

1- SOURCES AND OCCURRENCES OF POROSITY AND MICROCRACKS

1.1 Intrinsic Sources (Other Than Sintering)

The importance of porosity effects on properties which arise from its significant impact, as well as from its pervasive occurrence in most fabrication processes whether it is desired or not. Despite the frequent desire for no porosity for many applications, pores pervasively occur due to both **intrinsic** and **extrinsic** factors as well as physical and economical limitations. A basic step in understanding the effects of porosity is to be aware of its sources and occurrences. Intrinsic limitations on reducing porosity were outlined for sintering (Fig. A), where most or all pores start as open, intergranular pores and transition to closed, and even more in the transition to intragranular pores; the latter reflects a marked change in shape, i.e., rounded polyhedral to spherical pores.

Sources of porosity,

Both inter- and intragranular pores of similar scale can also be introduced by various processes, e.g., differential diffusion, annealing of radiation damage or dislocations (especially entangled ones from deformation)" stoichiometric changes, and phase changes due to reaction of constituents or impurities during, or after, sintering.

1.2 Extrinsic Sources in Sintering

There are other extrinsic aspects of processing that effect the amount and character of pores beyond the more intrinsic sources of porosity noted above, especially in sintering. Thus, more, and possibly somewhat larger pores commonly remain in sintered ceramics not only due to intrinsic effects, but also due to gases left in the originally open pores (e.g., due to firing in air rather than vacuum). Gases not soluble in the surrounding ceramic are entrapped in closed pores since they cannot be diffused out of the pore. Many other extrinsic sources of (commonly intergranular) pores exist, especially for sintered bodies. These other sources of pores, i.e., from the materials and forming operations used, contribute mainly to heterogeneity of the size, shape, and spatial distribution of the porosity.

The powders used for forming bodies often contribute larger, heterogeneous pores from heterogeneous particle sizes, shapes, or spatial distributions . Larger pores typically occur with agglomerates in the powder.

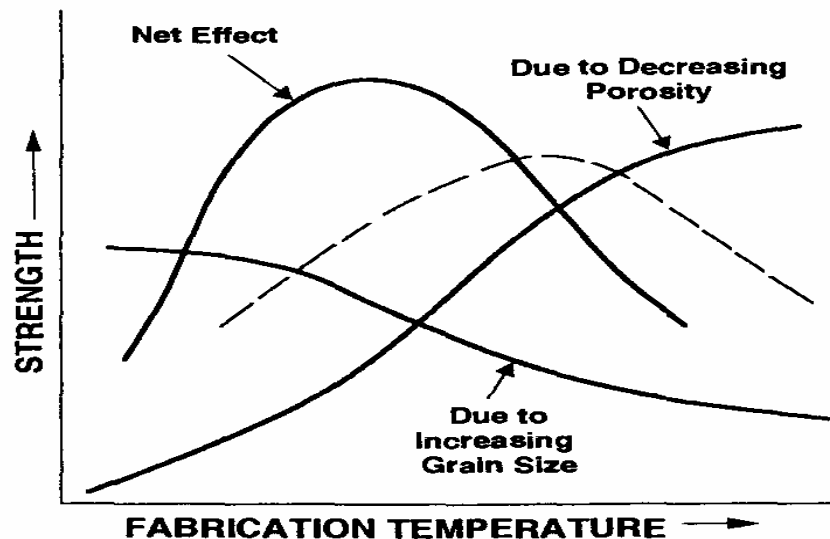


Fig (A)

1.3 Sources and Occurrence of Microcracks:-

The first of three basic sources of microcracks on specimen surfaces is from transient, local impact on the specimen surface, e.g., from rain drops, ice, dust, particles of sufficient sizes, velocities, and impact angles. The second, most prevalent and important source of such surface microcracks is from abrasive machining, which introduces two populations of cracks, one normal to the abrasive particle motion and the other parallel with it. The third source of microcracks, is from mismatched microstructural strains, especially from phase transformations (including crystallization of glasses) or thermal expansion of grains or particles in a body

