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CONDITIONS FOR ATTAINMENT OF THERMODYNAMIC EQUILIBRIUM FOR THE Ag/Hg SYSTEM

Influence of the particle shape parameter

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Following a previous study on the influence of the size of silver particles used in dental alloys on the conditions for the attainment of thermodynamic equilibrium, results are presented on the influence of the particle shape factor. Calorimetric results obtained using different particle forms are compared with those derived from a mathematical model in which it is considered that silver particles can assume a spherical or cylindrical (flat or narrow) shape. It appears that the thermal effects obtained by computation are closer to those obtained by calorimetric experimentation when the sphere of the model is transformed into either a disc or a rod.

For some time now, various research projects have been undertaken in order to improve the clinical behaviour of the most commonly used dental amalgams [1, 2]. In the alloy powders, the Cu percentage has been increased, and the spherical particles have been introduced. With regard to the latter, we have started a fundamental study to determine the influence of the particle shape on the amalgamation reaction. In dentistry, the choice of the calorimetric method was quite new [3, 4], and we first had to limit our measurements to the simple binary Ag/Hg system. For the Ag/Hg system, reproducibility difficulties appeared when we tried to determine the excess enthalpy values [5]. For example, the mass thermal effect varies with the origin and size of the silver particle [6]. In a previous paper [7], we compared experimental results obtained by calorimetry with the numerical results relating to a theoretical model taking into account the size of the silver grains, considered as spherical with an initial radius R_0. In this way, we were able to determine a critical initial radius $R_{0c} = 7$ μm, which allowed as to differentiate two

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groups of particles: small particles, which could be completely amalgamated, and large particles, which could not, whatever the initial Hg quantities used.

For the latter, we defined a domain of pseudosaturation, which thermodynamic equilibrium cannot be attained in the time considered for the calorimetric measurements. The extent of this domain increases when the initial radius R_0 is increased. By experimentation, it was seen [6] that the γ-phase behaviour for the initial stages of the reaction is such that:

1. the expansion of the γ-phase layer is limited to a value $e^* = 10$ µm;
2. the γ-phase dissolution in the Hg excess cannot be detected calorimetrically.

Thus, we saw how particle size is a factor in the appearance of this domain. Photo 1 depicts the silver particles used for the measurement. The grain shape seems cylindrical rather than spherical. In the present study, we have used the same methodology (calorimetric/theoretical results) to study the influence of the particle form factor on the existence of this domain.

Materials and methods

Calorimetric experimentation

A Seteram C.R.M.T. calorimeter was used. Ag (Lyon-Allemand) powder washed in 10 vol% H_2NO_3 solution and cleaned Hg (Prolabo-Hg, washed 4 times by allowing it to fall in drops through a 3 vol% H_2SO_4 solution) were placed in a divided cell (Fig. 1), and brought into contact once thermal equilibrium had been reached (25°). The Ag–Hg reaction is endothermic, and the shape of the thermogramm obtained, in terms of time, shows a rapid decrease in reactivity, characterizing an incomplete reaction.

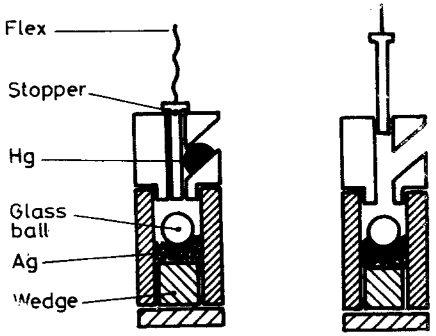

Fig. 1 Divided calorimetric cell. (The stopper is withdrawn once thermodynamic equilibrium is reached. The glass ball is used to check the Hg flow.)

Models

Following the first experimental results, which showed the influence of the size, origin and surface state of the silver particles on the recorded thermal effects, we conducted complementary investigations (M.E.B. measurements, electron microprobe analysis, calorimetric examination). Thus, Photo 1 shows a silver particle after its Hg reaction for a given mass ratio ($\theta = m_{Hg}/m_{Ag}$).

