JOURNAL OF MATERIALS SCIENCE 19 (1984) 2599–2605

Rearrangement phenomenon developed inside powder compacts: theoretical model expressing the associated shrinkage

C. SERVANT
Laboratoire de Métallurgie Physique, associé au CNRS no. 177, Bâtiment 413, Université Paris-Sud, 91405 Orsay Cedex, France

F. KHAN-BEHAR, G. CIZERON
Laboratoire de Structure des Matériaux Métalliques, Bâtiment 465, Université Paris-Sud, 91405 Orsay Cedex, France

A distinct new Stage 0 has been resolved which precedes the normal Stage 1 in the sintering curves of iron powder composed of smooth spherical particles. It can, therefore, be resolved only under conditions of high-speed dilatometry, where the errors induced by heating are minimized. The temperature and pressure dependence of Stage 0 suggests that this kinetic regime is related to the relaxation of tangential interparticle stresses caused by incomplete compaction. To take into account the experimental results a model is proposed. The agreement between the dilatometric curves calculated from this model and the experimental ones is good.

1. Introduction

In an earlier study, carried out by high speed dilatometry, it was shown that the shrinkage associated with isothermal sintering occurs in two successive stages in the case of ex-carbonyl iron powder green pellets for sintering temperatures ranging from 500 to 800° C.

The observation of the first stage, referred to as Stage 0, is dependent upon the form of the particles, their size distribution, the value of the strength of compaction and the temperature of the thermal treatment. This phenomenon was related to a rearrangement of the particles of the green pellet, due to a relaxation of tangential interparticle stresses, in order to obtain their highest compactness.

In this paper, a theoretical model is proposed to describe the experimental results obtained earlier which have already been published [1].

2. Model describing the observed experimental shrinkage

2.1. Analytical representation of the size distribution of the particles

The radii distribution of the particles of the iron powder used is shown in Fig. 1 and is represented by a Type III Pearson function (shifted from the origin of the r_0 value), the expression of which is as follows

$$f(r-r_0) = \frac{1}{\gamma\Gamma(p)}\left(\frac{r-r_0}{\gamma}\right)^{p-1}\exp-\frac{(r-r_0)}{\gamma} \quad (1)$$

The values of the parameters of this function (for the powder under consideration in this paper), deduced from a fitting, are as follows:

$$p = 2; \quad \Gamma(p=2) = 1; \quad \frac{1}{\gamma} = \alpha = 4 \times 10^3\,\mathrm{mm}^{-1}$$

hence (2)

$$f(r-r_0) = \alpha^2(r-r_0)\exp-\alpha(r-r_0)$$

2.2. Influence of compaction and formation of contact area

The influence of the compaction leading to the formation of contact areas between the particles with a spherical form can be calculated from the Hertz theory ([2]. For two particles having the same radius and supporting a resultant strength $\bar{F}$ directed along the centre line of the two particles,

0022–2461/84 $03.00 + .12

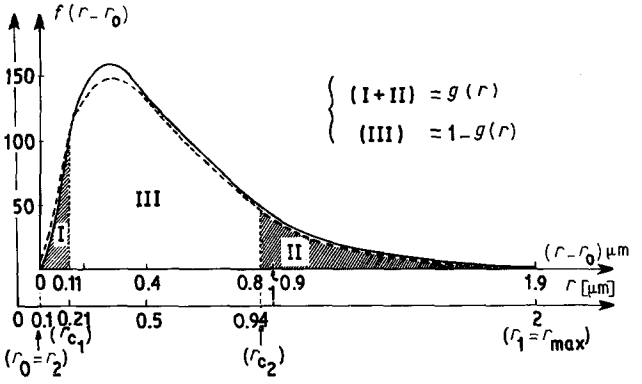

Figure 1 Size distribution of the radii of the particles of the iron powder used. ——— experimental curve, ... fitted curve.

the radius of the contact area a_{11} is expressed as follows:

$$a_{11} = 0.88\left(\frac{\bar{F}r}{E}\right)^{1/3} \tag{3}$$

where E is Young's modulus for the material under consideration.

