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HEAT TREATMENT OF SOLDERED JOINTS IN DENTAL CASTING GOLD ALLOYS

AN ELECTRON MICROPROBE ANALYSIS

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Samples of gold soldered assemblies from three different dental casting gold alloys were subjected to various homogenizing heat treatments. The distribution of available alloy components in the region of the gold-solder junction was investigated using electron-probe microanalysis. An extensive statistical treatment of the data was performed. Concentration differences between casting alloy and solder alloy were not levelled out to any great extent unless after prolonged heat treatment (3 hours) for one of the three alloys. However, this heat treatment caused grain growth and an increased amount of microporosities in the region of the joint. In the soldered assemblies from two of the three casting alloys microphases with a composition different from the original alloys appeared at the gold-solder junction after heat treatment. The results show that homogenizing heat treatment of gold soldered assemblies should not be performed as a routine.

In previous investigations (*Schriever & Diamond,* 1952; *Maschinski,* 1970) it was demonstrated that potential differences occur between pairs of metallic fillings used in the same oral milieu to replace lost tooth structure. Furthermore it has been shown (*Söremark et al.,* 1962; *Bergenholtz et al.,* 1965) that metallic elements in dental alloy restorations migrate into the structures of the oral cavity. Presumably these metals have been dissolved out of the restorations as a result of electro-galvanic corrosion. Metallic dissolution from cast gold restorations can also occur in some cases even though restorations made from other alloys are not present in the mouth. This effect is often attributed to surface inhomogeneity of the alloy due to segregations and inclusions which are frequently found in dental gold castings (*Skinner & Phillips,* 1967).

Heat treatment of a dental gold casting has a tendency to level out con-

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centration variations due to intracrystalline segregation. This has been demonstrated by *Björn & Hedegård* (1965) and *Eick & Hedegård* (1968), using electron microprobe analysis. *Söremark & Hedin* (1969) induced corrosion on dental gold alloys by electrolyzing them in a commercial deplating unit containing a hot cyanide solution. It was found that heat treated specimens were attacked less than the untreated ones as revealed by changes of some distances in the specimens. These three investigations deal with single castings and in these cases heat treatment to level out concentration variations seems to make the material less subject to corrosion. However, this reasoning cannot be directly applied to soldered constructions where at least two alloys of different compositions are included.

The solder is usually a low-fusing alloy which is capable of wetting the parent metal. Many gold solders, and particularly the lower fusing types, are eutectic phase mixtures. This implies a certain inhomogeneity of the solder itself and can increase the likelihood of corrosion. (*Skinner & Phillips*, 1967).

El-Ebrashi et al. (1968) in a very careful study investigated the properly heated and overheated gold-soldered joints by electron microscopy. They found a distinct demarcation and no diffusion between the solder and the parent alloy in the properly heated joints. In the overheated joints no distinct interface of solder and parent alloy was seen and a greater amount of microporosities was found. In addition the grains were more irregular in the overheated joints. In this investigation the overheating of the solder was performed during the soldering process by holding the flame on the solder assembly for ten seconds after the solder was molten. Oxide formation was observed in both the properly heated and the overheated joints. However, it was more pronounced in the latter. The authors conclude that although a complete diffusion between the solder and parent alloy should result in a superior metallurgical joint, such a joint cannot be produced in dental gold soldering because of the unavoidable microporosity and oxide formation. In addition to this investigation previous observations (*Turbyfill*, 1939; *Ryge*, 1958) have indicated that an atomic diffusion occurs between solder and parent alloy if the solder is overheated. The same effect can occur at lower temperatures, although not as readily, if the heating is sufficiently prolonged (*Skinner & Phillips*, 1967).

The way in which the effects of heat treatment influence corrosion in an oral milieu has not been studied to any great extent. However, in a clinical study *Hedegård* (1958) demonstrated that heat treatment of gold-soldered castings (bridges) at 725°C for 70 min resulted in a decreased tendency to discolouration of the restorations and less risk of subjective discomfort. In this study and in a text-book (*Hedegård*, 1971) he therefore recommends that cast and soldered gold constructions should be heat treated (»homogenized») before being finally installed.

Partially contradictory opinions concerning the heat treatment of gold-soldered assemblies are thus revealed in the literature. In order to estimate the *concentration* levelling out effects of heat treatment of different kinds the distribution of individual alloy components in the region of the gold-solder junction has to be studied. The purpose of the present study was: to investigate whether, on gold-soldered assemblies, any changes of the distribution of available alloy components occur in the region of the joint after different kinds of conventional heat treatments.

MATERIALS AND METHODS

Alloys investigated. Commercial dental casting gold alloys of the types which are commonly used for fixed crown and bridge restorations and for details of removable partial prosthesis were used. The alloys investigated correspond to types III (A) and IV (C) according to ADA specification No 5 1969, while the alloy (B) lies between type III and IV according to the same specification. The solder (melting range 765—820°C) is of a type commonly used especially for hard gold restorations. For detailed information about the chemical composition, see Table I.

Sample preparation. To avoid inclusions due to extraneous factors in the investing, casting, soldering and polishing techniques the samples were prepared as follows.

20 g of each casting alloy were placed in a preheated crucible of recrystallised Al_2O_3 (Degussit AL 23 containing $>99.5\ \%\ Al_2O_3$) and melted in an electrically heated furnace in an argon (Aga, quality SR) atmosphere. The melting temperature was held at 100°C above the liquidus temperature of the alloy in question. The crucible with the molten alloy was shaken before it was removed from the furnace to make sure all the metal was molten. After melting the alloy was allowed to cool in air for one minute and then quenched by rapidly cooling the crucible in water at room temperature. For each of the three alloys investigated four parent samples were prepared in this way. Each sample formed as a round plate with a diameter of about 25 mm and 2—3 mm thick, was then divided into twelve pieces, each approximately the same size, using an air-cooled fine-toothed saw. The pieces were each given a number and ten were randomly grouped in pairs. The remaining two pieces, marked »e» and »g» were used to represent the 'as cast' condition.

Table I.