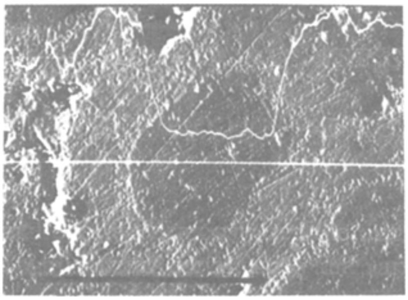

Photo 1 Microprobe examination of an amalgamated particle after a 3-θ reaction. The variation of the relative [Hg] is represented by the graph above the median line. The points of the analysis are represented on this line. The particle comprises a residual silver core and a peripheral γ-phase layer

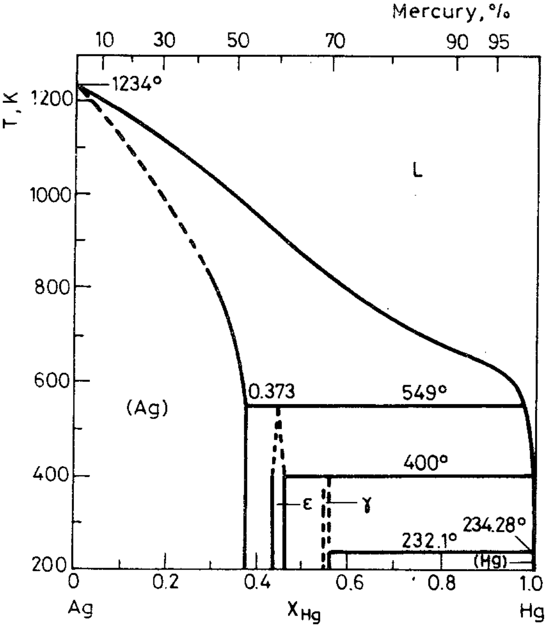

Fig. 2 The Ag–Hg phase diagram [8, 9]

Two concentric layers can be differentiated. The microprobe analyser gave the composition of each: residual pure Ag in the core, and a γ-phase layer surrounding it, with a thickness of about 10 μm. It may be noted that, for a given time, during which no particular thermal effect is detectable, we did not observe the results predicted from the Ag/Hg phase diagram (Fig. 2).

Consequently, we elaborated a theoretical model by formulating the following hypothesis: whatever the relative mass ratio may be, the γ-phase is the only one that forms spontaneously, and its growth towards the Ag core is limited to a thickness $e=e^*$ of about 10 μm.

Sphere model

The complementary experimentation and the above hypothesis enabled us to elaborate a preliminary model, taking into consideration spherical silver particles with an initial radius R_0 (Fig. 3).