For two particles of different radii, r_1 and r_2, this expression becomes:

$$a_{12} = 0.88\left[\frac{\bar{F}}{E} \times \frac{2}{\left(\frac{1}{r_1}+\frac{1}{r_2}\right)}\right]^{1/3} \tag{4}$$

So, for the two preceding cases, the maximum pressure exerted on the centre of the contact area is:

$$p_{11} = 1.5 \times \frac{\bar{F}}{\pi a_{11}^2}$$

and

$$p_{12} = 1.5 \times \frac{\bar{F}}{\pi a_{12}^2} \tag{5}$$

As was determined experimentally, it was not possible to compact particles having exactly equal radii to obtain a green pellet with a convenient mechanical behaviour. It was then concluded that p_{11} was less then, or just equal to, the yield strength of the material (except in the case where compaction pressure is less than 750 MPa).

Therefore it has been deduced that on a large scale the green pellet cohesion depends upon the size distribution of the particles and that a more or less substantial plastic deformation takes place in the contact area of the particles during compaction. Thus, p_{12} can be expressed as follows:

$$p_{12} = \left[\frac{a_{11}}{a_{12}}\right]^2 \times p_{11}$$

and by substituting $r = r_1$ into Equation 3, p_{12} becomes:

$$p_{12} = \frac{1}{2}\left(1+\frac{r_1}{r_2}\right)^{2/3} \times p_{11} \tag{6}$$

Taking into account the extreme values of the radii of the particles of the iron powder used ($r_2 = 0.1\,\mu m$ and $r_2 = 2\,\mu m$),

$$p_{12} \simeq 4.8 p_{11} \qquad \text{with } p_{11} \leqslant \sigma_E \tag{7}$$

From Bowden and Tabor, [3] it can be considered that a homogeneous irreversible plastic deformation occurred in the whole contact area when $p_{12} \simeq 3\sigma_E$. This condition is well verified by Equation 7.

Thus, in the case of a green pellet compacted from the powder under consideration, some contact areas exist for which $p_{12} > 3\sigma_E$; this suggests that the $g(r)$ fraction of the powder particles (Zones I and II on Fig. 1) is plastically deformed in an irreversible way. These particles begin to sinter as soon as the sample is heated up to the temperature of the isothermal treatment, while the remaining fraction $1-g(r)$ of the particles (Zone III on Fig. 1) – which are deformed during compaction under a pressure $p < 3\sigma_E$ – can rearrange themselves during the rapid heating and the very early parts of the thermal treatment, and can then sinter when the particles have reached their final position.

2.3. Calculation of the fraction $g(r)$ of the particles plastically deformed during compaction

From Equation 6, and by substituting $p_{12} = 3\sigma_E$ and $p_{11} = \sigma_E$, we can reach the ratio of the radii $r_1/r_2 = 9.40$, for the particles able to deform in an irreversible way during compaction. Therefore, in the powder used, the very small particles are deformed irreversibly when they are in contact with the very large (this is in the case of systems

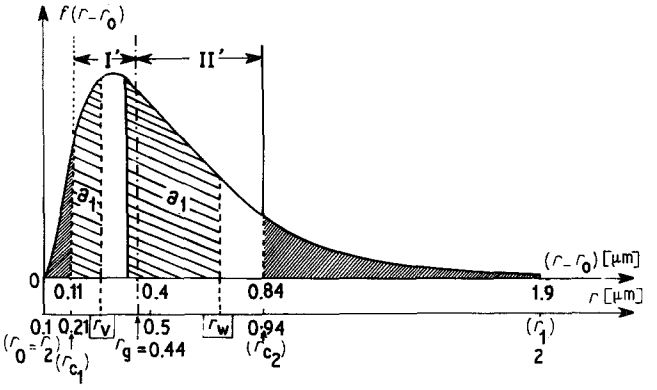

Figure 2 Evolution of the $1-g(r)$ fraction of the particles able to rearrange themselves.

resulting from the association of particles belonging respectively to Zones I and II on Fig. 1).