Chemical composition in weight per cent of the alloys investigated. Code: 1 = specimen which was melted and quenched specially for the chemical analysis, 2 = specimen from one of the original parent samples of each alloy (marked »g»), 3 = alloy formulas provided by the manufacturer

Alloy	Code	Au	Ag	Cu	Pt	Pd	Zn	In	Ir
A	1	74.7	10.3	11.0	0.46	3.5	0.57	<0.1	0.01
	2	74.0	10.4	11.0	0.46	3.5	0.51	<0.1	0.01
	3	74.0	10.5	11.0	0.50	3.5	0.50		
B	1	71.0	10.0	12.9	0.01	6.2	0.58	<0.1	<0.01
	2	70.7	10.0	12.9	<0.01	6.3	0.71	<0.1	<0.01
	3	70.0	10.5	13.0		6.0	0.50		
C	1	66.9	10.6	12.3	9.6	0.1	0.52	<0.1	0.09
	2	66.7	11.3	12.2	8.2	0.1	0.21	<0.1	0.07
	3	68.0	12.0	12.5	7.0		0.50		
Solder	1	70.0	5.2	15.2	2.87	<0.1	0.83	∼5	0.05
	3	71.0	5.5	15.0	2.75		0.75	∼5	

One pair (marked »f») of the five pairs from two of the four parent samples of each alloy was then annealed at 800°C for one hour, *i.e.* a homogenizing heat treatment of conventional type was performed. After this heat treatment the »f» pair of pieces together with the remaining four pairs (a, b, c, d) from each of the parent samples were prepared for soldering together. A slight diamond-grinding of the areas to be soldered was performed during water-cooling to make them fit. The two pieces of every pair were then placed together with a solder gap of 0.1—0.2 mm using no soldering investment but wet asbestos to keep them fixed.

During the soldering procedure general principles of soldering were observed. Sufficient flux to cover the joint area only was used. The two parts to be joined were preheated and the solder was melted using a gas blowpipe. The applied solder flew at once and the flame was immediately removed. The soldered assemblies were allowed to cool in air for one minute before quenching in water at room temperature and cleaning in a commercial acid cleaner (Jel-Pac)* for dental gold castings.

Heat treatment of the soldered assemblies. Various heat treatments followed by bench cooling for one minute and then quenching in water at room temperature were performed. The marked samples were treated as follows:

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* J. F. Jelenko & Co., Inc. New York, U. S. A.

a: no further heat treatment after soldering,
b: heat treatment for 3 hours at 700°C after soldering,
c: heat treatment for 1 hour at 700°C after soldering,
d: heat treatment for 1 hour at 700°C after soldering, and then hardening heat treatment from 450°C to 250°C for 30 min followed by quenching,
e, g: representing the 'as cast' condition (extra samples),
f: heat treatment for 1 hour at 800°C before soldering and for 1 hour at 700°C after soldering.

The same inert-atmosphere furnace was used in all heat treatments except in the hardening heat treatment where a porcelain furnace of the common type was used.

Mounting and polishing the specimens. After the different treatments the a—d and f specimens were mounted in methyl methacrylate resin. The surface was prepared with silicon carbide paper, through 600 grit and polished with diamond paste, 6 μ, 1 μ and 1/4 μ. Four series of the a—d specimens and two series of the f specimen were produced from each alloy giving in total 54 samples ($4 \times 4 \times 3 + 2 \times 1 \times 3 = 54$).

The accuracy of the temperature measurements. The temperature control of the furnace, ±10°C, was carried out with a platinum versus platinum — 10-per cent rhodium thermocouple. The temperature was measured close to the crucible inside the furnace tube (60 cm by length and 5.5 cm inner diameter) using other thermocouples of the same type. The thermopotentials were measured by a Leeds and Northrup Student's potentiometer (cat no 7645) and read to ±0.02 mV. A Norma galvanometer (measuring range 0.0018-20 μA) was used as a zero point instrument. Before every reading a standardization with a Weston Normal cell (1.01859 V at 20°C) was performed. The accuracy of the measured temperatures was ±2°C.

Chemical analysis. The chemical composition of each alloy was determined by X-ray fluorescence analysis. The analysis was completed with atomic absorption spectrophotometry for Au, Cu and Zn. Two specimens of each casting alloy were analysed. One was the previously mentioned specimen marked »g» from one series of each casting alloy. The other was obtained by melting two grams of each alloy in the melting furnace used before. Immediately after melting the alloy was quenched in water at room temperature. In addition two grams of the solder alloy were treated in the same way and analysed. (Analytica, AB, Sollentuna, Sweden.)

Electron probe microanalysis. In the present study an electron-probe of the type Cameca MS 46 was used. (Swedish Institute for Metal Research, Stockholm, Sweden.)

Before the investigation the specimen surface was very slightly etched with diluted aqua regia to reveal the microstructure. The casting alloys as well as the solder alloy still showed marked segregations after the heat treatments and after a pilot study it was decided to use a prolonged beam in order to get a mean analysis of matrix and segregations. In this way changes in the element distribution across the gold-solder junction could be observed more easily. The beam used for the line analysis was 200 μm long and 1 μm wide. The line analysis was started in the cast alloy at a distance of 250 μm from the solder junction and proceeded across the junction into the middle of the soldered joint. In the case of a very narrow joint the line analysis proceeded further into the cast alloy on the other side of the soldered joint. In this way a line of about 350—500 μm was scanned by progressively moving the specimen at a rate of 68 μm/min under the electron beam. Simultaneously the X-ray emission intensity of two elements was recorded on charts moving at 5 cm/min. On the specimen surface marks of the burn at the beginning and the end of the scanned line were used to define the analysed region. The sample was brought back to the starting position and the same line was scanned again until X-ray emission data for all the elements in the specimen had been obtained (Fig. 1). Before each run the graphs were calibrated so that the background X-ray emission intensity was read as zero on the graph. Correction for absorption was obtained according to *Philibert* (1963). The mass absorption coefficients were taken from *Theisen* (1965). Each curve was recorded at a distance of ½ cm on the graph.

During the course of the investigation some microphases were found at the gold-solder junction of heat treated specimens from the alloys B and C. These structures were further investigated using electron microprobe point analysis.

Light microscopic observation. For each specimen a microphotograph was taken of the area over which the electron beam had travelled. The microstructure of the alloy could then be correlated with specific points on the graphical plots of the X-ray emission data for each element.

Statistical methods

The concentration curves are considered as a non-deterministic function X of an independent variable t where t corresponds to scanning length *i.e.*