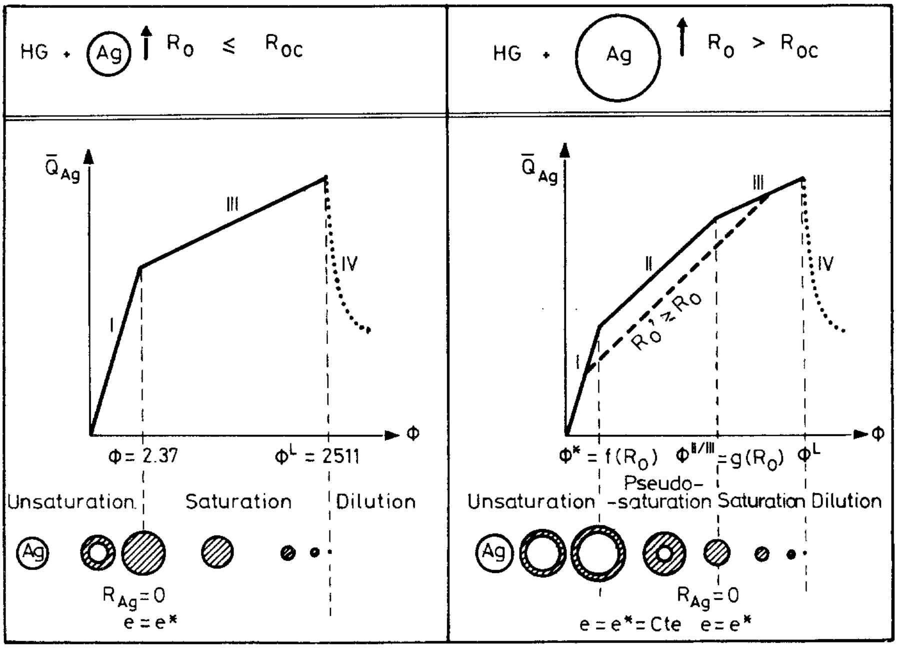

Fig. 3 Sphere model: theoretical thermal effects *vs.* ratio θ for different values of R_0. The structure of the particles is represented at the bottom of this diagram for each domain. For $R_0 \leq R_{0c}$: when θ increases, with $\theta \leq \theta^L$, there are only domains I and III. For $R_0 > R_{0c}$: When θ increases, with $\theta \leq \theta^L$, there are then three domains. Domain II increases with R_0, which restricts domains I and III

Depending of the R_0 value, after reaction we can have either a completely amalgamated particle with radius R, or a partially amalgamated particle, where the residual silver core has radius R_{Ag}.

Depending on the θ value, the reaction products can be as follows:

Domain I: $Ag+\gamma$

This is a domain of unsaturation. When θ increases, the γ-phase layer grows. Finally, the upper limit of the domain is reached when the silver core disappears. At this point, if $R_0 \leqslant R_{0c}$, then $\theta = \theta^{\gamma} = 2.367$; if $R_0 > R_{0c}$, then $\theta = \theta^* < \theta^{\gamma}$.

Domain II: $Ag+\gamma+L$

This is a domain of pseudosaturation, and it appears only with the particles for which $R_0 > R_{0c}$. At the $\theta = \theta^*$ value, each particle seems to be amalgamated, but there is a residual silver core; and when $\theta > \theta^*$, an Hg excess appears. The γ-phase layer has thickness e^*. In domain II when θ increases, the silver core becomes smaller as a consequence of two simultaneous phenomena:

(a) γ-phase dissolution at the grain boundary,

(b) γ-phase formation at the periphery of the Ag-core. Domain II ends at the $\theta^{II/III}$ value, when the pure Ag core disappears.

Domain III: $\gamma+L$

At $\theta = \theta^{\gamma}$ (for $R_0 \leqslant R_{0c}$) and $\theta = \theta^{II/III}$ (for $R_0 > R_{0c}$), the particles are completely amalgamated. With further increase in θ, the Hg-saturated phase appears, following dissolution of the γ-phase in the Hg excess.

Domain IV: 1

This appears when the γ-phase particle is completely dissolved.

It is characterized by an unsaturated Hg solution (1-phase) which results from dilution of the L-phase.

Cylinder model

So as to introduce the shape factor ($\xi_0 = 2R_0/L_0$), we considered the case of cylindrical particles (with radius R_0 and length L_0) closer to the profile of the silver grain we had available. The theoretical development will be published in a future paper.

We can classify the cylinder shapes as follows:

When $0 < \xi_0 < 1$, we have rods.

When $1 < \xi_0 < \infty$ we have dics.

If $\xi_0 = 1$, we have "cuboïds" with $2R_0 = L_0$.

Critical initial dimensions

As with the sphere model, we can define the critical initial dimensions as being those of a cylinder for which, when $e = e^*$, $\theta = \theta^* = \theta^\gamma$. If any given cylindrical particle is taken with characteristic dimensions P_d (smaller dimension) and G_d (larger dimension), it can be stated that it is the growth of the γ-phase in the direction of the small dimension which determines the disappearance of the residual Ag core.

The critical dimension (P_{dc}) value is calculated as follows:

For the rods: $P_d = 2R_0$ and $P_{dc} = 2R_{0c}$, with:

$$R_{0c^2}+2\frac{\alpha_x}{\beta}\frac{(e^*)^2}{L_0}R_{0c}-\frac{\alpha_x}{\beta}(e^*)^2\left(1+\frac{2e^*}{L_0}\right)=0$$

For the discs: $P_d = L_0$ and $P_{dc} = L_{0c}$, with:

$$L_{0c^2}-2\frac{e^*}{\left(\frac{e^{*2}}{R_0}\right)\cdot\frac{\alpha_x}{\beta}}\left[1+\frac{2e^*}{R_0}\cdot\frac{\alpha_x}{\beta}\left(1+\frac{e^*}{R_0}\right)\right]L_{0c}+$$

$$+4\frac{(e^*)^2}{\left(\frac{e}{R_0}\right)^2}\left(1+\frac{e^*}{R_0}\right)^2=0$$

For the "cuboïd", $P_d = G_d$. The relationship turns out to be the same as for the spheres:

$$R_{0c} = e^*\sqrt[3]{\alpha/\beta} = 7\ \mu\mathrm{m}$$

where α and β are specific parameters for the Ag/Hg system. It can be seen that, for all cylinders where $\xi_0 \neq 1$, the value of P_{dc} is a function of G_d. These functions are represented in (Fig. 4).

