

VLIV PLYNU ZACHYCENÉHO V PÓRECH PŘI SLINOVÁNÍ A SOLARISACE KERAMICKÝCH TĚLES

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Souhrn

Byly vyšetřovány účinky nedifundovatelných plynů, zachycených v pórech keramických těles. Ukazuje se, že nedifundovatelné plyny zachycené v průběhu druhého stupně slinovacího procesu v pórech keramických těles nebrání materiálu, aby dosáhl vysokého stupně slinutí ve výši 95-98 % teoretické hodnoty. V tomto případě však hutná keramická tělesa obsahují stacionární bublinky v rovnovážném stavu.

Při růstu zrna jsou unášeny stacionární bublinky pohybem zrn a shlukují se, v důsledku čeho vznikají rovnovážné bublinky při objemu větším, než je součet objemu primárních stacionárních bublinek. V soulase s energetickým polem hranice zrn nastává koalescence bublinek přednostně po hranicích zrn, kde se bublinky spojují a vytvářejí velké integranulární dutiny. Shora popsané chování bylo potvrzeno řadou pokusů s kyslíčkem uranickým.

ВЛИЯНИЕ ГАЗА ЗАХВАЧЕННОГО В ПОРАХ В ТЕЧЕНИЕ СПЕКАНИЯ И СОЛЕРИЗАЦИЯ КЕРАМИЧЕСКИХ ТЕЛ

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Резюме

Было осуществлено исследование воздействия недиффундируемых газов, захваченных в порах керамических тел. Показывается, что недиффундируемые газы, захваченные в порах керамических тел в течение второй степени процесса спекания, не составляют препятствия для того, чтобы материал достиг

достичь высокой плотности спекания в пределах от 95 до 98 % теоретической величины. Но в этом случае плотные керамические тела содержат стационарные пузырьки в равновесном состоянии.

Во время роста зерен стационарные пузырьки уносятся вследствие движения границ зерен и эти пузырьки скопляются (коалесцируют), вследствие чего доходит к образованию равновесных пузырьков с большим объемом, чем представляет сумма объема первичных стационарных пузырьков. В согласии с энергетическим полем границы зерен образуются коалесценция пузырьков преимущественно на границах зерен, где пузырьки соединяются и образуют большие межгранулярные раковины.

Выше приведенное поведение было подтверждено рядом опытов с двуокисью урана.

EINFLUSS DES WÄHREND DER SINTERUNG UND SOLARISATION DER KERAMISCHEN KÖRPER IN POREN AUFGEFANGENEN GASES

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Zusammenfassung

Es wurde die Untersuchung der Wirkungen von nichtdiffundierbaren, in Poren der keramischen Körper aufgefangenen Gase, durchgeführt.

Es hat sich gezeigt, dass die während der zweiten Etappe des Sinterungsprozesses in Poren der keramischen Körper aufgefangene nichtdiffundierbare Gase dem Material kein Hindernis in den Weg legen um den hohen Grad von 95 % - 98 % des theoretischen Wertes der Sinterungsdichte erreichen zu können. In diesem Fall aber enthalten die dichten keramischen Körper stationäre Bläschen in ausgeglichene Zustand.

Beim Kornwachstum werden die stationäre Bläschen durch die Korngrenzsbewegungen zerrissen und agglomerieren mit den

neuentstehenden ausgeglichenen Bläschen bei einem Inhalt, der die Summe der primären stationären Bläschen überhöht.

In Übereinstimmung mit dem energetischen Korngrenzfeld, entsteht auf den Korngrenzen vorzugsweise die Koaleszenz, wo sich die Bläschen verbinden und formen grosse intergranuläre Kavernen.

Oben zusammengefastes Verhalten wurde bestätigt durch eine ganze Versuchsreihe mit dem Urandioxyd.

THE EFFECT OF THE GAS TRAPPED WITHIN PORES DURING THE SINTERING
AND THE SOLARIZATION OF THE CERAMIC BODIES

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SUMMARY

The effects of non-diffusible gases trapped within the pores of the ceramic bodies were examined. It is shown that the non-diffusible gases trapped during the second stage of the sintering process in the pores of the ceramic bodies do not hinder the material to reach a high sinter density such as 95. - 98 % of the theoretical value. In this case, however, the dense ceramic bodies contain stationary bubbles in the equilibrium conditions.