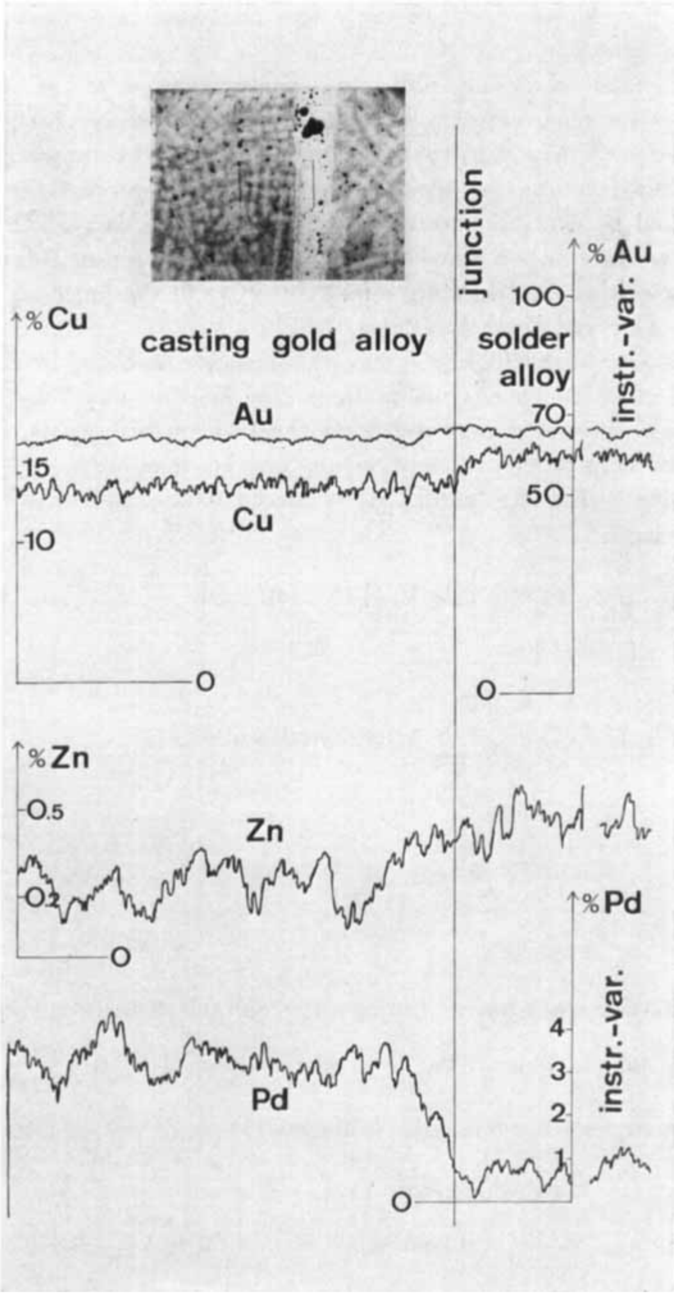

Fig. 1. Distribution of Au, Cu, Zn, Pd as obtained by line scanning with the electron probe over the surface of a specimen which was heat-treated before and after soldering (B4f). The marks on the microphotograph indicate the scanned line across the gold-solder junction.

time. Each continuously drawn curve is a realization of a non-stationary stochastic process.

Most methods of dealing with non-stationary time series are based on techniques for removing or filtering out the non-stationary part, leaving behind a series which can be treated as stationary. Since the statistical properties of stationary series do not change with time, these properties can be summarized by computing certain functions from the data which in this study is assumed to be a sample from a stationary time series. This assumption is somewhat dubious since effects do occur in the junction between the cast alloy and the solder alloy.

A stationary stochastic process may be adequately described by the lower moments of its probability distributions. The lower moments include *e.g.* the mean μ, variance σ^2, and covariance function. In this way the relations within and between concentration curves may be described.

Assuming a stationary normal series specify its autocovariance function for time lag u

$$\gamma(u) = E\left[(X(t)-\mu)\,(X(t+u)-\mu)\right],$$

which is estimated by

$$c(u) = \frac{1}{N}\sum_{t=1}^{N-u}(x(t)-\bar{x})\,(x(t+u)-\bar{x}),$$

where

$$\bar{x} = \frac{1}{N}\sum_{t=1}^{N} x(t),$$

and N is the sample size.

To normalize c(u) when comparing series with different scales of measurement the sample autocorrelation function is defined by $r(u) = \frac{c(u)}{c(0)}$.

For a completely random series (white noise)

$$\mathrm{Var}(r(u)) = 1/N$$

in which case a 95 per cent confidence interval för r(u) is ± 0.44.

Some concept of the interactions between two processes can be obtained by regarding a cross covariance function of a bivariate stationary stochastic process.

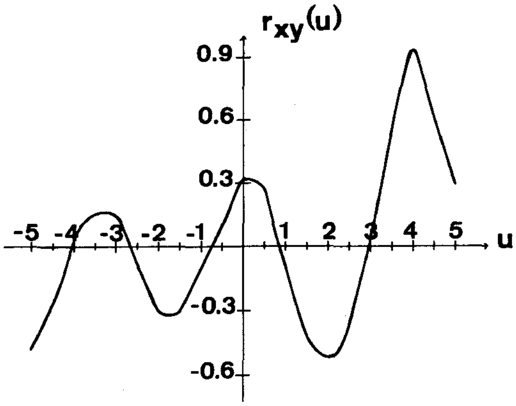

Fig. 2. Sample autocorrelation function for smoothing concentration points of Au in the specimen A4b (Computed according to *Dixon*, 1967).

If the stochastic processes X(t) and Y(t) are assumed to be stationary we define the cross covariance function between X(t) and Y(t+u) by

$$\gamma_{xy}(u) = E[(X(t)-\mu_x)\ (Y(t+u)-\mu_y)].$$

$\gamma_{xx}(u)$ is the autocovariance function (see above) and $\gamma_{xx}(0) = \sigma_x^2$ the mean square value of X(t).

If the study concerns two processes with possibly different scales of measurement or different variances it is necessary to define the cross correlation function as

$$\varrho_{xy}(u) = \gamma_{xy}(u)/\sqrt{\gamma_{xx}(0) \cdot \gamma_{yy}(0)} = \gamma_{xy}(u)/(\sigma_x \cdot \sigma_y).$$

The sample cross correlation function will be denoted $r_{xy}(u)$.

For two uncorrelated series of white noise we have Var $(r_{xy}(u)) = 1/N$. Thus results in the range ±0.44 can almost certainly be expected. However even larger values, such as $r_{xy}(0)$ may not necessarily indicate a real relationship because uncorrelated series may give spuriously large cross covariances as a result of large autocovariances within the two series (*Jenkins & Watts*, 1968).

Discrete representation of a concentration curve x′(t) is obtained by sampling values in a distance of h meter. Due to the noise from the recorder of Cameca 46 a moving average of 3 terms is computed for each value by putting

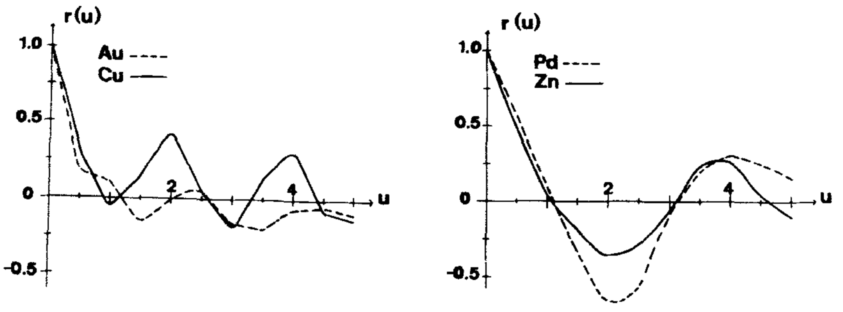

Fig. 3. Sample cross correlation function for concentration points derived from Au and Cu and from Pd and Zn in the specimen A4b (Computed according to *Dixon*, 1967).]

$$x'(t) = \frac{1}{3} \sum_{i=-1}^{1} x' \quad (t+ih).$$

In this case $h = 7 \cdot 10^{-6}$ m. The sample mean value of n smoothed concentration points is calculated from the formula

$$x(t) = \frac{1}{n} \sum_{i=1}^{n} x_i'(t)$$

where $x_i'(t)$ is a value at time t and i the running index of the realization.