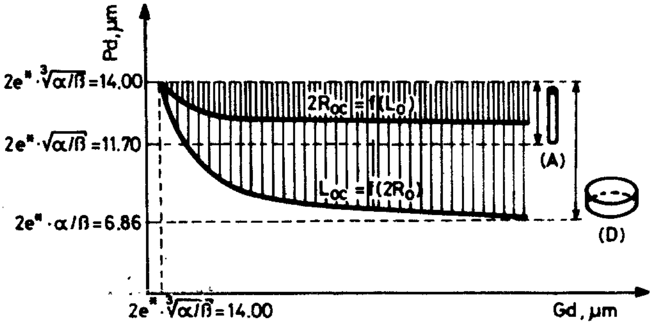

Fig. 4 Cylinder model: The cylinders (rods or discs) whose P_d value varies in the area bounded by the $P_{dc} = f(G_d)$ curve cannot be completely amalgamated at $\theta < \theta^{\mathrm{II/III}}$

Results

A knowledge of the correlations between P_{dc} and G_d theoretically allows specification of the conditions for attainment of thermodynamic equilibrium. As with the sphere model, we can consider the Hg reaction with the Ag cylinders in domains I–IV. For each, the model provides a knowledge of:

The geometry of the particle

This is expressed by using reduced variables:

$$x = \frac{R_{\mathrm{Ag}}}{R_0} \quad y = \frac{R}{R_0} \quad u = \frac{L_{\mathrm{Ag}}}{L_0} \quad v = \frac{L}{L_0}$$

with R and L as the radius and length of the cylinder after reaction, and R_{Ag} and L_{Ag} as the radius and length of the residual Ag core.

Introduction of an isotropic constraint leads to the relations:

$$u = 1-\xi_0+\xi_0 x$$

$$v = 1-\xi_0+\xi_0 y$$

which added to the mass balances, yields the functions $x(\theta)$, $y(\theta)$, $u(\theta)$ and $v(\theta)$.

For example, in the domain of pseudosaturation, x is the solution of the following equation:

$$x^3+\left[\frac{1-\xi_0}{\xi_0}+3\gamma\left(\frac{e^*}{R_0}\right)\right]x^2+\gamma\left(\frac{e^*}{R_0}\right)\left[3\left(\frac{e^*}{R_0}\right)+ +2\left(\frac{1-\xi_0}{\xi_0}\right)\right]x-K = 0$$

where

$$K = \left\{\frac{1-a\theta}{\xi_0}-\gamma\left(\frac{e^{*2}}{R_0}\right)\left[\left(\frac{e^*}{R_0}\right)+\frac{1-\xi_0}{\xi_0}\right]\right\}$$

with a and γ as specific parameters of the Ag/Hg binary.

The masses of the different phases formed

These are expressed with the reduced variables $u_\gamma = m_\gamma/m_{\mathrm{Ag}}$, $u_L = m_L/m_{\mathrm{Ag}}$ and $u_{\mathrm{Ag}} = m^c_{\mathrm{Ag}}/m_{\mathrm{Ag}}$, with m^c_{Ag} the Ag mass in the residual core.

These masses are functions of x, y, u and v, and they are obtained by using mass balance and geometrical considerations.