During the grain growth, the grain boundary movements sweep the stationary bubbles and these bubbles coalesce, originating new equilibrium bubbles with volume larger than the sum of the volume of the primary stationary bubbles. In accordance with the grain boundary energy field, the coalescence of the bubble occurs preferentially at grain boundaries, where the bubbles link and form large intergranular cavities. The behaviour described was confirmed by a series of experiments on urania.

1 - Introduction

The gas trapped in the pores at closure may inhibit the rate of pore closure (1, 2). This effect causes the densification rate to decrease as density increases; in this line, Coble (3) has shown that nitrogen

(or air), argon and helium at one atmosphere inhibit sintering of alumina to the theoretical density and that theoretical density is achieved if the atmosphere is hydrogen, oxygen or vacuum. Monsour and White (4) have shown that the diffusion rates of gases trapped in the pores of the uranium sintered bodies control the pore evolution: if the diffusion is very fast, all the pores shrink; if the diffusion is very slow, pores shrink until the gas pressure inside them reach the value of $2\gamma/r$, where γ is the surface tension of the material and r is the radius of curvature of the pore; in intermediate cases, gases diffuse under a pressure gradient from smaller pores (which will shrink) to larger pores (which will grow). Amato and Colombo (5-7) have shown that the occurrence of a regression of the fired density, (solarization), of steam and hydrogen sintered uranium bodies is due to the gases, originated from the organic compounds added to the powder in order to make easier the pressing operation; these gases are not able to diffuse in the ceramic bodies and are trapped in closed pores of the material. In conclusion, it is ascertained that the non-diffusible gases trapped in the closed pores are responsible for the following phenomena:

- i. to inhibit sintering to the theoretical density;
- ii. to generate a regression of the fired density of the ceramic bodies submitted for long time at high temperature treatment.

Scope of this paper is a discussion on the mechanism which regulates the above summarized phenomena.

2 - The sintering inhibition originated by the gas trapped within the pores

A pore is a place surrounded by solid material where no solid material exists. When a relatively high gas pressure exists in the pore, it is named bubble. An equilibrium spherical bubble is a bubble where the gas pressure, p , is balanced by a surface tension restraint, γ , (in the range of 1000 erg/cm^2 for ceramics), such that the following relation be satisfied:

$$p = \frac{2\gamma}{r} \quad (1)$$

where r is the equilibrium radius for a bubble with gas trapped at the pressure p .

Now, the pore size distribution of the ceramic bodies submitted to the sintering process is as shown in figure 1: it is apparent that the open porosity can be divided in two fractions, one made of coarse voids having diameters larger than 0.2μ and one, the large majority, made with fine pores with diameters ranging from 0.2μ to a value lower than the detection threshold of the porosimeter, i.e. 0.04μ .

Now, since the pores at the closure have a value of the internal pressure of non-diffusible gases of about one atmosphere, it is easy to calculate the radius of the equilibrium bubbles, assuming, of course, that no grain growth and no pore coalescence occur during this step of the sintering process.

However, it is possible to write that a spherical bubble with a non-diffusible gas trapped within it may shrink until the following relation is satisfied:

initial pressure of non-diffusible gases \times initial bubble volume =
 = final pressure of non-diffusible gases \times final bubble volume.

Since the initial pressure of non-diffusible gases is approximately 1 atmosphere, it is possible to write the following relation:

$$1 \text{ atm} \times \frac{4}{3} \pi r_0^3 = \frac{2\gamma}{r_f} \times \frac{4}{3} \pi r_f^3 \quad (2)$$

where r_0 is the initial radius of the bubble and r_f is the radius of the bubble obtained when the internal pressure of non-diffusible gases is balanced by the surface tension.

So, for each diameter of the pore of the ceramic bodies submitted to the sintering process, it is possible through the relation (2), to calculate the value of the equilibrium bubble diameter. The Table 1 summarizes the values of equilibrium bubble diameter of each value of initial pore diameter: it can be seen that, first of all, the fine porosity, which is the large majority, is absorbed by the sintered bodies and practically disappears, secondly, the coarse porosity does not disappear because it reaches the equilibrium bubble diameter with sizeable dimension of the bubble.

The main conclusions that can be drawn from these considerations are that a ceramic body with non-diffusible gases trapped in the pores may reach during the sintering process fired density very near to the theoretical value (97-98% T.D.), even if fired densities equal to the theoretical value are theoretically impossible to achieve.