Taking into account the extreme values of the radii $r_{min} = 0.1\,\mu m$ and $r_{max} = 2\,\mu m$ of the particle distribution, the limits of the $g(r)$ fraction of the particles plastically deformed during compaction can be calculated.

$$r_1 = 2\,\mu m \rightarrow r_{c_1} = 0.21\,\mu m$$

$$r_{c_2} = 0.94\,\mu m \leftarrow r_2 = 0.1\,\mu m \quad \text{(see Fig. 1)}$$

The $g(r)$ fraction is therefore represented by the sum of the two hatched areas (I and II) on Fig. 1. Its value can be calculated from the integrals of functions of the same type as mentioned in Equation 2:

$$g(r) = \alpha^2 \int_0^{R_1} R \exp(-\alpha R)\, dR + \int_0^{R_{max}} R \exp(-\alpha R)\, dR - \int_0^{R_2} R \exp(-\alpha R)\, dR, \quad (8)$$

where

$$R = r - r_0 \quad r_0 = r_2 = 0.1\,\mu m \quad R_1 = r_{c_1} - r_0$$

$$R_{max} = r_{max} - r_0 \quad R_2 = r_{c_2} - r_0$$

Hence $g(r) = 0.222$.

2.4. Evolution of the fraction $1-g(r)$ of the particles which can rearrange themselves

This fraction is, of course, equal to 0.778. In order to continue the calculations, three hypotheses have been made:

(a) all of the particles which belong to Area III in Fig. 1 can be classed as a system of pairs for which $r_w/r_v = cte$. In fact, by simple simulations consisting of modifying the respective positions of particles of different dimensions, it has been shown that the smaller particles start moving before the bigger ones; this means that any rearrangement phenomenon involves the conjoint motion of two particles of different mean dimensions.

So Area III is divided in two parts (I' and II') (Fig. 2), situated on both sides of a r_g value defined by the relationship

$$\frac{r_{c_2}}{r_g} = \frac{r_g}{r_{c_1}} = K$$

$$\text{i.e. } r_g = (r_{c_1} r_{c_2})^{1/2} = 0.444\,\mu m$$

Then the K parameter is equal to 2.115 and can be written:

$$\frac{r_w}{r_v} = K \quad \text{with} \quad \begin{matrix} r_g < r_w < r_{c_2} \\ r_{c_1} < r_v < r_g \end{matrix}$$

The value of the maximum pressure exerted in the centre of the contact area developed between particles of radii equal to r_w and r_v, respectively, can also be calculated. From Equation 6 we have:

$$p_{12} = p_{max} \simeq 1.35\,\sigma_E \quad \text{with } p_{11} \simeq \sigma_E$$

(b) All pairs of particles (r_w, r_v) are supposed to be unable to rearrange themselves at the same time; thus at time t only one fraction of the particles having a radius equal or less than r_v could take part in the process. This fraction is represented by the area a_1 on Fig. 2. As the pairs consisting of smaller particles must rearrange first, it can be seen that the abscissa of the line limiting the a_1 area on the left is coincident with r_{c_1}. On the other hand, if the abscissa of the line which is the upper limit of the area a_1 is equal to r_w, one can write:

$$\frac{1}{r_1} + \frac{1}{r_2} = \frac{1}{r_w} + \frac{1}{r_v} = \frac{1}{r_v}\left(1 + \frac{1}{K}\right) \quad (9)$$

By combining Equations 9, 4 and 5, r_v can be

expressed by:

$$r_v = \frac{0.242E\bar{F}^{1/2}}{(p_{12})^{3/2}} \times \left(1+\frac{1}{K}\right)$$

$\bar{F}$ is the average resultant strength exerted on the particles considered at any time t. At time $t=0$ we have $p_{12}=p_{max}$ and

$$r_v = r_{c_1} = \frac{0.242E(\bar{F}_{max})^{1/2}}{(p_{max})^{3/2}} \times \left(1+\frac{1}{K}\right)$$

Then the following relationship can be deduced:

$$\frac{r_v}{r_{c_1}} = \left[\frac{\bar{F}}{\bar{F}_{max}}\right]^{1/2} \times \left[\frac{p_{max}}{p_{12}}\right]^{3/2} \quad (10)$$

The pressure p_{12} represents the effective stress σ_{eff} which allows the rearrangement phenomenon to develop. This stress decreases with increasing time; such an evolution is consistent with the fact that if $r_v > r_{c_1}$, $p_{12}=\sigma_{eff}$ is lower than $p_{max} \simeq 1.35\sigma_E$. In order to taken into account the decrease of σ_{eff}, a third hypothesis will be put forward. It must be remarked that $\bar{F}$ (the effective mean strength exerted on the particles at time t) is decreasing simultaneously as σ_{eff}. Hence $\bar{F}$ becomes progressively smaller than F_{max}. However, the difference between the two strengths cannot be very great because the sintering between particles increases the cohesion of the green pellet by creating simultaneously a mean strength of cohesion which is opposed to a very significant decrease of $\bar{F}$. Therefore in the following it is considered that $\bar{F} \simeq \bar{F}_{max}$. Hence:

$$\frac{r_v}{r_{c_1}} \simeq \left[\frac{p_{max}}{\sigma_{eff}}\right]^{3/2} \quad (11)$$

