but the decrease in E was only 1.3 %. The $E-T$ curve showed a slight peak at 31° C, the significance of which is not clear. From the minimum E value near 76° C the

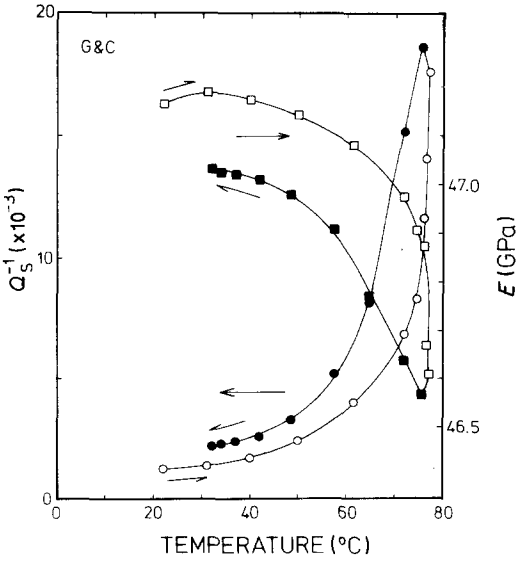

Figure 4 Temperature dependence of mechanical damping, Q_S^{-1} (round symbols), and Young's modulus, E (square symbols), for G & C.

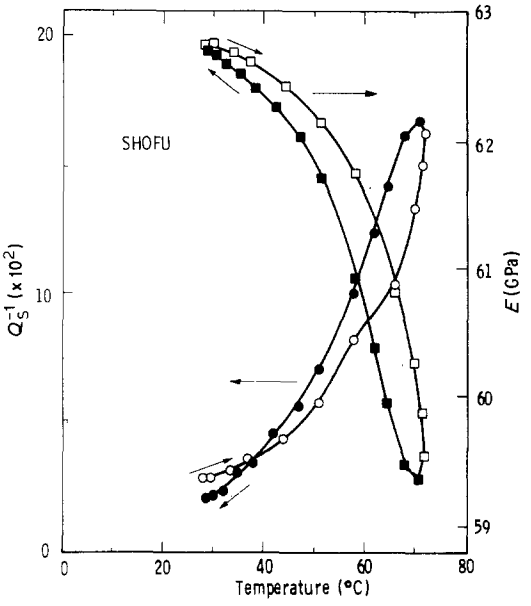

Figure 5 Temperature dependence of mechanical damping, Q_S^{-1}, and Young's modulus, E, for Shofu.

increase in E with decrease in temperature was only about 1 %.

For Shofu the values of mechanical damping were the largest of all those for the dental amalgams examined here, reaching a maximum of about 1.7×10^{-1}. Hence this alloy is extremely efficient at damping out mechanical vibrations at 60–80° C. The $Q_S^{-1}-T$ curves showed an increase of a factor of 6 for heating and some hysteresis for cooling. The $E-T$ curve for heating indicated a 5% decrease, while the curve for cooling showed hysteresis.

A summary of the behaviour of these four

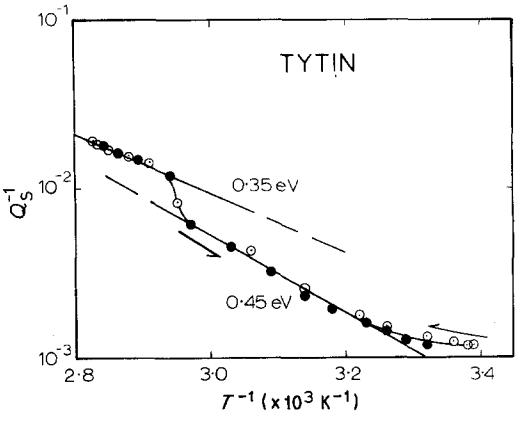

Figure 6 Arrhenius plot of mechanical damping, Q_S^{-1}, for Tytin.

