Journal of the European Ceramic Society **9** (1992) 245–250

Stuijts Memorial Lecture 1991: Some New Developments in Ceramic Science and Technology*

A. J. Burggraaf

University of Twente, Laboratory of Inorganic Chemistry, Materials Science and Catalysis, PO Box 217, 7500 AE Enschede, The Netherlands

(Received 16 December 1991; revised version received 28 January 1992; accepted 12 February 1992)

Abstract

Exciting opportunities exist for the imaginative refinement of ceramic micro(nano)structures. Examples are given illustrating progress in the design, preparation and characterisation of such structures.

Auf dem Gebeit der bildlichen Auflösung keramischer Mikro- oder Nanostrukturen existieren interessante Möglichkeiten. Hierzu werden einige Beispiele vorgestellt, die den Fortschritt im Design, in der Herstellung und in der Charakterisierung solcher Strukturen veranschaulichen.

L'affinage imaginatif des micro(nano)structures céramiques présente des possibilités intéressantes. Des exemples sont donnés, illustrant le progrès dans la conception, la préparation et la charactérisation de telles structures.

1 Introduction to the Stuijts Memorial Award Lecture

In a lecture with a certain focus on micro and nanostructural effects, we should realise that Leo Stuijts contributed in an important way to the acknowledgement of the effect of ceramic microstructures on the final properties of ceramics both in and outside the field of ceramic science. That the notion 'microstructure' is accepted now was certainly not self-evident 30 years ago. Coming from the field of solid state chemistry, I can assure the reader that microstructural effects were considered by solid state chemists and physicists as a curiosity of a scientifically somewhat underdeveloped field. Just in that period, my somewhat older colleague and friend, Leo Stuijts, convinced me of the importance of microstructures and consequently of the importance of technological factors. It has influenced my career in a profound way. Today the situation has changed. The notion 'microstructure' has been accepted rather well in several fields outside ceramic science and recent developments towards nanostructures gain the attention of even solid state physicists.

In the first Stuijts Memorial lecture, Professor R. J. Brook already identified a number of important fields. His conclusion was that the prevailing attitude of researchers in ceramic science and technology should be a 'pragmatic pattern of development based on a good understanding of the possible contributions of generalised mechanisms'. I can agree with that statement. However, *quantitative predictions* are hardly possible, because several mechanisms almost always act simultaneously in ceramic systems. This gives, however, opportunities for *imaginative* approaches, which should form an essential ingredient of the above mentioned framework. In a time in which fewer and fewer young people choose a scientific or technological career, I hope to show that both science and technology can be an adventure provided imagination plays a role.

Finally, good contact between research institutions and the problems and needs of society and industry is necessary to promote a good balance in efforts to solve short term needs on the one hand and to realise long term possibilities for solving persistent problems on the other hand. Only this balance can guarantee a platform for stable R & D and for future industrial competitiveness.

In my lecture today I shall try to elaborate just these imaginative aspects by inspecting some current new developments and possibilities for advanced ceramics.

---

* Given on the occasion of the Second Meeting of the European Ceramic Society, 12 September 1991, in Augsburg, Germany.

Journal of the European Ceramic Society 0955-2219/92/$05.00

2 General considerations, focal points and conceptions

Focal points in this paper are developments in and possibilities for:

(i) sophisticated (advanced) microstructures. A certain focus is given on nanostructure materials in layers (membranes, coatings) as well as in bulk materials.
(ii) the role of new (sophisticated) preparation technologies
(iii) synergy effects in the development of (nano)-structures in layers and in bulk materials.

Some important developments and themes are summarised in Table 1; this can serve as a background for the considerations given below.

2.1 Synergy effects

Recently, interesting nanostructures have been reported in both dense bulk ceramics and in both porous and dense ceramic films (membranes).[1,2] A closer inspection reveals that in both subfields, similar conceptions and phenomena are used, sometimes in an opposite way.

It has been shown that ordering of rather uniformly sized nanoparticles (5–15 nm) by collapse of a system of weak agglomerates can lead to a well-packed system in both ceramic membranes and in bulk green compacts with grain as well as pore sizes in the nanometer range and with sharp pore (grain) size distributions (this is called 'State B'). A mild disorder in the obtained green compact is preferred to provide sintering dense bulk ceramics as well as porous composite films after sintering.