Table 2.1 Hierarchy of the Categories of the Porosity Dependence of Properties

Category/level of porosity dependence	Examples of properties/uses
I) No dependence on porosity	Lattice parameter, unit cell volume, thermal expansion, emissivity (but not emittance)
II) Dependence only on the amount of porosity	Density, much dielectric constant data, heat capacity per unit volume
III) Dependence on both the amount and character of porosity	
A. Flux or stress dominant in the solid phase	Mechanical properties. Electrical and thermal conductivity at low to moderate temperature and porosity (finer).
B. All flux in the pore phase and filtration	Surface area and tortuosity, e.g., for catalysts
C. Flux in both pore and solid phases	Thermal conductivity, with larger and more open pores at higher temperature

2.1 HIERARCHY OF POROSITY IMPACTS ON PROPERTIES

hierarchy, of porosity dependence of properties is considered here (Table 1). Basic but simple considerations show that there are three broad categories of porosity

dependence that increase in their complexity of dependence on porosity in a hierarchal fashion. At the lowest level, there are properties that have no dependence on porosity; typically, these are those that depend only on the local atomic bonding and are not affected by pores. Thus, properties such as lattice parameter and derivative properties such as unit cell volume fall in this first category, as do melting and boiling temperatures, ablation energy, and emissivity. An important extension of these atom bonding determined properties to macroscopic behavior that does not depend on porosity is **thermal expansion**.

The second hierarchal category consists of those properties dependant only on the amount, and not the character, of porosity. This category consists of properties dependant only on the mass in a given volume and not the specifics, i.e., the microstructure, of its distribution within that volume. This includes density, heat capacity (per volume), and much dielectric constant data. Such properties follow a rule of mixtures relation for the volume fractions of the pore phase (P) and the solid phase (I - P):

$$X = X_s (I - P) + X_p P$$

where X = the property of the body, X_s = the solid property (i.e., at P = 0), and X_p = the property of the pore phase (often zero, but not always, e.g., typically about I for the refractive index and dielectric constant).

The third, largest, most complex and important category in the hierarchy of the porosity dependence consists of those properties dependant on both the amount as well as the character of the porosity. **Three important sub-sets of this are** (following the designations in Table 1):

- A) properties determined only by flux or stress transmission through the solid but not through the pore, phase,
- B) properties determined only by flux through the pore phase (e.g., filtration), and
- C) properties dependant on transmission through both the solid and pore phases.

It is important to note that some properties can change categories with the nature of the porosity or the conditions. Thus, many properties, including most or all mechanical and conductive properties, of bodies with tubular pores aligned parallel with the stress or flux axis follow a I - P dependence, which is that of Category II properties (and the upper limit of porosity dependence of properties). Mechanical and conductive properties of other pore structures all fall below this 1 - P dependence, i.e., have greater rates of property decreases, typically in a nonlinear fashion over

reasonable P ranges. The dielectric constant of bodies with substantial fine porosity, high dielectric constant material, or both, deviate below the rule of mixtures relation (apparently when surface charges on the pores becomes significant) moving it from Category II to Category III. At lower temperatures and finer, closed porosity where convective and radiative heat transfer across and between pores are insignificant, thermal conductivity falls in Category III A; however, as temperature and the size, amount, and openness of pores increases, thermal conductivity transitions to Category III C, and at high temperatures and porosity can approach Category II B due to thermal transport by radiation. some properties are difficult to categorize, e.g., dielectric breakdown where the stress is in the solid phase, but much of the actual breakdown may occur via the pore phase.

There is also a hierarchy of property dependences for microcracks, which are of interest as an extreme of pores for their occurrence in a number of materials, and for their use to modify properties, e.g., to increase toughness and resistance to more extreme thermal shock. The hierarchy for microcracks has overall similarity to, but also some differences from, that for porosity.

So Flaws(pores & cracks) in the material added during processing, final machining, or testing, or while in service.

General physical properties include:-

1- Density:- there are three types of density:

a) Green density:- represents the mass of a material before firing divided by its total volume it is significant in:

* Consider a good indicator for material toughness (dry toughness), whereas increments in green density increase dry toughness.