For example, in domain II, we have:

$$u_\gamma = \frac{\varrho_\gamma}{\varrho_{\text{Ag}}}[y^2 v - x^2 u]$$

$$\mu^c_{\text{Ag}} = ux^2$$

$$\mu_L = \frac{1 - \mu^c_{\text{Ag}} - \mu_\gamma \alpha^\gamma_2}{\alpha^L_2} = \frac{\theta - \mu_\gamma \alpha^\gamma_1}{\alpha^L_1}$$

with

$$\alpha^\gamma_1 = x^\gamma_1 \cdot \frac{M_{\text{Hg}}}{M_\gamma}, \quad \alpha^L_1 = x^L_1 \cdot \frac{M_{\text{Hg}}}{M_L}$$

and

$$\alpha^\gamma_2 = x^L_2 \frac{M_{\text{Ag}}}{M_\gamma}, \quad \alpha^L_2 = x^L_2 \cdot \frac{M_{\text{Ag}}}{M_L}$$

where x^Φ_i is the molar fraction of i in a given Φ-phase.

The thermal effects

Mass quantities (for one-Ag-gr are used for these. We have:
$\bar{Q}_{\text{Ag}}$ for the overall thermal effect,
$\bar{Q}^\gamma_{\text{Ag}}$ and $\bar{Q}^L_{\text{Ag}}$ for the contributions of the γ and L-phases to $\bar{Q}_{\text{Ag}}$.
Then,

$$\bar{Q}_{\text{Ag}} = \bar{Q}^\gamma_{\text{Ag}} + \bar{Q}^L_{\text{Ag}}$$

with

$$\bar{Q}^\gamma_{\text{Ag}} = \mu_\gamma \cdot \frac{h^E_\gamma}{M_\gamma} \quad \text{and} \quad \bar{Q}^L_{\text{Ag}} = \mu_L \frac{h^E_L}{M_L}$$

To summarize after the development of the expressions of these different functions for each domain, it appears that, with this model, thermodynamic equilibrium can possibly take place:

(1) if $\theta \geqslant \theta^\gamma$ for particles with $P_d \leqslant P_{dc}$;
(2) if $\theta > \theta^{\text{II/III}}$ for particles with $P_d > P_{dc}$.

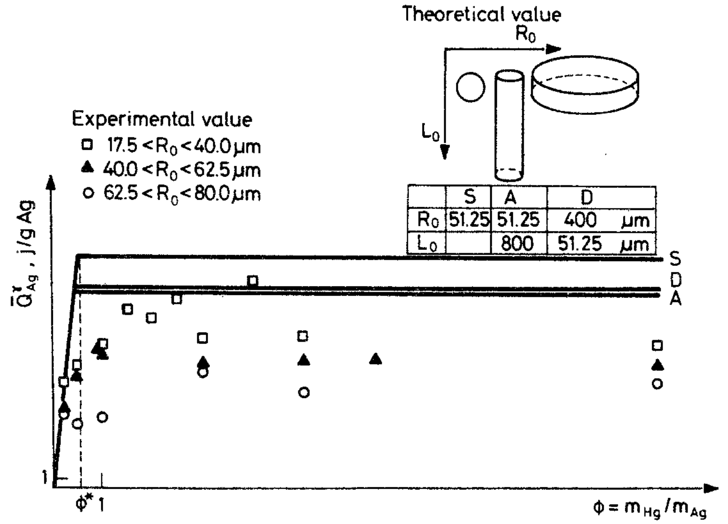

Fig. 5 The theoretical thermal effects have been calculated for spherical particles with a theoretical radius R_0, which is comparable to the mean radius of the silver particles used for the calorimetric experimentation ($R_0 = 51.25$ μm). The theoretical results are larger than the experimental ones. In the same way, the thermal effects have been calculated for cylindrical particles (rods and discs) where the small dimension is equal to the radius of the sphere. The theoretical and experimental results coincide better, particularly in the case of the rods

Results and discussions

Figure 5 illustrates the changes in the experimental and theoretical thermal effects as the mass ratio varies. We can see that:

(1) For the experimental method, the reaction becomes less complete when the particle size increases.

(2) The experimental values are noticeably lower than the theoretical ones calculated for spherical particles (S)

(3) When the shape factor (I: discs, A: rods) is taken into account, the theoretical values are closer to the experimental values. Thus, it appears that when one of their dimensions (P_d) is equal to the radius sphere, such discs or rods would give less complete reactions than observed with spheres. (In this case P_{dc} decreases as G_d increases.)