The required very fine-grained and non- or weakly-agglomerated precursor particles can be obtained by wet chemical synthesis (colloidal processing, sol–gel methods) or by gas phase synthesis. A general scheme to obtain 'State B' and from this state final products is given in Figure 1.

An interesting observation is the fact that with a given material, the same green compact microstructure can lead to supported porous ceramic membranes with a pore structure which is stable up to 1100°C as well as to fully dense bulk ceramics with grains of 0·1 μm sintered at the same temperature! The solution to this apparently contradictory situation is the fact that in thin layers densification and microstructure development is constrained by layer support interactions.

Table 1. Important developments and themes

Structural ceramics
- improvement of reproducibility and of reliability→defect elimination
- improvement of toughness while maintaining high strength
- design concepts for ceramics→tailor made component design
- ultra high temperature strength
- high wear and corrosion resistance (coatings, bulk)

Functional ceramics
- development of sophisticated micro (nano)structures
- grain boundary engineering
- ceramic coatings (layers)

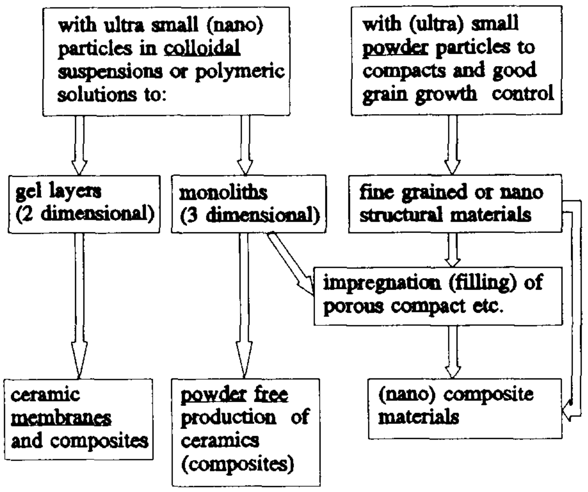

Fig. 1. General scheme for synthesis of (ultra) fine grained green compacts (state B) and products.

Particle reorganisation in the early state of sintering seems especially to be very important to create sufficient contact points and to obtain low sintering temperatures and ultra-fine grained ceramics. If this reorganisation step is inhibited locally (by hard agglomerates), differential sintering results and (micro) defects are formed. If this particle reorganisation is hindered homogeneously by interaction with the support, densification and gain growth are hindered and a stable membrane results.

A typical example is the microstructural development of TiO_2. Unsupported TiO_2 films (thickness 30 μm) sintered at 300°C have a grain size of 5–10 nm and a porosity of about 30% with pores of about 5 nm. Sintered at 600°C the density and grain size are about 95% and 60 nm, respectively.[4] TiO_2 ceramic membranes with a thickness of 3–10 μm on a porous α-Al_2O_3 support maintain the microstructure mentioned for the 300°C unsupported membranes until temperatures above 600°C with only a small loss in porosity. Moreover, the anatase–rutile phase transformation at 500°C shown by the unsupported material and by bulk material is inhibited until about 700–800°C! The stresses and strain relaxation in these ceramic layers can be measured directly with a newly developed method.[5]

Modelling of these processes with two dimensional sintering models (known in the literature) to which constraints (boundary conditions) are added seems to be useful; results from membrane experiments and from modelling can give insight into bulk sintering phenomena.

2.2 Typical aspects of consolidated (porous or dense) nano-crystalline materials.

Brief reviews of ceramic nano-crystalline systems have been given by Burggraaf *et al.*[1,2] Characteristic points are: (i) particle sizes are in the range of 1–100 nm; (ii) a large-fraction of atoms is in the grain boundary region or in a region with a characteristic physical length (Debye length, domain size); (iii) transport properties are changes, e.g. enhanced diffusivity and deformability (ductile!) and (iv) physical properties are changed, e.g. magnetic and electrical behaviour, quantum effects occur (photo electrochemical/catalytical behaviour), solid solubility is enhanced.