3 - Regression of fired density of ceramic bodies originated by the equilibrium bubbles

When the grain growth occurs within the sintered ceramic bodies, for instance, when the bodies are submitted for long time to a high temperature treatment, the equilibrium bubbles may be swept to the grain boundaries and coalesce together. In this case, however, since the bubbles, before the collision, have the equilibrium pressure between the pressure of non-diffusible gases trapped within the pores and the pressure due to the surface tension, after coalescence, since the new bubble radius is larger, the new equilibrium $2\gamma/r$ pressure must be lower. Consequently, there exists an excess pressure of the gas, not balanced by surface tension, which causes a strain field in the matrix, thereby setting up a vacancy gradient, and vacancies diffuse into the bubbles until the pressure is again balanced by the surface tension. The net result then, after volume adjustment, is that the new bubbles occupy a larger volume than the sum of the initial bubbles and consequently the external dimension of the sintered body must increase. In order to give a general idea of this swelling phenomenon it can be seen that if two equilibrium bubbles of equal volume coalesce, the radius of the new bubble before the swelling, is $1.26 r_0$, while the radius of the new equilibrium bubble, therefore after swelling, obtained through the resolution of the following relation:

$$2 \left(\frac{2\gamma}{r_0} \right) \left(\frac{4\pi}{3} r_0^3 \right) = \left(\frac{2\gamma}{r_e} \right) \left(\frac{4\pi}{3} r_e^3 \right) \quad (3)$$

is $r_e = 1.41 r_0$.

In order to have a better knowledge of the coalescence and swelling

phenomena, it is not needless to add that, according to the Nichols' experiments (8), the coalescence is a surface diffusion controlled process, while the swelling requires volume diffusion of vacancies and so occurs at a decidedly slower rate.

A confirmation of the above summarized behaviour has been obtained through some experiments performed on sintered urania bodies. While urania bodies without bubbles submitted to long time - high temperature treatment increase the grain size and the fired density (fig. 2), urania bodies with bubbles show, after an appropriate heat treatment, bubbles aligned according to a sort of a three-dimensional, largely intergranular network (fig. 3). Since the bubbles swelling occurs by stress induced vacancies diffusion, also in this case, as in the creep rupture studies of Hull and Rimmer (9), the zone of growing bubbles must be the grain boundaries; consequently it can be seen that the growing bubbles merge together at grain boundaries (fig. 4), ending up in macroscopic intergranular cavities (fig. 5).

4 - Conclusions

The main conclusions drawn from the above speculative remarks are the following:

- i. the size of the pores of the ceramic bodies submitted to the sintering process is such that non-diffusible gases trapped in the pores do not prevent that the ceramic bodies reach very high fired density (97-98% of the theoretical value); however, these ceramic bodies have very small equilibrium bubbles;

- ii. when grain growth occurs in dense ceramic bodies having equilibrium bubbles, the material swells and the equilibrium bubbles coalesce in large intergranular cavities.

5 - References

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Table 1 - Equilibrium bubble diameters for different diameter of initial pore of the ceramic body submitted to sintering treatment.

Initial diameter (μ)	Equilibrium diameter	
0.01	7.56	A
0.02	4.42	A
0.03	8.13	A
0.04	12.52	A
0.05	17.50	A
0.06	23.01	A
0.07	28.99	A
0.08	35.42	A
0.09	42.27	A
0.1	0.0049	μ
0.2	0.0140	μ
0.3	0.0257	μ
0.4	0.0396	μ
0.5	0.0553	μ
0.6	0.0727	μ
0.7	0.0917	μ
0.8	0.1120	μ
0.9	0.1336	μ
1	0.156	μ
2	0.442	μ
3	0.813	μ
4	1.252	μ
5	1.750	μ
6	2.301	μ
7	2.899	μ
8	3.542	μ
9	4.227	μ
10	4.951	μ
20	14.004	μ
30	25.728	μ
40	39.501	μ