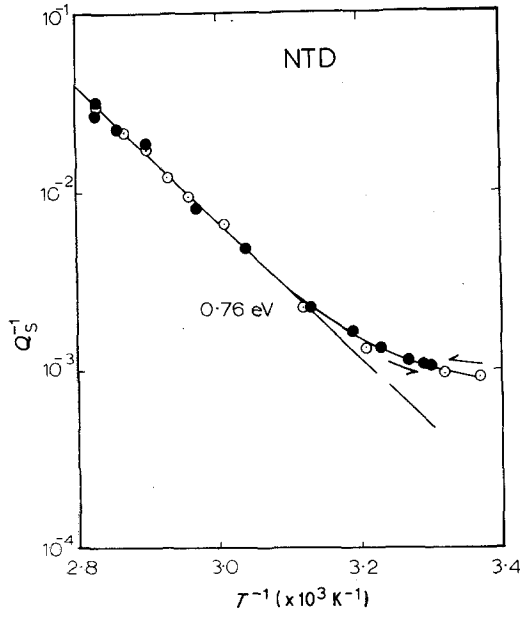

Figure 7 Arrhenius plot of mechanical damping, Q_S^{-1}, for NTD.

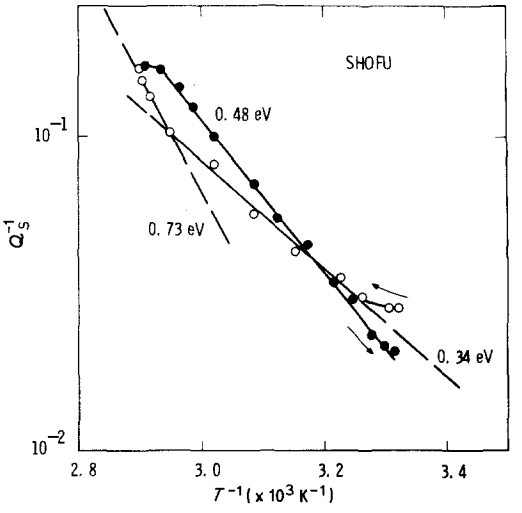

Figure 9 Arrhenius plot of mechanical damping, Q_S^{-1}, for Shofu.

amalgams is given in Table III. Since all the amalgams showed a rapid increase in Q_S^{-1} at between 65 and 70° C, it is likely it is the $\gamma_1 \rightarrow \beta_1$ transformation, via its effect on the damping characteristics of the alloys, that is being observed. Certainly for G & C and Shofu the transformation seems irreversible within the time-frame of the tests. The ternary phase diagram for Ag–Hg–Sn is complex [8] and the usual additions of Cu, Zn, etc. in amalgams will certainly modify it. However, it is well known that solid amalgams "sweat" Hg at temperatures near 70° C. Thus the phase change $\gamma_1(Ag_2Hg_3) \rightarrow \beta_1$ that takes place when the specimens are heated to 70° C is accompanied by the formation of liquid Hg. The presence of a liquid within the alloy is consistent with our observations of large increases in Q_S^{-1} as the temperature traversed the range 60 to 80° C. Similar variations in mechanical damping have already been reported for a melting metallic component (Pb) within a ternary alloy system (free-machining brass: Cu–Zn–Pb) [9].

Although the microstructure of dental amalgams is complicated [10], an attempt has been made to relate the temperature dependence of the mechanical damping to the fundamental diffusion process(es) that occur(s) during the aging of dental amalgams. From the Arrhenius plots in Figs 6 to 9 effective activation energy values are obtained which are related to the activation energies for diffusion of the various components in the amalgams. In Table IV the effective activation energies derived from the present investigation are compared with the reported activation energies for diffusion of

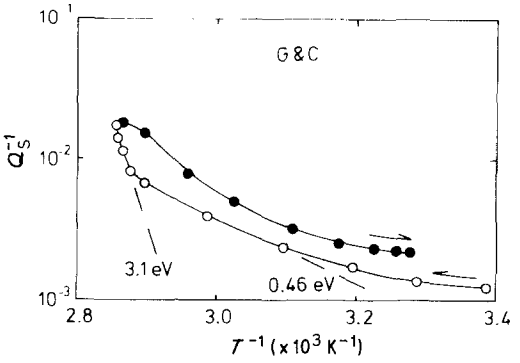

Figure 8 Arrhenius plot of mechanical damping, Q_S^{-1}, for G & C.