Groups of nanocrystalline materials to be distinguished are: (i) *porous* ceramic bodies like aerogel bulk monoliths and ceramic membrane structures; (ii) *dense* nanocrystalline materials (ceramics, metals and composites including nano dispersions) and (iii) nano phase surface layers (e.g. ion implanted layers). Some examples of dense nanostructures are given in Table 2. Nanodispersions are defined here as composite systems built up of a (sub)micron particle matrix of phase A, with a dispersion within it of nano sized particles of phase B.

Nanostructural dense materials mentioned in Table 2 exhibit interesting properties like superplastic deformation with large strain rates (see section 3.1) while microporous membranes (pore diameter < 2 nm) exhibit molecular sieving properties (see section 3.2).

2.3 Some advanced (preparation) technologies

Interesting sophisticated preparation technologies to obtain special micro (nano)structures are:

1. Impregnation and filling of (preformed) porous matrices using (i) solution–precipitation; (ii) gas phase deposition processes like CVD or CVI (Chemical Vapour Infiltration); (iii) molten metals followed by oxidation. If sol–gel processes are used, the porous matrix is already a nanostructure with both particles and pores in the nanosize range (Figure 1).
2. Synthesis of composites (bulk as well as films) from mixtures of organic polymers (containing considerable numbers of metals or metalloids in the polymeric chain) with ceramics or metals.[17] For bulk materials, use can be made of the good shaping properties of polymers. After pyrolysis of the organic polymer, metal carbides, nitrides or carbonitrides are formed within the matrix resulting in composite systems. The porosity and the shrinkage during sintering is diminished. This can be beneficial (see below). For membrane materials, the chemical nature of the pore structure as well as the effective pore size is changed. This results in nanofiltration properties (separation of medium sized molecules or highly charged ions).

Table 2. Types of advanced (sophisticated) nanostructures)

Nanostructural dense materials
(a) nanostructural matrix:
        grain diameter ≤ 100 nm
        density $\geq 90\%$
    $ZrO_2 - Y_2O_3$ ss, TiO_2, CaF_2, MgO/TiO_2, Ag/MgO
    Dispersion of nanoparticles in (sub)micron matrix
    —domain pinning in ferrites
    —flux pinning in superconductors
    —carbide or nitride nanoparticles in Al_2O_3 or MgO
        (Niihara) to improve high temperatures properties
'Duplex' structures with coated particles
Composites with continuously changing composition (bonding technology)

3. Colloidal processing and coating of submicron particles followed by consolidation techniques.
   Duplex structures (Table 2) obtained by the coating of particles have been reported in the literature and can yield interesting composites and/or improve forming technologies (compatability of components in binary colloidal mixtures, higher particle concentrations in suspensions, better phase distribution in binary composites). Finally grain growth kinetics and grain boundary characteristics can be manipulated by the coating of particles.
4. Use of self healing mechanisms with technologies like hot- or sinter-forging or viscous sintering (see point (c) below).
5. Biological (mimetic) procedures.

Some of the above mentioned technologies might be used to solve the problem of (micro) defect formation during the sintering of powder compacts. The larger the shrinkage, the larger the risk of (local) differential sintering and if relaxation mechanisms are not sufficiently active, the larger the extent of (local) defect formation and consequently bad process reproducibility and product reliability (Table 1). Powder free routes (Figure 1) give no solution unless shrinkage is diminished or very homogeneous porous microstructures can be obtained together with very slow processing rates. The main strategic routes to improve the (micro) defect structure in sintered powder compacts are:

(a) Decrease or avoid shrinkage. This can be obtained by the filling of porous compacts followed by reaction (see 2.3 point 1).

(b) 'Homogenisation of shrinkage rate'. This implies that local differences in shrinkage rate must be eliminated or are allowed to relax by adaptation of their local environment. Introduction of a mild degree of disorder in particle compacts by the use of particles having a small but finite distribution width seems advantageous. Phase transformations must be controlled (inhibited or slowed down). The use of weak, well-defined agglomerates consisting of small (nano sized) elementary particles is necessary to obtain ultra fine grained ceramics. If fractal structures are present the size of the (agglomerate) particles should be small.

(c) Use of self healing mechanisms.