These smoothed sampled average mean curves are put together in Figures 5–24.

Under given assumptions (see above) consider $\varrho = \gamma_{xy}(0)/\sigma_x\sigma_y$ as a measure of linear correlation between X and Y (Fig. 3 and $u = 0$). Table II shows point estimates r of ϱ.

The table is computed using the logarithmetic transform

$$\begin{cases} z_r = \frac{1}{2} \ln \frac{1+r}{1-r} & : r \geq 0 \\ z_r = -z_{-r} & : r < 0 \end{cases}$$

where z_r, for a moderate sample size N, is approximately normally distributed with expected value

$$\xi = \frac{1}{2} \ln \frac{1+\varrho}{1-\varrho} + \frac{\varrho}{2(N-1)}$$

and variance $1/(N-3)$. (*Fischer*, 1921)

Define the weighted mean value of the z_{r_i} : s (i = 1, . . ., n) as

$$\bar{z}_n = \frac{\sum_{i=1}^{n} (N_i - 3) z_{r_i}}{\sum_{i=1}^{n} (N_i - 3)} .$$

If the term $\frac{\varrho}{2(N-1)}$ is neglected $E[\bar{z}_n] = \xi$ and $\mathrm{Var}\,[\bar{z}_n] = 1/\sum_{i=1}^{n} (N_i - 3)$

This means that $\bar{z}_n$ may be used as a point estimate of ξ. A confidence interval to the value of ξ on the $(1-\alpha)$ — level may now be calculated by the formula

$$P\left(\xi \in \left[\bar{z}_n \pm \frac{Z_{1-\alpha/2}}{\sqrt{\sum_{i=1}^{n} (N_i - 3)}}\right]\right) = 1 - \alpha$$

(*Snedecor & Cochran,* 1967)

Retransforming the confidence limits into the original space by the transform

$$r = r(z) = \frac{e^{2z} - 1}{e^{2z} + 1} = \tanh\, z$$

(*Bennet & Franklin,* 1954)

a confidence interval to ϱ may be established. (Table II). The confidence interval shows if the null hypothesis: $\varrho = \varrho_0$, shall be rejected or not.

RESULTS

Chemical composition. The chemical compositions of the alloys as revealed by X-ray fluorescence analysis and atomic absorption spectrophotometry agree well with the alloy formulas provided by the manufacturer (Table I). In the chemical analysis iridium was found to be present in very small amounts in all the alloys investigated. Iridium is a commonly used grain refining agent in many dental gold alloys. As an alloying element in platinum it imparts added corrosion resistance to this metal.

Table II.

Interval estimate of ϱ *for some alloy compositions and treatments with high* $r(\bar{z}_n)$*-values. In addition the corresponding values for the specimen B4f are given*

Alloy composition and treatment	Elements	Casting alloy $r(\bar{z}_n)$ (Conf. interval)	Solder alloy $r(\bar{z}_n)$ (Conf. interval)
Ac	Zn/In	0.41 (0.06:0.67)	0.48 (0.15:0.71)
Bd	In/Pd	−0.61 (−0.79:−0.33)	−0.45 (−0.71:−0.09)
Cb	Au/Pt	−0.55 (−0.75:−0.24)	−0.66 (−0.82:−0.41)
B4f	Pd/Zn	−0.61 (−0.89:0.03)	0.21 (−0.58:0.80)

Microscopic observations. Most samples which were heat-treated for three hours after soldering had an increased grain size and a greater amount of microporosities in the gold-solder region in comparison with the rest. In all the samples from the alloy C and some of the samples from the alloy B the microphotographs revealed that after heat treatment for one and three hours respectively a new structure appeared at the junction between the cast alloy and the solder alloy (Fig. 4). By the use of electron microprobe point analysis these structures were investigated. Their compositions are given in Table III. As can be seen from the table there are microphases with compositions that are rather different from the original alloys. However, in regions with a decreased concentration of gold and silver the platinum content is markedly increased thus preserving the nobility of the alloys.

Electron microprobe data from line analysis. In the present study no inclusions due to extraneous factors in the laboratory techniques were found. Line scanning had revealed for each specimen the distribution of alloy components as is shown in Fig. 1. In those specimens where the line scan had proceeded across the whole soldered joint into the cast alloy on the other side, the distribution pattern of the elements was similar on both sides of the soldered joint. The height of a curve was read for each element at a distance of $\frac{1}{2}$ cm on the graph. Using these values the recorded mean composition of each element in a specimen could be obtained. However, when comparing the effects of different heat treatments performed only a smaller region close to the gold-solder junction was taken into consideration.

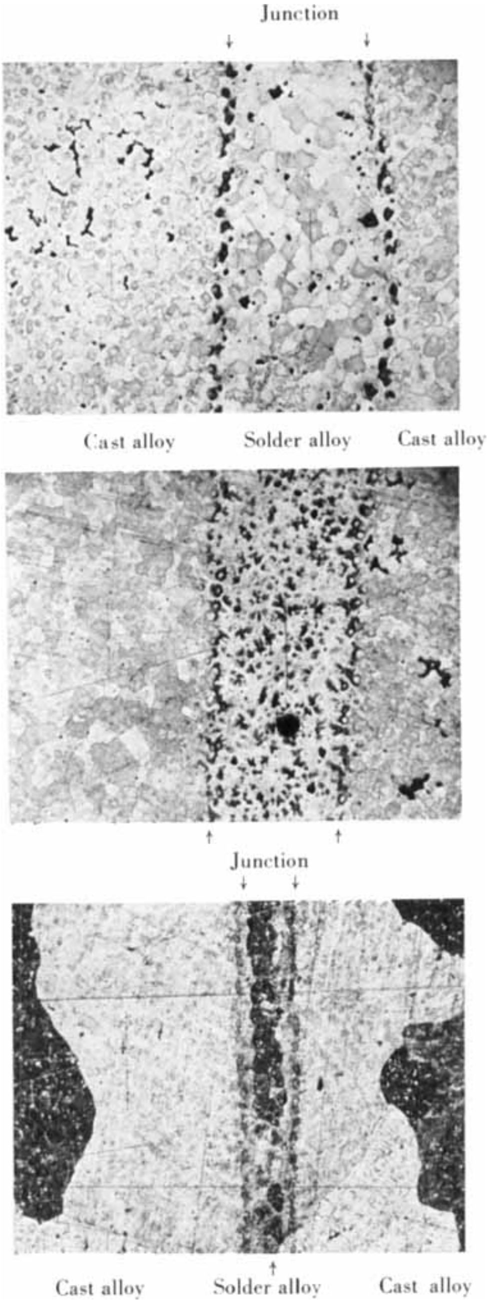

Fig. 4. Light microscopic pictures showing new structures emerging at the gold-solder junction after homogenizing heat treatment for three hours (C4b upper) and one hour (C1d middle and B3c lower). Magn. × 100.