(c) It is considered that the relaxation of the stresses takes place according to the hyperbolic law suggested by Crussard [4] and that the value of σ_{eff} is independent of the temperature in the range (500 to 800° C). Thus one can write

$$\sigma_{eff} = \frac{Cte}{t_0^m\left(1+\frac{t}{t_0}\right)^m} \quad (12)$$

with $1.0 < m < 1.5$ for the ferrous materials.

To evaluate the constant of Equation 11, it was considered that at $t=0$

$$\sigma_{eff} = p_{max} = \frac{cte}{t_0^m}$$

hence $cte = p_{max}t_0^m$ and, consequently,

$$\sigma_{eff} = \frac{p_{max}}{\left(1+\frac{t}{t_0}\right)^m} \quad (13)$$

In this expression t_0 is a parameter which is dependent upon the temperature, according to a law of the type

$$t_0 = t_0^0 \exp\left[\frac{\Delta H_2}{RT}\right] \quad (14)$$

where ΔH_2 is the activation energy for the relaxation of the stresses, and t_0^0 is the time from which the rearrangement begins with the above hyperbolic law.

By combining Equations 11 and 13 one obtaines:

$$\frac{r_v}{r_{c_1}} = \left[1+\frac{t}{t_0}\right]^{3m/2} \quad (15)$$

Using these different formulations, it is now possible to calculate the variation of the total shrinkage acquired by the sample.

2.5. Shrinkage acquired by the sample

2.5.1. Shrinkage associated with the rearrangement of a certain type of particle

The shrinkage value due to the rearrangement of these particles cannot exceed the maximum value equal to 1/3 of the variation of the density of the green pellet compacted under 500 MPa (d_1) and 1500 MPa (d_2) respectively (i.e. showing or not showing the rearrangement phenomenon). It is found that:

$$\left(\frac{\delta l}{l}\right)_{max} \leqslant \frac{1}{3}\left(\frac{d_2-d_1}{d_2}\right) = 7 \times 10^{-3}$$

When $t>0$, the fraction a_1 of the total number of particles able to rearrange themselves is equal to:

$$g(r_v-r_0)-g(r_{c_1}-r_0)$$

For time t, the shrinkage associated with the rearrangement will have the value as follows:

$$\left(\frac{\delta l}{l}\right)_r = \left(\frac{\delta l}{l}\right)_{max} \times [g(r_v-r_0)-g(r_{c_1}-r_0)] = \phi(t)$$

By including $x=\alpha(r-r_0)$ it follows that

$$x_v = \alpha(r_v-r_0) \quad x_{c_1} = \alpha(r_{c_1}-r_0) = 0.44$$

and

$$g(r-r_0) = g(x/\alpha) \quad (16)$$

Taking into account Expression 2, we can write:

$$g(x/\alpha) = \int_0^x x \exp -x \, dx$$

Finally:

$$\left(\frac{\delta l}{l}\right)_r = \epsilon\left(\frac{\delta l}{l}\right)_{max} \times \left[g\left(\frac{x_v}{\alpha}\right) - g\left(\frac{x_{c_1}}{\alpha}\right)\right]$$

ϵ is a standard constant which translates the fact that the $1-g(r)$ fraction which is available for rearrangement is equal to 0.778 and not to unity.

$$\left(\frac{\delta l}{l}\right)_r = \epsilon\left(\frac{\delta l}{l}\right)_{max} \times [(1+x_{c_1})\exp(-x_{c_1}) - (1+x_v)\exp(-x_v)] = \phi(t) \quad (17)$$