Hot- and sinter-forging processes as well as hot extrusion are characterised by the occurrence of extensive shear stresses. If large strains can be obtained, as is the case with systems showing (super)plastic deformation, healing of (micro) defects is observed as soon as a certain threshold value of strain is surpassed (see further section 3.1).

Viscous sintering (glasses or glass ceramic composites) sometimes provides an effective mechanism for the removing of voids.

Relaxation processes can be promoted in green compact synthesis by the use of small weakly bound particles obtained, e.g. by the use of drying controlled chemical agents (DCCA).

3. Some illustrative examples

3.1 Dense nanostructure materials and hot/sinterforging processes

Interesting developments in superplastic deformation technology (hot and sinter-forging) are based on the following advantages:

1. Rather complicated shapes can be realised.
2. Strain rates up to $10^{-2} s^{-1}$ are possible by appropriate doping (0,3% Mn or Cu oxide) of zirconia ceramics with grain sizes of 0·3–1·0 μm (Chen, Wakai[8,9]).
3. Many materials can be superplastically deformed provided that the grain size is about 1 μm or smaller (Chen, Wakai, Carry). Strains up to 800% have been reported (Nieh).[14]
4. Defect healing is observed after extensive shear deformation (> 60%).
5. Sinter-forging is suitable for near net shaping of ceramic composites in a single step and for production of ultra fine grained ceramics.
6. Use of ceramics with nano sized particles yields interesting effects (Boutz/Burggraaf).[6,16]

Boutz *et al.*[6] recently performed hot forging experiments with ceramics of zirconia containing 2·6 mol% Y_2O_3 (2·6Y-TZP with grain sizes of 0·2 μm). At 1300°C they found an increase by a factor of 50 in the strain rate compared with ceramic with comparable composition, made from commercially available powder (Tosoh TZ 3Y), with a grain size of 0·4 μm. Both systems have a relatively low impurity concentration. The effect of impurities is a question of vigorous debate in the literature.[18,19] Recently Boutz *et al.*[16] used sinter-forging (starting with green compacts with particle and pore sizes around 7–10 nm) to produce ceramics with a grain size of 100 nm and a density of 94%. This result was obtained at the relatively low temperature of 1100°C in 22 minutes using a (initial) pressure of 84 MPa. Den Exter *et al.*[7] could produce composites of Al_2O_3 containing 15 weight% zirconia with a density of 98% and grain size of 0·9 μm (Al_2O_3) and 0·3 μm (ZrO_2) in a sinter-forging process at 1450°C in 15 minutes. No preferential orientation of the particles occurred and the ceramic material exhibited a very homogeneous phase distribution.

3.2 Porous ceramic membrane structures

Overviews of ceramic membrane synthesis, structures and properties have been reported by Burggraaf and Keizer.[10,11] The most frequently used type of ceramic membrane consists of an asymmetric composite structure built up of:

(i) A porous support (for mechanical strength) with a thickness of about 2 mm and a pore diameter of 1–15 μm. Materials used are αAl_2O_3, zirconia, carbon or steel.

(ii) On top of one side of the support is applied an 'intermediate' layer with a thickness of 10–100 μm and pores with a diameter in the range of 0·1–1·5 μm.

(iii) On top of the intermediate layer is applied a very thin layer (by sol–gel technology) with a thickness of 2·0–10 μm. The pore structure is characterised by a very sharp pore size distribution which can be centered around diameters of 3 nanometer (as a minimum value) up to about 50 nm. Porosities are in the range of 30–50 vol%, particle diameters range between 5–100 nm. The structure is thermally stable at high temperatures. It is obtained by the ordering of nanoparticles by collapse of weak agglomerates into a well packed layer system during the drying of the gel layer.

(iv) The top layer mentioned under (iii) can be modified by liquid phase as well as gas phase deposition techniques[1,10,11] as mentioned in 2.3.1.