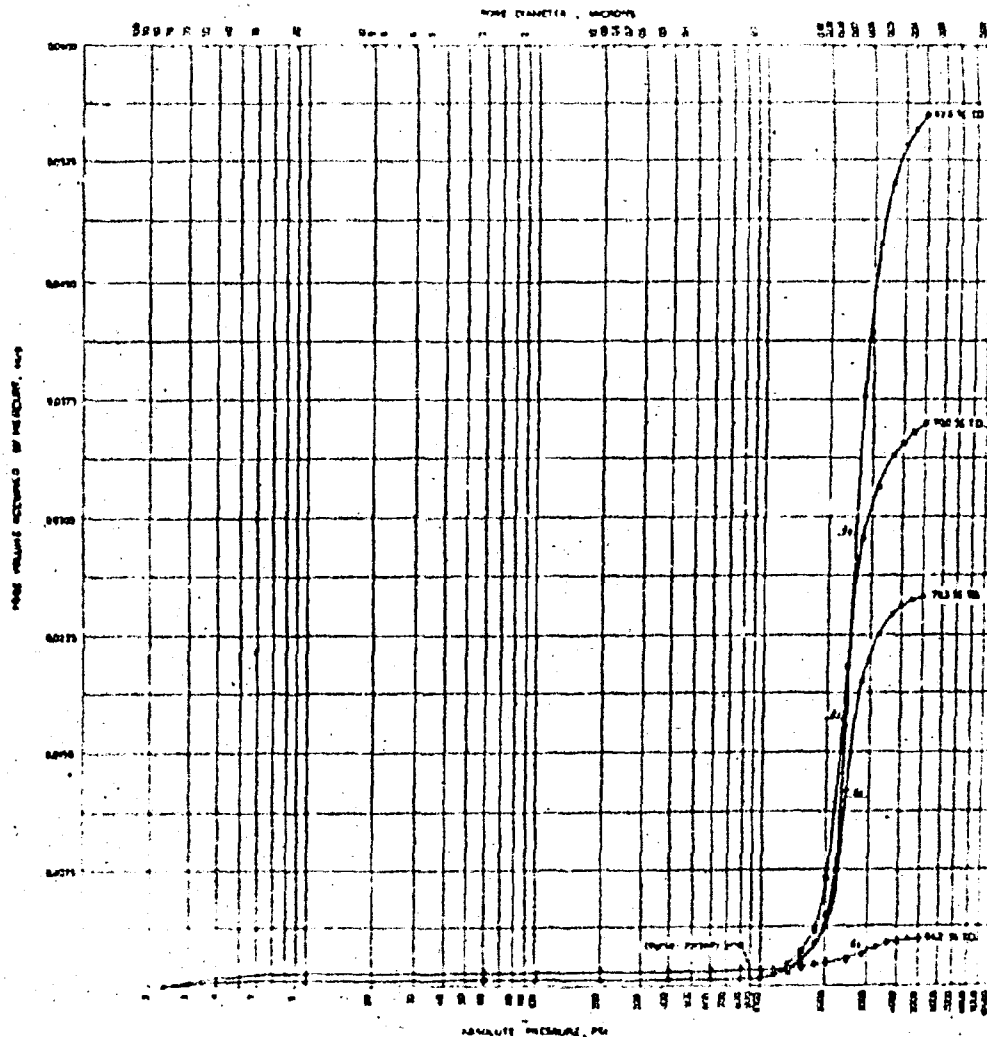


Fig. 1 - Open pore distribution for uranium bodies submitted to different densification treatment (determination carried out through AMINCO Winslow apparatus).

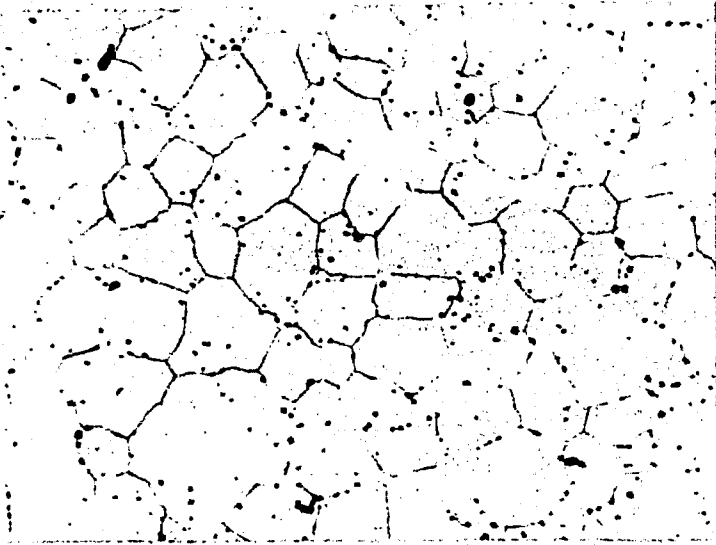


Fig. 2 - Urania bodies without bubbles (thermal etched, 250 x)