From Relation 16, it follows that:

$$\frac{x_v}{x_{c_1}} = \frac{r_v - r_0}{r_{c_1} - r_0} \simeq \frac{r_v}{r_{c_1}}$$

because r_0 is very small ($\simeq 0.1\,\mu m$) and can be neglected. Thus from Equation 15

$$\frac{x_v}{x_{c_1}} = \left(1+\frac{t}{t_0}\right)^{3m/2}$$

Therefore:

$$\phi(t) = \epsilon\left(\frac{\delta l}{l}\right)_{max} \times \left\{(1+x_{c_1})\exp(-x_{c_1}) - \left[1+x_{c_1}\left(1+\frac{t}{t_0}\right)^{3m/2}\right]\exp\left[-x_{c_1}\left(1+\frac{t}{t_0}\right)^{3m/2}\right]\right\}$$

2.5.2. Shrinkage associated with the sintering of the particles put in contact by compaction

This shrinkage concerns the fraction $g(r)$, which will be referred to as β from now on. It can reasonably be supposed that the sintering of these particles is related to a kt^n law; the associated shrinkage is then expressed by:

$$\left(\frac{\delta l}{l}\right)_{f_1} = \beta k t^n \quad (18)$$

with

$$k = k_0 \exp\left[-\frac{\Delta H_1}{RT}\right] \quad (19)$$

In this expression ΔH_1 is equal to the activation energy of the acting sintering mechanism.

2.5.3. Shrinkage associated with the sintering of the particles which are first rearranged

This shrinkage takes into account the fraction $[g(x_v/\alpha) - g(x_{c_1}/\alpha)]$ of the particles which are able to rearrange themselves [the maximum value of which is $1-g(r)$].

If it is supposed that the sintering of this fraction depends upon the rate of the rearrangement phenomenon, the associated shrinkage can be expressed by the convolution product as follows:

$$\left(\frac{\delta l}{l}\right)_{f_2} = k\int_0^t (t-t_r)^n \times \frac{d[\phi(t_r)]}{dt_r}\,dt_r \quad (20)$$

The function $\phi(t)$ has been defined in Equation 17. In Equation 20, t_r is the time from which a given pair of particles (r_w, r_v) is rearranged and begins to sinter.

2.6. Total shrinkage concerning the sample

The theoretical equation describing the curve of the shrinkage recorded can be expressed from Equations 17, 18 and 20, as follows:

$$\left(\frac{\delta l}{l}\right)_t = \left(\frac{\delta l}{l}\right)_r + \left(\frac{\delta l}{l}\right)_{f_1} + \left(\frac{\delta l}{l}\right)_{f_2}$$

or

$$\left(\frac{\delta l}{l}\right)_t = \phi(t) + \beta k t^n + k\int_0^t (t-t_r)^n \frac{d[\phi(t_r)]}{dt_r}\,dt_r \quad (21)$$

Whenever the second derivative of the second term of Equation 21 is equal to zero, the theoretical curve will exhibit a change in slope. It will be recalled that the experimental curves show just such an anomaly – which is in the main shown by an apparent acceleration of the shrinkage – when the greater part of the rearrangement phenomenon has taken place.

In practice, the convolution product has no analytical expression, so its second derivative cannot be calculated. Consequently, only values for different paramters of Equation 21 can be chosen. For different temperatures the theoretical curves can be calculated from these values and compared with the experimental curves registered for these same temperatures. It should be mentioned that the temperatures under consideration range only from 500 to 800° C, because experimentally, the rearrangement phenomenon is only observed in that temperature range [5].

The following parameters were used:

(i) $\beta = 0.222$; $n = 0.32$ (the exponent of the equation corresponding to the more probable sintering mechanism, i.e. where the intergranular mechanism plays a role); k (depending on k_0); and $\Delta H_1 = 125.4\,kJ\,mol^{-1}$. The values of k used for the different temperatures considered in this paper were determined from isothermal dilatometric experiments carried out with relatively low speed [6] and are indicated in Table I.

TABLE I Values of the parameters k and t_0 fitted in terms of temperature

T (K)	k ($\times 10^3$) (low speed dilatometry)	k ($\times 10^3$) (high speed dilatometry)	t_0 (min)
828	4.94	1.85	200
855	7.59	4.25	120
873	8.50	5.50	100
898	11.56	8.56	76
923	13.32	12.50	50
968	15.86	16.66	40

(ii) $(\delta l/l)_{max} = 7 \times 10^{-3}$; $\epsilon = 1.298$; $x_{c_1} = 0.44$; $m = 1$; t_0 was evaluated from Equation 14 with $t_0^0 = 0.04$ min and $\Delta H_2 = 50.1\,kJ\,mol^{-1}$.