This process yields composite layers consisting of γAl_2O_3, TiO_2, ZrO_2, C or glass (partially) filled with layers, plugs or particles of e.g. Ag, MgO, ZrO_2, CeO_2, V_2O_5 or SiO_2. Most interesting are structures where the pores of αAl_2O_3 membranes are plugged at their entrance only. Using SiO_2 or binary SiO_2–TiO_2 or SiO_2–ZrO_2 systems, amorphous plugs of about 30 nm covered by a thin layer of about 30 nm of the same material were obtained (Uhlhorn/de Lange/ Keizer/Burggraaf[12,13]). These ultra thin plug/layers have pore diameters in the range of 0·5–1·0 nm (micropores). These systems show molecular sieving properties.

An interesting variety is the possibility to make sandwich structures consisting of a series of thin layers (each 2–4 μm thick) on each other. The thin layers can have different composition, e.g. Al_2O_3–TiO_2 sandwich structures.

The combinations of (i) and (ii) mentioned above is used for microfiltration applications (food, biotechnological, beverage industry). The combination of (i) to (iii) is used for ultrafiltration and vapour phase separation. Finally the complete membrane system (i) to (iv) can be used for nanofiltration (medium sized molecules; highly charged ions), gas and vapour phase separation (petrochemical industry) and in catalytically active membrane reactor systems. An example of this is the separation of hydrogen (H_2) from other gasses or from (de)hydrogenation reactions with the above mentioned microporous membranes. Fluxes of 300 $m^3\ m^{-2}\ day^{-1}\ bar^{-1}$ are obtained for H_2 with selectivities up to 200 while the conversion and selectivity of several chemical reactions could also be considerably increased.[15]

Finally, the use of nanostructured membrane layers in electro-optical devices and sensors and the use of ceramic coatings for high temperature corrosion protection should be mentioned.

Conclusions

1. Synthesis of sophisticated microstructures has been realised, especially in nanostructure layers (porous membranes, coatings) and nano-dispersed bulk composites. A variety of new or improved properties can be obtained: e.g. nanofiltration and molecular seiving, (electro) optical devices, improvement of magnetic and (super)conductive properties, high temperature strength, wear resistance.
2. Interesting possibilities for some sophisticated preparation technologies exist:
   (a) Impregnation and filling of (preformed) porous matrix structure using:
      (i) gas phase reactions
      (ii) molten metals followed by oxidation
      (iii) solutions/precipitation
   (b) Synthesis of composites (bulk and films) from organic polymer–chemical/metal mixtures.
3. Interesting new characterisation method(s) are emerging, e.g. Atomic Force and Scanning Tunneling Microscopy; characterisation of grain boundary structures and nanoscale details.

References

1. Burggraaf, A. J., Keizer, K. & van Hassel, B. A., Nano phase ceramics, membranes and ion implanted layers. In *Surfaces and Interfaces of Ceramic Materials*, ed. L. C. Dufour, C. Marty and G. Petot-Ervas, Kluwer Academic Publishers, 1989, pp. 705–25.
2. Burggraaf, A. J., Theunissen, G. S. A. M. & Winnubst, A. J. A. Synthesis and properties of nano phase ceramics and composites. In *Euroceramics, Vol. 1, Processing of Ceramics*, ed. G. de With, R. A. Terpstra, R. Metselaar, Elsevier, London, 1989, pp. 1.8–1.12.

3*a*. Theunissen, G. S. A. M. Microstructure, fracture toughness and strength of ultra finegrained tetragonal zirconia ceramics, PhD Thesis, University of Twente, Enschede, The Netherlands, February 1991.

3*b*. Boutz, M. M. R., Theunissen, G. S. A. M., Winnubst, A. J. A. & Burggraaf, A. J., Grain growth during sintering of nanocrystalline Y and/or Ce-doped tetragonal zirconia. In *Proceedings Symposium Mat. Res. Soc., Vol. 196*, San Francisco, USA, 1990, pp. 87–93.

4. Kumar, K. P., Zaspalis, V. T., Keizer, K., Burggraaf, A. J., Okubo, T., Morooka, S. & Nagamoto, H., Nanostructural evolution in supported and unsupported titania membrane, MRS Spring '92, Symposium Materials for Separation Technology, April 27–May 1, San Francisco, U.S.A.

