Minimal pore size reached upon sintering

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Abstract. Analytical expression for minimal (critical) pore size reached upon sintering was derived. It has been shown that a pore size in a given material cannot be stable below some critical value characteristic of this material.

1. Introduction

As is known, thermomechanical processing of materials is accompanied by mass transfer caused by diffusion and drift of dislocations, which leads to a decrease in pore sizes and to an increase in material density. These processes can occur even in the absence of external pressure and interpore gas pressure [1]. The driving force of these processes is a decrease in the free energy of material due to a decrease in the free surface area under the action of surface tension forces. The application of external compressive pressure can be expected to result in further decrease in material porosity.

Shape of an individual pore, plastic deformation of material around a pore, and strain-induced distribution of vacancies have been analyzed in [2-3]. The latter factor (as well as strain magnitude) were found to play a key role in the kinetics of mass transfer responsible for pore healing. When the pore volume is less than the critical volume, the pore is energetically more profitable to heal, and when the pore volume is larger than the critical volume, the pore is energetically more favorable to grow [4, 5]. An expression for a minimal pore size in the absence of applied pressure was suggested in [1].

In this work, we aimed at determining a minimal pore size under applied pressure as in conditions of hot isostatic pressing (HIP).

2. Results and discussion

For a spherical pore with radius \( R \) and interpore pressure \( P_i \) under external pressure \( P_0 \), the problem can be formulated in terms of Lamé equation [6-7]. Accordingly, the distribution of radial \( \sigma_r \) and tangential \( \sigma_t \) strains around the pore can be described by Eqs. (1) and (2):

\[
\begin{align*}
\sigma_r &= -P_i \frac{R^3}{r^3} + P_0 \frac{(R^3 - r^3)}{2r^3} \quad (1) \\
\sigma_t &= P_i \frac{R^3}{2r^3} - P_0 \frac{(2r^3 + R^3)}{2r^3} \quad (2)
\end{align*}
\]

where \( r \) is running pore radius.

In the absence of applied pressure and at \( P_i = 0 \), pressure inside the pore is equal to the Laplace pressure \( (P_L) \):

\[
P_L = \frac{2\alpha}{R} \quad (3)
\]
where $\alpha$ is surface tension. This magnitude also contributes to the formation of deformation mode: In this case, the effect of the internal pressure $P_i$ can be represented as the sum of the gas pressures inside the pore $P_G$ and the Laplace pressure $P_L$: $P_i = P_G - P_L$.

The stresses are maximal at $r = R$:

$$\sigma_r = P_L - P_G$$

$$\sigma_t = -\frac{P_L - P_G}{2} - \frac{3P_0}{2} \quad (5)$$

Then the main normal strains can be represented in the form:

$$\sigma_1 = \sigma_r = P_L - P_G \quad (6)$$

$$\sigma_2 = \sigma_3 = \sigma_t = -\frac{P_L - P_G}{2} - \frac{3P_0}{2} \quad (7)$$

Plastic deformation around the pore gets started at some critical stresses. There exist several explanations for material deformation when equivalent strains $\sigma_{eq}$ exceed allowable stress $\sigma$. The theory of maximum-distortion-energy is based on the assumption of equal potential distortion energy accumulated to the moment of material creep upon both compound and simple stress. According to this theory for ductile materials [7], we have:

$$\sigma_{eq} = \left\{\frac{1}{2}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]\right\}^{1/2} \leq [\sigma] \quad (8)$$

Using (6–8), we obtain the expression for $\sigma_{eq}$:

$$\sigma_{eq} = \frac{3(P_L - P_G + P_0)}{2} \quad (9)$$

Let us now admit that $\sigma = \sigma_{0.2}$. If $\sigma_{eq} = \sigma_{0.2}$, the pore begins to deform until its healing. Hence, expressions (3) and (9) can be used to derive an analytical expression for critical pore size $R_{cr}$:

$$R_{cr} = \frac{6\alpha}{2\sigma_{0.2} + 3P_G - 3P_0} \quad (10)$$

The results of calculations for some metals at room temperature, $P_G = 0$ (pressing and sintering in vacuum) and $P_0 = 100$ MPa (isostatic pressing) are collected in Table 1. A decrease in $\sigma_{0.2}$ with increasing temperature favors an increase in $R_{cr}$, while the applied pressure decreases it. The increase in external pressure leads to the fact that large pores begin to collapse, that is, the critical pore size increases.

It follows that a minimal pore size in porous materials is restricted by a calculated value of $R_{cr}$. 
Table 1. Properties [8–15] and critical pore radius for some metals at room temperature.

| Material                   | $\alpha$, N/m [7–11] | $\sigma_{0.2}$, MPa [7] | $R_{cr}$, nm ($P_0 = 0$) | $R_{cr}$, nm ($P_0 = 100$ MPa) |
|----------------------------|----------------------|-------------------------|---------------------------|-------------------------------|
| Iron                       | 1.90                 | 170                     | 34                        | 285                           |
| Chromium                   | 2.20                 | 190                     | 35                        | 165                           |
| Titanium                   | 1.70                 | 300                     | 17                        | 34                            |
| Cobalt (annealed)          | 1.97                 | 300                     | 20                        | 39                            |
| Copper (cold-worked)       | 1.75                 | 380                     | 14                        | 23                            |
| Molybdenum (annealed)      | 2.60                 | 570                     | 14                        | 19                            |
| Nickel (deformed)          | 1.82                 | 686                     | 8                         | 10                            |
| Tungsten                   | 2.80                 | 760                     | 11                        | 14                            |

3. Conclusions
Plastic compression of pores occurs under the action of surface tension force and applied external pressure. By comparing main stresses with creep limit, we managed to derive the expression for a minimal pore size that can exist in a given material.

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