Using the above values of the parameters, the agreement between the experimental and calculated curves was not good enough. Some of the parameters were fitted and the best fitting was obtained with the following values, for the whole range of temperature considered: $\beta = 0.1275$; $x_{c_1} = 1$, $\Delta H_1 = 113.7\,kJ\,mol^{-1}$; k (cf. Table I, for the high speed dilatometry); $\Delta H_2 = 75.2\,kJ\,mol^{-1}$; t_0 (cf. Table I).

For the temperature of 873 K, Fig. 3 gives an example of the very good agreement between the two curves. This justifies the hypothesis made to translate the total instantaneous shrinkage acquired by the sample.

The discrepancies found between the calculated and fitted values of β and x_{c_1} are probably related to the approximations made to estimate the values of p_{11} and p_{12}. Those discrepancies related to the value of ΔH_1, fitted from dilatometric curves recorded with high or low speed, may be due to the fact that for these latter experiments the shrinkage translated by the convolution product of Equation 21 was not taken into account.

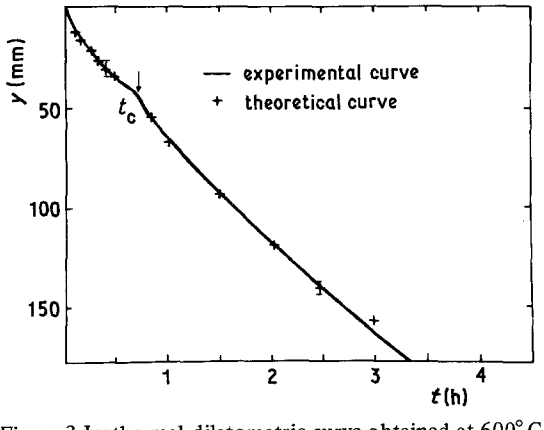

Figure 3 Isothermal dilatometric curve obtained at 600° C from a green pellet compacted under a pressure of 500 MPa and heated at high speed (———) and a curve fitted from the model proposed in this paper.

Furthermore, the values of t_0 indicated in Table I result from fitting with a new value of ΔH_2, greater than $50.1\,kJ\,mol^{-1}$, and with the t_0^0 coefficient having the new value 3×10^{-3} min.

2.7. Influence of the compaction pressure on the rearrangement phenomenon.

For samples sintered at the temperature of 582° C, it was shown that the rearrangement phenomenon was very noticeable when the compaction pressure was equal to 500 MPa and disappeared for 1000 MPa. This fact can be explained as follows:

When the pressure of compaction P increases to P', the number of systems of particles of Types I and II deforming irreversibly (cf. Fig. 1) must increase. This fact does not mean, however, that the pressure p_{12} acting between the particles is greatly different from the value $p_{12} \simeq 3\sigma_E$ established above [3] (cf. Section 2.2).

Furthermore, the systems of particles belonging only to Type III remain elastically strained. However, it can be reasonably supposed that when the strength of compaction increases, the pressure exerted in the corresponding zones of contact tends to exceed σ_E; this can be expressed as $n\sigma_E$ (with $1 < n < 3$).

Reconsidering Equation 6 with the new values $p_{12} \simeq 3\sigma_E$ and $p_{11} = n\sigma_E < p_{12}$, it follows that

$$K' = \frac{r_1'}{r_2'} = 2\left(\frac{3}{n}\right)^{3/2} - 1 \qquad (22)$$

where r_1' and r_2' are the analogous radii to r_1 and r_2 (cf. [2]) that must be considered when the pressure of compaction increases from P to P'.

Equation 22 clearly shows that if $n > 1$, $K' < 9.4$, therefore r_1' must decrease and r_2' increases. In fact, if the upper limit of the size distribution of the particles of the powder used $r_1' = r_1 = 2\,\mu m$ is not considered, the above relation shows that when n increases, r_2' decreases; if now the lower limit $r_2' = r_2 = 0.1\,\mu m$ is considered, r_1' must decrease.

This analysis finally shows that when the strength of compaction P increases, the hatched area (I + II) on Fig. 2 increases and the $1 - g(r)$ fraction decreases.

The rearrangement phenomenon regarding the $1 - g(r)$ fraction of the particles and, in particular,

the point of inflection which is associated with the function $\phi(t)$, must disappear if $x'_{c_1} > 1.33$ for $m = 1$ in Equation 17.