(4) After M.E.B. observations (Photo 2), it may be noted that the silver grains used for the calorimetric experimentation present various shapes and sizes, even in a given granulometry group. For a numerical simulation we considered 3 groups of

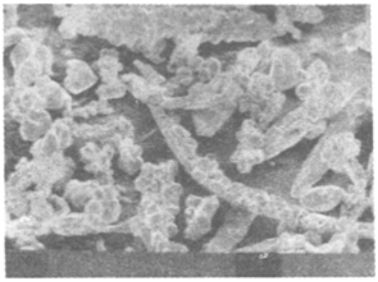

Photo 2 M.E.B. examination of electrolytic silver particles used for calorimetric experimentation. (1) The manufacturer indicated a powder particle size range of 35 µm to 80 µm. The actual range is wider, since many grains are larger than 80 µm. (2) A certain heterogeneity is also apparent: the grain shape, tended more towards a cylindrical than a spherical form

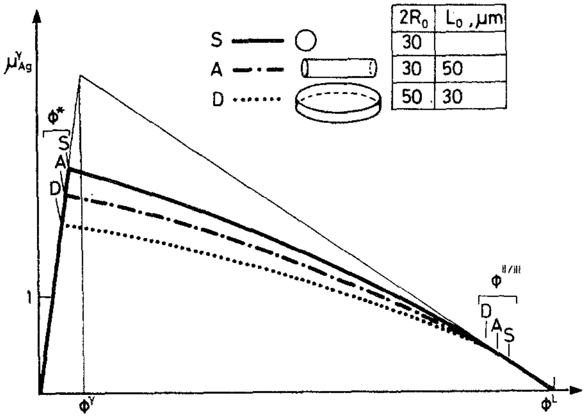

Fig. 6 Correlation of the mass of the γ-phase formed *vs.* the θ increase. Spherical (S) or cylindrical (A, D) particles could have come from a 50 µm—mesh sifting. The θ—scale is not respected ($\theta^{\gamma} = 2.367$ and $\theta^L = 2511$). The spherical particles give a more complete reaction

Ag powders (spheres, discs and rods) which could have come from a 50 µm mesh sifting. (In Fig. 6, in which the scale of the θ values is not respected, we have represented the changes in the γ-phase quantities formed with increase in Φ.

Conclusion

It can be concluded that the heterogeneity of the shape and size of the Ag particles can be an important parameter in the dispersion of the experimental values for the thermal effect.

In fact, this study, which was primarily conducted for dental research, demonstrates how the calorimetric determination of excess enthalpies can be difficult for all metal powder/liquid systems. However, it allowed quantitative specification of the conditions for attainment of thermodynamic equilibrium, particularly for the Ag/Hg system.

In dentistry, this study will lead to calorimetric experiments at 50° (for Ag–Hg), and to application of this method to the compound systems (Sn/Cu/Hg) used for dental amalgams.

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Zusammenfassung — Nach einer vorangehenden Untersuchung über den Einfluß der Größe von für Dentallegierungen verwendeten Silberteilchen auf die Bedingungen zum Erreichen des thermodynamischen Gleichgewichtes wird nun über den Einfluß der Teilchenform berichtet. Dabei werden kalorimetrische Ergebnisse von verschiedenen Teilchenformen mit denen verglichen, die man mittels eines mathematischen Modelles erhielt, bei dem angenommen wird, daß die Silberteilchen in Kugel- oder Zylinderform (flach oder schmal) zugegen sind. Es zeigte sich, daß man sich bei den errechneten Werten für die thermischen Effekte der kalorimetrisch bestimmten Werten besser nähert, wenn die Kugeln im Modell durch Ansteigen der einen Dimension in Scheiben oder Stäbchen ausarten.

Резюме — Продолжая ранее проведенное исследование, касающееся влияния размеров частиц серебра в зубных сплавах для достижения термодинамического равновесия, авторы представили результаты, касающиеся влияния формы частиц серебра. Калориметрические измерения различных форм частиц были сопоставлены с таковыми, выведенными на основе математической модели, в которой предполагалось, что частицы серебра могут быть сферической или цилиндрической форм. Кажется очевидным, что значения вычисленных термических эффектов являются более близкими к таковым, полученным калориметрическим методом, где сферическая модель представлена увеличением одного из размеров круга или стержня.