Table III

Composition in weight per cent of microphases emerging in the region of the gold-solder junction after heat treatment

Specimen	Time for heat treatment (hours)	Phase localization	Weight per cent						
			Au	Ag	Cu	Pt	Pd	Zn	In
C4b	3	Junction	45	2.0	15.6	28.5		1.2	5.7
		Nearest to the junction in the cast alloy (two different phases)	48.7	4.6	21.8	23.0		1.0	
			61.6	12.2	14.9	4.2		0.2	0.3
		Nearest to the junction in the solder alloy	64.0	6.7	17.5	4.2		0.5	3.6
C1d	1	Junction	54.3	3.2	18.2	21.0		1.2	1.5
		Nearest to the junction in the cast alloy (two different phases)	60.1	7.2	15.9	14.8		0.7	
			71.0	11.5	12.7	2.9		0.2	
		Nearest to the junction in the solder alloy(two different phases)	64.5	6.7	15.9	8.4		0.7	3.4
			71.0	8.6	15.0	2.6		0.4	1.9
B3c	1	Junction	69.4	7.8	14.5	1.7	2.6	0.5	1.8
		Nearest to the junction in the cast alloy	70.9	10.1	13.0	0.3	5.3	0.4	
		Nearest to the junction in the solder alloy	69.4	7.3	15.2	1.4	2.4	0.5	2.8

A moving average of three terms for each of 10 sampling points in the parent alloy and 7—10 sampling points (depending on the width of the soldered joint) in the solder alloy was determined. The modified concentration points are plotted in Figs 5—24. Each figure shows the obtained effects from heat treatments for an element and an alloy. In the figures the curves a, b, c, d are mean value curves of four modified concentration curves, and the curves f of two. The difference in maximal variation of amplitude of the plotted curves in Figs 5—24 with regard to different heat treatments are collected in Table IV, V and VI, representing the alloys A, B and C respectively. In addition the difference between the corresponding mean value of the concentration of each element in parent alloy and solder alloy are given in these tables together with the corresponding standard deviation. Differences in maximal variation of curve amplitude with regard to effects

Table IV.

Some characteristic measurements of concentration points. Symbols: MV = the difference in concentration mean values between cast alloy (A) and solder alloy. SD = corresponding standard deviation. AMP = difference in maximal variation of amplitudes (curves from Figs. 5—11)

		Type of treatment				
		a	b	c	d	f
Au	MV	0.73	—1.43	—0.13	0.27	0.62
	SD	2.33	2.97	2.91	2.71	1.41
	AMP	2.25	2.49	2.52	2.03	1.63
Ag	MV	1.17	0.99	2.14	1.88	2.23
	SD	0.98	1.07	1.41	0.98	0.88
	AMP	1.53	1.53	3.35	2.19	3.02
Cu	MV	—2.94	—1.71	—3.01	—2.23	—2.17
	SD	1.06	0.78	0.93	1.03	0.82
	AMP	3.68	2.29	3.79	2.62	2.83
Pt	MV	—0.97	—0.66	—0.78	—0.86	—0.81
	SD	0.57	0.58	0.68	0.51	1.34
	AMP	1.19	0.95	1.36	1.02	1.15
Pd	MV	1.85	0.93	1.36	1.77	1.57
	SD	0.68	0.72	0.62	0.59	0.59
	AMP	2.35	1.84	1.72	1.92	2.02
Zn	MV	—0.04	0.04	—0.03	—0.09	—0.11
	SD	0.07	0.14	0.14	1.26	0.14
	AMP	0.07	0.08	0.11	0.15	0.21
In	MV	—2.49	—0.86	—1.98	—2.02	—1.73
	SD	0.68	0.49	0.86	0.75	0.62
	AMP	3.11	1.31	2.94	2.67	2.21

of alloy composition in specimens subjected to the same heat treatment are collected in Table VII.

To estimate the value of calculated results the dependence of time within curves as well as interactions between curves without any treatment effects must be taken into consideration. To obtain some concept about these phenomena autocorrelation function and crosscorrelation function have been examined using data (c. 20 concentration points) from the beginning of

Table V.

Some characteristic measurements of concentration points. Symbols: MV = the difference in concentration mean value between cast alloy (B) and solder alloy. SD = corresponding standard deviation. AMP = difference in maximal variation of amplitudes (curves from Figs. 12—18)

		Type of treatment				
		a	b	c	d	f
Au	MV	—2.72	—2.34	—3.70	—2.43	—2.64
	SD	2.43	3.18	3.34	2.64	1.70
	AMP	3.59	3.76	5.97	2.87	4.28
Ag	MV	2.06	1.65	1.96	2.42	2.65
	SD	0.76	0.86	0.95	1.20	0.81
	AMP	2.44	2.06	2.35	2.97	3.29
Cu	MV	—1.88	—1.40	—1.27	—0.88	—2.15
	SD	0.66	0.89	0.86	0.51	0.65
	AMP	2.04	2.03	1.90	1.14	2.49
Pt	MV	—1.67	—1.29	—1.16	—1.00	—1.63
	SD	0.90	0.49	0.55	0.59	1.09
	AMP	2.05	1.62	1.51	1.33	1.93
Pd	MV	3.28	2.82	2.96	3.53	3.20
	SD	1.16	0.93	1.12	1.03	0.95
	AMP	4.10	3.74	3.51	4.63	3.83
Zn	MV	—0.15	—0.01	—0.02	0.00	—0.13
	SD	0.11	0.13	0.08	0.10	0.13
	AMP	0.23	0.13	0.04	0.07	0.24
In	MV	—2.93	—1.99	—2.54	—2.93	—2.79
	SD	0.68	0.75	0.65	0.85	0.89
	AMP	3.59	2.54	3.04	3.38	3.40

the scanned line farthest away from the soldered joint, where no levelling out effects of heat treatment have been noted. The autocorrelation function shows that in most cases a time lag of h*) meter seems to be enough to avoid dependence in successive sampled points (Fig. 2). Apart from the small value of r(1) in Fig. 2 it is also noteworthy that some autocorrelation functions seem to be periodic. This means that the concentration levels of

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*) $(h = 7 \cdot 10^{-6} m)$

Table VI.