By considering $x'_{c_1} = 1.388$, from Equation 16 we can evaluate $r'_{c_1} = 0.447\,\mu m$. Then it can be deduced that:

$$K' = \frac{r'_1}{r'_2} = \frac{2}{0.447} = 4.474$$

Then $r'_{c_2} = 4.474 \times 0.1 = 0.447\,\mu m$.

The values of r'_{c_1} and r'_{c_2} calculated in this way are identical: this situation is related to the case where none of the pairs of particles are able to rearrange themselves [i.e. $g(r) = 1$ and $1 - g(r) = 0$].

It was shown before that:

$$r_v = \frac{0.246(\bar{F})^{1/2}E}{(p_{12})^{3/2}}\left(1 + \frac{1}{K}\right) \qquad (23)$$

hence it can be inferred that

$$\bar{F} = \frac{(p_{12})^3(r_v)^2K^2}{[0.246(1+K)]^2E^2} \qquad (24)$$

It has previously been established that when the pressure of compaction is equal to 500 MPa the fraction of the particles plastically strained is equal to 0.1275 and the fraction of particles which are able to rearrange themselves is then equal to 0.8725. An average pressure acting inside the green pellet can therefore be evaluated as follows:

$$p_{12} \simeq 0.1275\,(3\sigma_E) + 0.8725\sigma_E = 1.255\sigma_E$$

Given that

$$r_v \simeq \bar{r} \simeq 0.444\,\mu m = 4.44 \times 10^{-7}\,m$$

$$K = 9.4$$

$$\sigma_E = 1.96 \times 10^8\,Pa$$

$$p_{12} = 2.46 \times 10^8\,Pa$$

$$E = 1.96 \times 10^{11}\,Pa$$

It can be found that $\bar{F} = 1.03 \times 10^{-9}\,N$.

For the pressure P' for which all the particles are plastically strained, p_{12} approximates to $3\sigma_E = 5.88 \times 10^8\,Pa$. As $K' = 4.74$ and $\bar{r}' = 4.47 \times 10^{-7}\,m$, $\bar{F}' = 1.17 \times 10^{-8}\,N$.

By supposing that the relation between $\bar{F}$ and P is of the same type as that expressed by Equation 24, one can then evaluate:

$$P' = \left[\frac{\bar{F}'}{\bar{F}}\right]^{1/2} P = 1115\,MPa$$

This value is in good agreement with that (1000 MPa) for which the rearrangement phenomenon is no longer observed on the experimental dilatometric curves.

3. Conclusion

The theoretical shrinkage curves of green pellets of ex-carbonyl iron powder, with a quasi-spherical form, recorded with a high speed dilatometer and showing a size distribution of the particles, can be described by the following relation:

$$\left(\frac{\delta l}{l}\right)_t = \phi(t) + \beta k t^n + k\int_0^t (t - t_r)^n \frac{dg(t_r)}{dt_r}\,dt_r$$

In this expression, $\phi(t)$ represents the shrinkage related to the rearrangement of the powder particles; the corresponding activation energy is of the order of 75 kJ mol^{-1}, while the activation energy for the sintering itself which develops when the rearrangement is over is of the order of 114 kJ mol^{-1}. The rearrangement phenomenon is only observed when the pressure of compaction does not exceed a value, which was estimated of the order of 1100 MPa.

Acknowledgements

The authors are grateful to Professor Werner Brandt of New York University for many helpful discussions and interest in this work.

References

1. F. BEHAR, C. SERVANT and G. CIZERON, *Scripta Metall.* 8 (1974) 1331.
2. H. HERTZ, "Gesammelte Werke", Vol. 1 (1895).
3. F. P. BOWDEN and D. TABOR, "Friction and Lubrication of Solids", Vol. 1 (Clarendon Press, Oxford, 1958) p. 11.
4. C. CRUSSARD, Thèse de Doctorat ès-Sciences, Université Paris-Sud, Orsay (1963).
5. F. BEHAR-KHAN, Thèse de Doctorat ès-Sciences, Université Paris-Sud, Orsay (1976).
6. F. BEHAR, C. SERVANT and G. CIZERON, *Int. J. Powder Met.* **11** (1975) 117.

Received 29 September
and accepted 3 November 1983