* Consider a good indicator for interrelate process happening between grains after firing by comparison it with density of materials after firing. Green density increases by increasing 1)compaction pressure. 2)decreasing applied compaction rate. 3)decreasing particles hardness. 4)particle size. 5)particle size distribution.

b) Apparent density(bulk density):- it's a ratio between fired mass and exterior volume (total volume)

c) True density:- its also called true specific weight and it's the ratio between fired mass to the volume of solid part only and it's a constant property foe each material.

2- Porosity and water Absorption:- Most ceramic products can be classed as pores solids, in which the continuity of the solid matter is interrupted by voids of different kinds.

In general there are two main types of pores: open and sealed or closed pores.

Open pores are voids which are accessible to penetrate by a fluid they exist because of the imperfect packing of the particles of the material and also due to escape of gases during drying and firing processes.

Sealed pores are formed on firing when bubbles of gas are frozen into the glassy matrix, or when open pores are sealed by molten materials.

Two types of porosity

- a) **Apparent porosity:-** is the ratio of the open pores volume to the total volume of the object.
 - b) **True porosity:-** is the ratio of the open and closed pores volume to the total volume of the object.
 - c) **Water absorption:-** is the ratio of open pore volume to the dry weight of the test piece.
- 2- **Specific gravity:-** is the ratio of material density to the water density at 4°C or it's the ratio between ceramic material weight to the weight of water volume equal to the volume of solid material part.

In calculating these physical properties we depend on the ASTM standard (C-373-88) and each test result is the average of three samples.

Procedure and Calculation:

- 1- Drying the test specimens to constant mass by heating in an oven at 150°C, followed by cooling in a desiccator. The dry mass (D), was determined to the nearest 0.01 g.
- 2- Immersing the specimens in a pan of distilled water and boiling them for 5 h, taking care that the specimens are covered with water at all times. Using setter pins or some similar device to separate the specimens from the bottom and sides of the pan and from each other. After 5 h boiling, allowing the specimens to soak for an additional 24 h.
- 3- After impregnation of the test specimen in water, then the suspended mass (S), was determined to the nearest 0.01 g, while suspended in water.
- 4- After determination of the suspended mass, each specimen was blotted lightly with a moistened cotton cloth to remove all excess water from the surface. The saturated

mass (M), was determined to the nearest 0.01 g after rolling the specimen lightly on the wet cloth.

Excessive blotting of specimen will introduce error by withdrawing water from the pores of the specimen. Make the weighing immediately after blotting, the whole operation being completed as quickly as possible to minimize errors caused by evaporation of water from the specimen.

Calculate the exterior volume, V, in cubic centimeters, as follows:

$$V = M - S \quad (1)$$

Calculate the volumes of open pores V_{OP} and impervious portions V_{IP} in cubic centimeters as follows:

$$V_{OP} = M - D \quad (2)$$

$$V_{IP} = D - S \quad (3)$$

The apparent porosity, P, expresses as a percent as:

$$P = \{(M - D)/V\} * 100 \quad (4)$$

The water absorption, A, expresses as a percent as:

$$A = \{(M - D)/D\} * 100 \quad (5)$$

Calculate the true density, T:

$$T = D/(D - S) \quad (6)$$

Bulk density:

$$B = D/V \quad (7)$$

Calculate the specific gravity with respect to water at 4°C, using ASTM standard (C 329 – 88) the *Pycnometer method* as follows:

$$S.G = (W - p)/\{(W_1 - p) - (W_2 - W)\} \quad (8)$$

Where:-

p = weight of the stoppered pycnometer .

W = weight of the stoppered pycnometer and specimen.

W1 = weight of the stoppered pycnometer filled with water.

W2 = weight of the stoppered pycnometer, specimen, and water.

Reference:

- 1- "POROSITY OF CERAMICS AND ITS EFFECTS ON PROPERTIES", Roy W. Rice.
- 2- "Calculating in ceramic", R. Griffith.
- 3- " Ceramic tests and calculations", A. I. Andrews.
- 4- ASTM manuals.