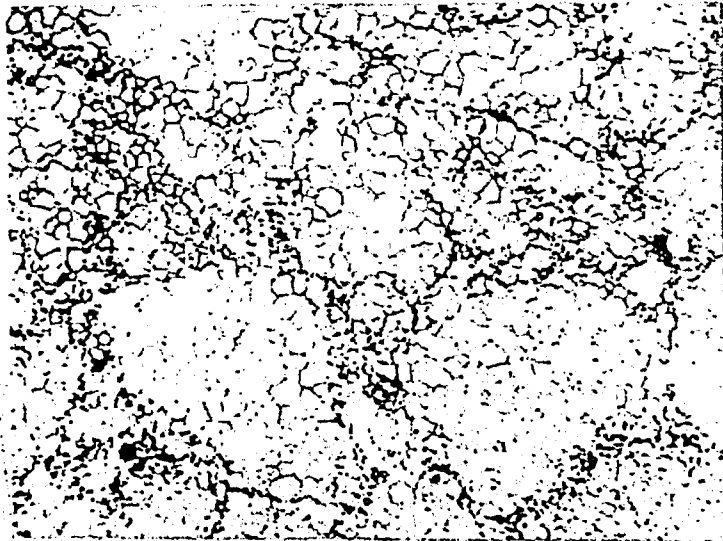


Fig. 3 - Urania bodies at the initial bubble coalescence (thermal etched, 300 x)

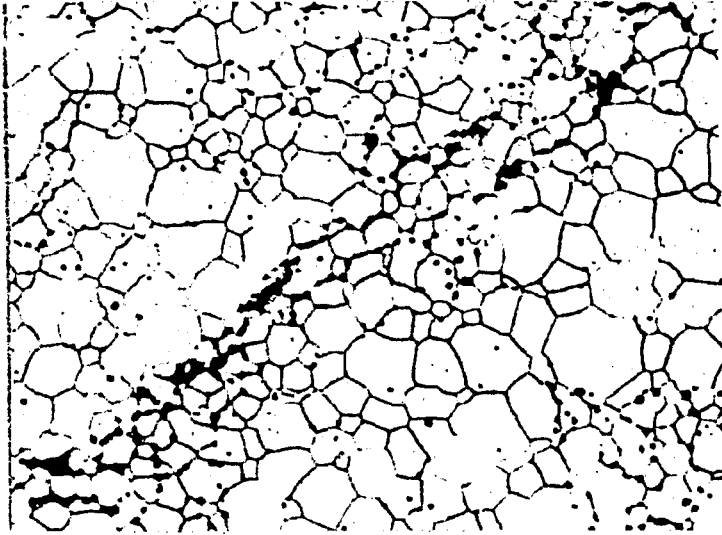


Fig. 4 - Urania bodies during the bubbles alignment (thermal etched,
750 x)

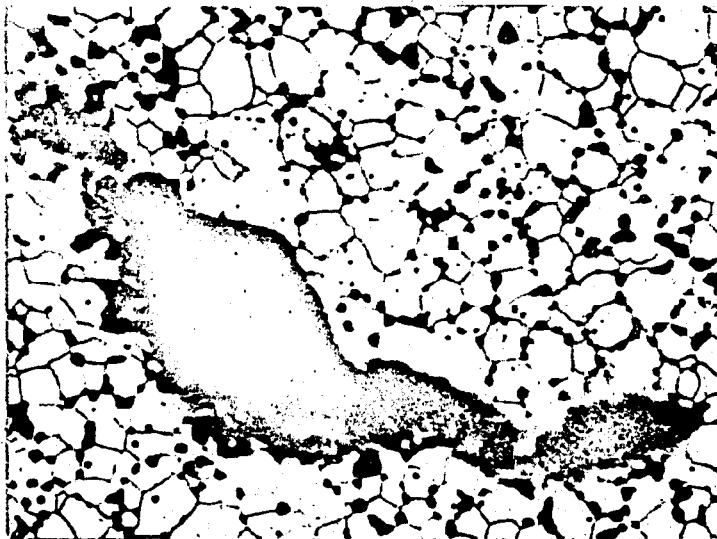


Fig. 5 - Intergranular cavities in sintered urania bodies originated
by equilibrium bubbles coalescence (thermal etched, 750 x)