Some characteristic measurements of concentration points. Symbols: MV = the difference in concentration mean value between cast alloy (C) and solder alloy. SD = corresponding standard deviation. AMP = difference in maximal variation of amplitudes (curves from Figs. 19—24)

		Type of treatment				
		a	b	c	d	f
Au	MV	0.07	—1.99	—1.18	—0.39	—1.63
	SD	2.62	3.73	2.59	3.10	2.66
	AMP	2.12	5.42	2.55	3.34	3.81
Ag	MV	1.95	2.47	2.25	0.42	1.54
	SD	1.29	1.20	1.12	1.15	1.32
	AMP	3.12	3.33	3.02	1.91	3.01
Cu	MV	—0.55	—1.53	—1.31	—0.43	—0.66
	SD	1.05	1.07	0.92	0.98	0.88
	AMP	1.22	2.19	1.86	1.22	1.73
Pt	MV	3.72	3.87	3.26	3.54	3.77
	SD	1.07	2.23	1.70	1.34	0.96
	AMP	4.84	6.02	3.27	4.40	4.52
Zn	MV	—0.04	0.05	0.00	—0.03	0.26
	SD	0.08	0.64	0.13	0.14	0.64
	AMP	0.13	0.32	0.14	0.08	0.29
In	MV	—2.72	—2.15	—2.65	—1.79	—1.66
	SD	0.72	1.26	0.98	0.89	0.78
	AMP	3.43	3.43	3.51	2.65	2.44

Table VII.

Difference in maximal variation of amplitudes of the curves in Figs. 5—24 for three casting gold alloys of different composition in regard to treatment

	Treatment and alloy														
Element	a			b			c			d			f		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Au	2.25	3.59	2.12	2.49	3.76	5.42	2.52	5.97	2.55	2.03	2.87	3.34	1.63	4.28	3.81
Ag	1.53	2.44	3.12	1.53	2.06	3.33	3.35	2.35	3.02	2.19	2.97	1.91	3.02	3.29	3.01
Cu	3.68	2.04	1.22	2.29	2.03	2.19	3.79	1.90	1.86	2.62	1.14	1.22	2.83	2.49	1.73
Pt	1.19	2.05	4.84	.95	1.62	6.02	1.36	1.51	3.27	1.02	1.33	4.40	1.15	1.93	4.52
Pd	2.35	4.10	—	1.84	3.74	—	1.72	3.51	—	1.92	4.63	—	2.02	3.83	—
Zn	.07	.23	.13	.08	.13	.32	.11	.04	.14	.15	.07	.08	.21	.24	.29
In	3.11	3.59	3.43	1.31	2.54	3.43	2.94	3.04	3.51	2.67	3.38	2.65	2.21	3.40	2.44

the elements may vary in a periodic manner. The crosscorrelation function (Fig. 3) shows that in the specimen A4b Pd and Zn have a similar periodicity with time lag zero. In the area of the soldered joint the correlation between sampling points was calculated to get some idea of the changes in time for the studied concentration curves. If $|r(\bar{z}_n)|$ is large enough (depending on time dependence between concentration points) the statistican $r(\bar{z}_n)$ indicates whether the two curves have the same or different trends.

Error of methods due to the noise in the registration of concentration points and the notation of sampling values has been estimated to 2.15 and 0.1 and 0.5 weight per cent for Au and Zn and the group Ag, Cu, Pd, Pt, In respectively.

According to the alloy formulas provided by the manufacturer the solder alloy contains indium but no palladium while none of the parent alloys contain indium and the alloys A and B contain palladium. These specifications are on the whole confirmed by the analysis of the chemical composition as is shown in Table I. From the figures it is clear that after soldering indium has diffused into the parent alloys (Figs 11, 18, 24) and palladium has diffused from the alloys A and B into the solder alloy (Figs. 9, 16). This diffusion takes place rapidly during the soldering process and is in some cases increased after heat treatment.

The hardening heat treatment performed after the homogenizing heat treatment on one series (d) of each alloy did not seem to have any noticeable effect on the distribution of the alloy constituents.

Generally speaking the distribution of available alloy components as a function of heat treatment and alloy composition seems to be very difficult to estimate. In the alloy A (Table IV and Figs. 5—11) the concentration curves of Cu, Pt, Pd and In are somewhat levelled out after heat treatment for three hours (b) while the Au-, Ag- and Zn-distributions are hardly affected. The only elements for which concentration curves are levelled out at any heat treatment studied are Pd and In. The curves of Ag and Zn were not levelled out but on the contrary the differences increased after heat treatment for one hour.

In the alloy B (Table V and Figs. 12—18) heat treatment for three hours (b) levelled out the concentration curves of Ag, Pt, Pd, Zn and In to some extent while Au and Cu were not noticeably affected. Concerning heat treatment for one hour the difference in variation of amplitudes for the curves in some cases increased and in others decreased. For Pt and In heat treatment for one hour always levelled out the curves.

In the alloy C (Table VI and Figs. 19—24) heat treatment for three hours (b) increased the difference in maximal variation of amplitudes for curves representing each of the alloy constituents except In. More uneven effects were observed after the one hour heat treatments. Concerning the Au content an impoverished zone was observed close to the gold-solder junction while the opposite effect was found for Zn and Pt.

A comparison of the effect of alloy composition on the results of the various heat treatments performed (Table VII) indicates that the composition of parent alloy and solder alloy are mutually best levelled out in the alloy A. As could be expected heat treatment for three hours (b) in general gave a more even distribution of alloy components than heat treatment for one hour (c, d, f). However, the concentration levelling-out effects of heat treatments were not obtained to any great extent in the alloys B and C. In the alloy C especially heat treatment for three hours to level out concentration gradients had the opposite effect. These results are to some extent confirmed by the microphotographs of the specimen surfaces. In the alloy C the microphotographs revealed that new structures appeared at the junction between cast alloy and solder alloy on each of the heat treated soldered assemblies. The results of electron probe point analysis of these structures (Table III), on specimen C4b for example, are well supported by the composition curves shown in Figs. 19, 22, 23. New structures of a similar type appeared in some of the specimens from the alloy B after heat treatment for one and three hours (B1d, B2b, B3b and c, B4d).

The appearance of the microphases in the region of the gold-solder junction of the alloys B and C possibly made the occurrence of the levelling out of available alloy components more difficult.

DISCUSSION

Conditions within the oral cavity vary widely with respect to oxidation-reduction potentials and saliva composition. No currently known laboratory test shows adequate correlation with clinical performance. In the absence of a satisfactory test, past clinical experience has indicated that composition requirements give reasonable assurance of corrosion resistance. One condition is of course that the laboratory techniques do not involve methods which

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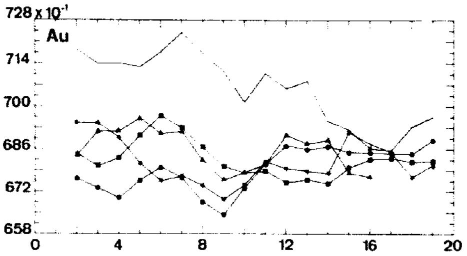
Figs. 5—24. Variation in distribution of available alloy components in soldered assemblies of the casting gold alloys A (Figs. 5—11), B (Figs. 12—18) and C (Figs. 19—24). Each curve is a mean value curve representing four (a, b, c, d) or two (f) average curves. Abscissa: equispaced ($7 \cdot 10^{-6}$m) sampled points. (Gold-solder junction between points 10 and 11.) Ordinate: concentration in weight per cent. ■ = a, ● = b, ★ = c, ▲ = d, — = f.