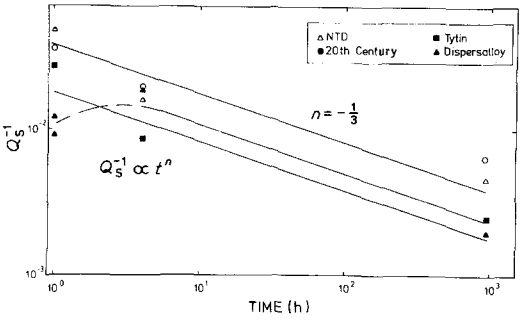

Figure 10 Time dependence of mechanical damping Q_S^{-1} for Tytin, Dispersalloy, NTD and 20th Century, aged at 37° C.

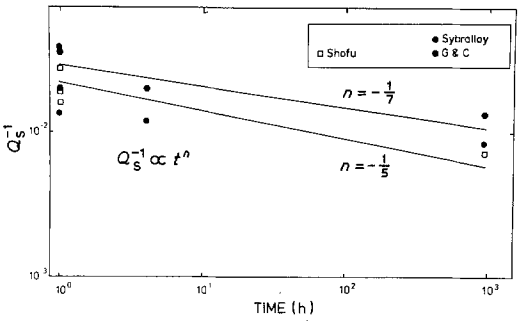

Figure 11 Time dependence of mechanical damping Q_S^{-1} for Sybralloy, Shofu and G & C, aged at 37° C.

various components. In the Arrhenius plots the "tails" on the curves for $10^3/T \gtrsim 3.2$ correspond to the thermal inertia in the specimen–furnace system and should be ignored. The Arrhenius plot for Tytin yields two values of effective activation energy, 0.35 and 0.45 eV, depending on temperature range. Both values are close to the value of 0.42 eV for the diffusion of Hg in $\gamma_1(Ag_2Hg_3)$ [11]. It is thus reasonable to suggest that the diffusion of Hg in the γ_1 phase influences the damping properties of this amalgam. For NTD the effective activation energy is 0.76 eV which is near the values of activation energy for either Sn diffusing in Ag_3Sn (grain boundary diffusion, 0.74 eV, see, [12]) or Hg diffusing in Ag_3Sn (volume diffusion, 0.81 eV, see [13, 14]). Thus the diffusion of Sn has an important influence on the damping in this alloy. The derived values of effective activation energy for G & C are 0.46 and 3.1 eV, depending on temperature range. The former value is similar to one of the values derived for Tytin and is close to the activation energy for Hg diffusing in γ_1 [11]. The high value of 3.1 eV cannot be correlated with any value from the literature for this system. Perhaps this value represents some complex diffusion-related process(es) such as grain growth, phase transformation, melting, etc. For Shofu the effective activation energies of 0.34, 0.48 and 0.73 eV can be correlated with the diffusion of Hg in γ_1 (0.42 eV, [11]) or the diffusion of Sn in the grain boundaries of Ag_3Sn (0.74 eV, [12]). From the present results it is evident that the varied chemical compositions and microstructures of the dental amalgams lead to several possible diffusion processes which affect the mechanical damping properties. At any given temperature the dominant mechanism for diffusion should reflect itself in the Arrhenius plots of Q_S^{-1}. The situation for NTD is simple while that for the other three amalgams is complex.

Finally, the plots of mechanical damping as a function of aging time (Figs 10 and 11) are discussed. These curves can be fitted to straight lines on log–log plots with some scatter. Thus the relation is of the form $Q_S^{-1} \propto t^n$, where $n = -\frac{1}{3}$ for Tytin, Dispersalloy ($t \geqslant 4$h), NTD and 20th Century, $n = -\frac{1}{5}$ for Sybralloy and Shofu, and $n = -\frac{1}{7}$ for G & C. The negative inverses of these exponents, i.e. 3, 5 and 7, are reminiscent of the exponents in the standard equations governing neck growth in model experiments on sintering [15]. The contact or neck width $x \propto t^{1/b}$, where $b = 2$ for viscous or plastic flow, $b = 3$ for evaporation–condensation, $b = 5$ for volume diffusion, $b = 6$ for grain boundary diffusion and $b = 7$ for surface diffusion. A simple approach is adopted to relate mechanical damping, as measured in the present study, to the sintering contact width, with the underlying assumptions that sintering of the dental alloy grains proceeds during and after compaction and that neck growth influences mechanical damping. Thus with aging time, the amalgams proceed from a state of separate grains immersed in Hg (at $t \sim 0$), to grains in contact with a partial Hg meniscus (for t small), to a compact solid with grains in firm, extensive contact