5*a*. Voncken, J. H. L., Lijzenga, C., Kumar, K. P., Keizer, K., Burggraaf, J. & Bonekamp, B. C., A new method for the measurement of stress in thin drying gel layers, produced during the formation of ceramic membranes. *J. Mater. Science*, **26** (1991) 472–8.

5*b*. Kumar, K. P., Zaspalis, V. T., Keizer, K. & Burggraaf, A. J., Stress development during drying of sol–gel derived ceramic membrane, *J. Non. Cryst. Solids*, submitted.

6. Boutz, M. M. R., Winnubst, A. J. A., Burggraaf, A. J., Nauer, M. & Carry, C., Low temperature superplastic flow of yttria stabilized tetragonal zirconia polycrystals. In *Proceedings of 2nd Eur. Cer. Soc. Conference*, 14 September 1991, Augsburg, Germany.

7. Den Exter, P., Synthesis, microstructure and mechanical properties of zirconia–alumina composites, PhD Thesis, University of Twente, Enschede, The Netherlands, December 1991.

8. Hwang, C. J. & Chen, I. W., Effect of a liquid phase on superplasticity of 2 mol%-Y_2O_3 stabilized tetragonal zirconia polycrystals. *J. Am. Ceram. Soc.*, **73** (1990) 1626–32.

9. Descamps, P., Tirlocq, J., Cambier, F. & Wakai, F., Comparison of superplastic behaviour of two different ceramic materials, Silicates Industriels 3–4, 47–61 (1991).

10. Burggraaf, A. J. & Keizer, K., Synthesis of Inorganic Membranes. In *Inorganic Membranes, Synthesis, Characteristics and Applications*, ed. R. Bhave, Van Nostrand Reinhold, London, 1991.

11. Burggraaf, A. J. & Keizer, K., Ceramic Membranes. In *Concise Enc. of Adv. Ceram. Materials*, ed. R. J. Brook, Pergamon Press, Oxford, 1991, pp. 62–67.

12. De Lange, R. S. A., Hekkink, J. H. H., Keizer, K. & Burggraaf, A. J., Microporous sol–gel modified membranes for hydrogen separation. In *Proceedings of ICIM-2*, 1–4 July, Montpellier, France, *Key Engineering Materials, Vols 61 & 62 (1991)*. Trans. Tech. Publishers, Zurich, Switzerland, 1992, pp. 77–82.

13. Uhlhorn, R. J. R., Keizer, K. & Burggraaf, A. J., Gas transport separation with ceramic membranes. Part II. Synthesis and separation properties of microporous membranes, *J. Membr. Sc.* (1992), accepted.

14. Nieh, T. G., McNally, C. M. & Wadsworth, J., Superplastic properties of a fine-grained yttria stabilized tetragonal polycrystal of zirconia, *Ser. Metall.*, **22** (1988) 1297.

15*a*. Zaspalis, V. T., Keizer, K. K. & Burggraaf, A. J., Porous and dense ceramic membranes in high temperature applications. In *Proceedings 2nd Int. Conf. on Inorganic Membranes (ICIM2)*, 1–4 July 1991, Montpellier, France (see Ref. 12).

15*b*. Zaspalis, V. T., Catalytically active ceramic membranes. Ph.D Thesis, November 1990, University of Twente, Enschede, The Netherlands.

16. Boutz, M. M. R., Winnubst, A. J. A., Burggraaf, A. J., Nauer, M. & Carry, C., Low temperature sinter-forging of Y-TZP ceramics, *J. Eur. Cer. Soc.*, submitted.

17. Passing, G., Schönfelder, H., Riedel, R. & Brook, R. J., Polymer derived ceramic components, *Proceedings 2nd Eur. Cer. Soc. Conference*, 11–14 September 1991, Augsburg, Germany.

18. Carry, C., Microstructures, grain boundaries and superplasticity in fine grained ceramics. In *Superplasticity in Metals, Ceramics and Intermetallics*, ed. M. Mayo, M. Kobayashi and J. Wadsworth, Mat. Res. Soc. Symp. Proc. vol. 196, 313–23 (1990).

19. Nieh, T. G., Wadsworth, J. & Wakai, F., Recent advances in superplastic ceramics and ceramic composites, *Int. Mater. Rev.*, **36** (1991) 146–61.