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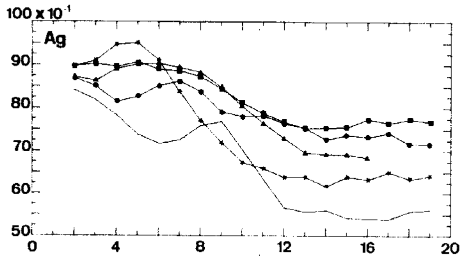

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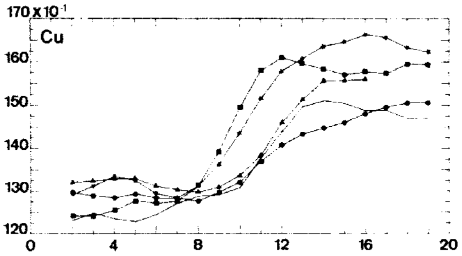

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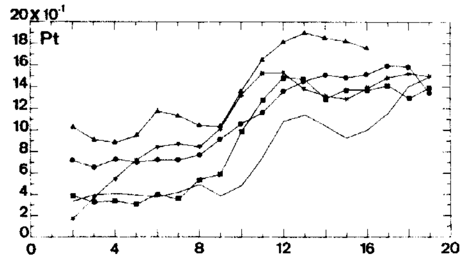

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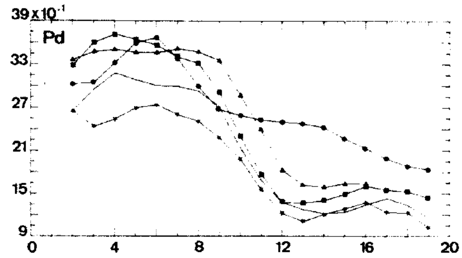

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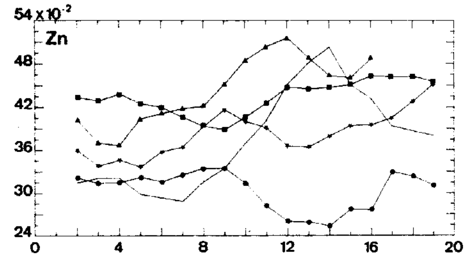

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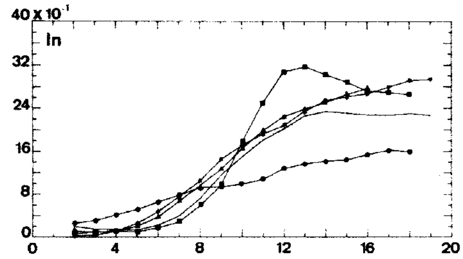

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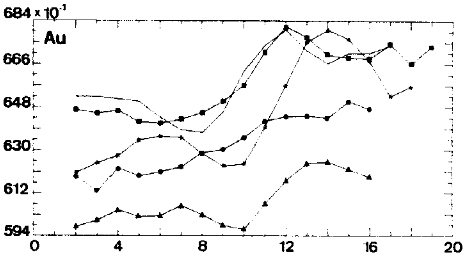

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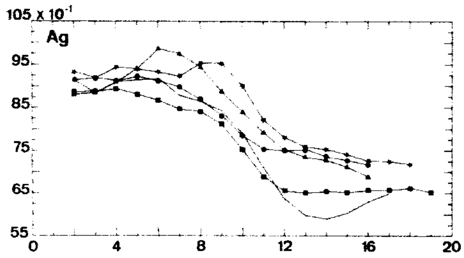

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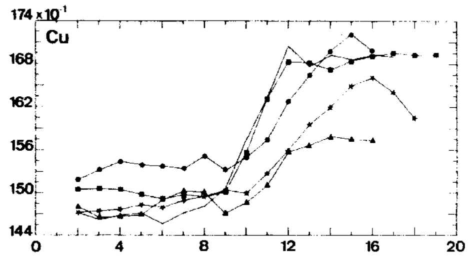

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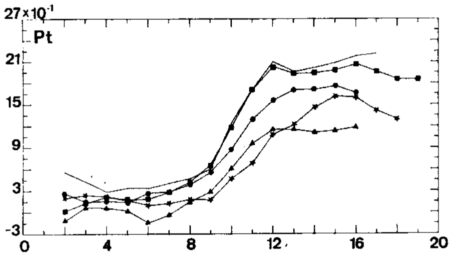

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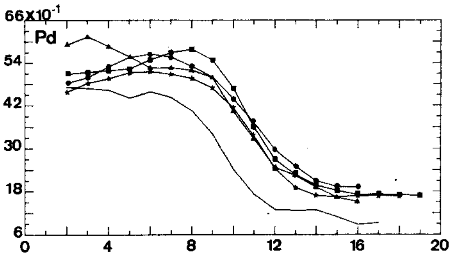

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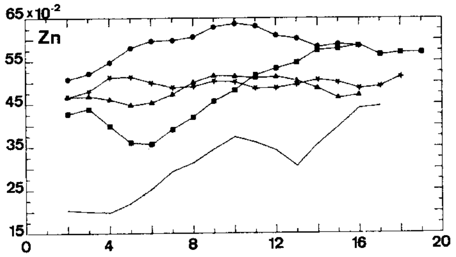

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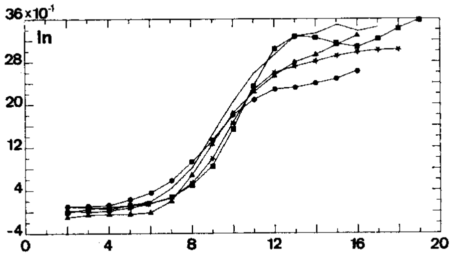

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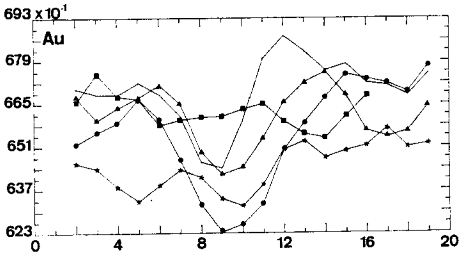

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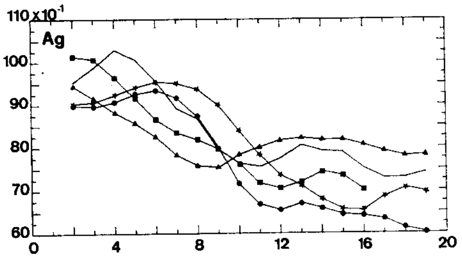