TABLE III Summary of the mechanical damping and Young's modulus data from the temperature dependence experiments on four dental amalgams

Amalgam	Increase in Q_S^{-1} for $T = 20$ to 80° C (Factor of)	Heating and cooling: same (s) or different (d)		Is there a rapid increase in Q_S^{-1} between 65 and 70° C?	Comment
		$Q_S^{-1}-T$ curves	$E-T$ curves		
Tytin	19	s	s	Yes	
NTD	32	s	d	Yes	Largest increase in Q_S^{-1}
G & C	15	d	d	Yes	$E-T$ curve had small peak at 31° C
Shofu	6	d	d	Yes	High Q_S^{-1} values

TABLE IV Comparison of effective activation energy values from the temperature dependence studies of mechanical damping with literature values for activation energies for diffusion

Amalgam	Effective activation energy (eV)	Nearest value of activation energy from literature (eV)	System	Reference
Tytin	0.35	0.42	Hg in γ_1	[11]
	0.45		(Ag_2Hg_3)	
NTD	0.76	0.74	Sn in Ag_3Sn grain boundaries	[12]
		0.81	Hg in Ag_3Sn	[13]
		0.81	Hg in Ag_3Sn	[14]
G & C	0.46	0.42	Hg in γ_1	[11]
	3.1	–		
Shofu	0.34	0.42	Hg in γ_1	[11]
	0.48	0.42	Hg in γ_1	[11]
	0.73	0.74	Sn in Ag_3Sn g.b.	[12]

and with Hg and other elements diffusing by several mechanisms. In mathematical terms, x increases from zero to a relatively large value. This causes Q_S^{-1} to fall from a relatively high value (when liquid Hg may be present) to lower values as the Hg diffuses into and/or around the grains. To a first approximation, then, $x^{-1} \propto Q_S^{-1}$. But since $x \propto t^{1/b}$ [15], then $Q_S^{-1} \propto t^{-1/b}$, which is the form of the observed dependences (Figs 10 and 11). If the outlined mechanical connection between the growth of contact width during grain sintering and the observed decrease in mechanical damping at 37° C is valid, then the results suggest that for Tytin, Dispersalloy, NTD and 20th Century the decrease in Q_S^{-1} with aging time may be related to sintering of grains by a diffusion mechanism involving vapour transport (of Hg, probably) through inter-grain pores. For Sybralloy and Shofu the mechanism may involve volume diffusion (of Hg in γ_1, probably), and the mechanism for G & C could involve surface diffusion. These mechanisms do not necessarily have to be the same as those noted for higher temperatures (> 37° C) in Table IV. In any case, the scatter in the data in Figs 10 and 11 precludes any definitive identification of the operative diffusion mechanism.

5. Summary

Measurements have been made with the PUCO technique of the Young's modulus and mechanical damping of eight silver dental alloys. Both the time dependence for aging at 37° C and the temperature dependence for the range 20 to 80° C were investigated. The E values were found to increase with aging time from around 17 GPa at 15 min and to saturate at about 70 GPa after 10^3 to 10^4 min. The Q_S^{-1} values increased rapidly by factors of between 6 and 32 over the temperature range 20 to 80° C and the E values decreased by 1.3 to 5%. These changes were probably connected with the $\gamma_1 \rightarrow \beta_1$ phase transformation. Arrhenius plots of the mechanical damping led to effective activation energies in the range 0.34 to 3.1 eV. Some of these values could be related to the reported activation energy values for the diffusion of various components in the amalgams, such as Hg in γ_1, Sn in Ag_3Sn grain boundaries and Hg in Ag_3Sn. The time dependence of the mechanical damping followed a relation of the type $Q_S^{-1} \propto t^n$, where n was $-\frac{1}{3}$, $-\frac{1}{5}$ or $-\frac{1}{7}$. This relation was correlated with the standard equations governing neck growth during sintering, $x \propto t^{1/b}$. A simple connection was developed between x and Q_S^{-1} and was interpreted in terms of various diffusion mechanisms.

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