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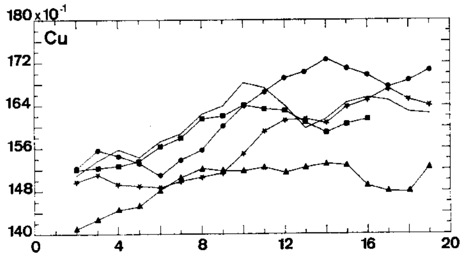

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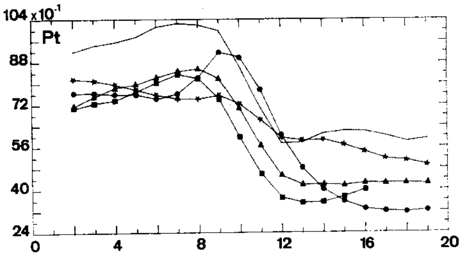

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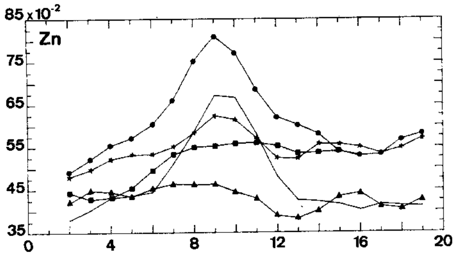

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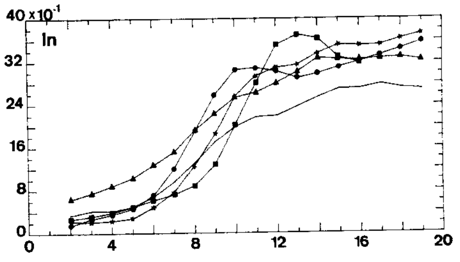

24.

influence uncontrollably the composition and distribution of the various alloy constituents. The composition can be determined quantitatively to a high degree of accuracy using spectroscopic or X-ray fluorescence techniques. However, until the development of the electronprobe microanalyzer there was no satisfactory way of determining the distribution of the various constituents in the material on a micron scale. The detection sensitivity of the electron probe is fairly low, being much poorer than the sensitivity obtained with the analytic methods previously mentioned. The main advantage with the electron probe is not its sensitivity but rather its ability to make a non-destructive analysis of very small volumes of material.

The electron microprobe is capable of carrying out point analysis with an accuracy of ±2%, provided sufficient care is taken in measuring the X-ray intensity and provided appropriate corrections are applied to convert the X-ray intensity values to weight per cent (*Weinberg,* 1970).

The accuracy is considerably worse during line scanning and area scanning. *Eick & Hegdahl* (1968) who studied the degree of segregation in dental casting gold alloys used line scanning. The average height of the concentration points recorded on the graphs was put equal to the mean composition as determined previously from other methods. In this manner the height of each of the concentration points was correlated with a specific percentage concentration value. The coefficient of variation was then used to define the degree of segregation on a quantitative basis.

No such transformations were done in the present study since the main purpose was not to estimate the alloy composition at a given point but merely to study changes in the element distribution in the region of the gold-soldered joint. Since these changes are most pronounced very close to the junction only concentration values from shorter parts (c. 70 μm) of the scanned lines on each side of the gold-solder junction have been taken into consideration.

Certain information about paired comparisons of curves may be given by $r(\bar{z}_n)$-statistican. However, a multivariate statistical model would correspond better to what actually happens due to heat treatment. Such a model would have been complex and as difficult to interpret as the $r(\bar{z}_n)$-statistican. To separate effects of treatment and effects of alloy composition from different levels of element concentration in solder and simultaneously to take the noise of registration into consideration will surely be an intricate task. As long as the degree of segregation is not properly defined these descriptive measurements may serve as a description of the interactions between and within the concentration curves. Summarizing these statistical measurements to a relevant measure of the degree of segregation would seem to be difficult in spite of the proposals suggested in the literature.

In the present investigation no inclusions were found in the specimens. This is probably due to the techniques used in producing the samples. In previous studies (*Söremark et al.,* 1966; *Eick & Hedegård,* 1968) it was established that inclusions due to extraneous factors in the investing, casting and polishing techniques are frequently found in dental gold castings.

Söremark et al. (1966) who studied the distribution of components of gold alloys as related to heat treatment found that the minor as well as some of the major constituents had an uneven distribution within the cast alloy. The various heat treatments performed did not change this uneven pattern as much as was expected. These results are in agreement with data from the present study. Our results indicate that a migration of elements across the gold-solder junction can occur during heat treatment. However, this migration of atoms, colloidal or ionic particles seems to be fairly uncontrollable as related to the alloys in total.

If one element is an integral part of only the parent alloy or the solder alloy the migration occurs mainly during the soldering process and is generally not influenced to any gret extent by subsequent heat treatment.

Theoretically complete equalization of the differences in composition between parent alloy and solder alloy, resulting in a very homogeneous structure, could take place at extremely high temperatures. However, grain growth, microporosities and oxide formation would then be unavoidable (*Skinner & Phillips,* 1967; *El-Ebrashi et al.,* 1968) resulting in an inferior joint with deteriorated mechanical properties. Partial equalization across the gold-solder junction can reduce the potential differences arising between differently composed metallic restorations in the oral milieu. However, according to the results of the present study microphases can appear in the region of the gold-solder junction after heat treatment. The composition of these microphases is more or less different from the composition of the parent alloy as well as the solder alloy thus creating conditions which promote corrosion. In addition the mechanical properties of these microphases are unknown, The presence of inclusions in many dental gold castings produced using conventional laboratory techniques makes the conditions still more complicated.

With no, or at least a minimum, migration of atoms or colloidal or ionic particles between the solder and parent alloy more favourable conditions are created. The chemical compositions of the two alloys are indeed different, but the possibility of corrosion occurring can to some extent be estimated, at least by empirical methods. In addition the mechanical properties of the two alloys are preserved and grain growth, microporosities and oxide formation are diminished or avoided.

In the present study the results have shown that the concentration curves for cast alloy and solder alloy are mutually best levelled out in samples from the alloy A. The microphotographs of the joints in the soldered assemblies from this alloy did not show any signs of formation of microphases at the junction. Theoretically it is possible that in these cases the resistance to corrosion can be improved by heat treatment. However, many of the microphotographs from this alloy also revealed that intracrystalline segregation still persisted within the parent alloy itself as well as within the solder alloy after heat treatment for three hours.

The main conclusion from the present study therefore is that heat treatment at high temperatures (»homogenizing heat treatment») of dental gold soldered assemblies made from the alloys investigated should not be performed unless a careful investigation has shown that no microphases appear after heat treatment. Although only three casting alloys of type III—IV have been studied the conclusion is, from a theoretical point of view, probably valid for most of the complex dental gold alloys in which the great amount of available alloy components will promote the formation of microphases especially at high temperatures. The recommendation, therefore, is that »homogenizing» heat treatment of gold soldered assemblies at high temperatures should not be performed as a routine.

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