Forming and sintering of multiphase bioceramics

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Composite bioceramic materials could find use in a wide range of biomedical applications; however, their processing technologies are quite complex or not sufficiently developed. In order to eliminate deleterious influences of powder inhomogeneities and to reduce the machining time of final components, a novel procedure for multiphase powders using wet pretreatment and direct forming of green bodies having the desired geometries was studied. During the experimental work alumina, yttria-stabilized zirconia, and their mixtures were used. The forming of discs and femoral heads was done by pressure casting of aqueous suspensions of powders. The measurements of physical, mechanical and tribological properties of sintered samples were performed; the results obtained showed the effectiveness of the process since the property values approached those of similar materials actually on the market, while requiring less machining labour.

1. Introduction
Due to their chemical and physical characteristics, ceramic materials have found many biomedical applications, particularly where the components are subjected to high stresses generated by mechanical loads, and severe wear. For instance, the reliability of alumina or zirconia-based bioceramic materials has been widely demonstrated by the ever-increasing number of implanted prosthesis. Unfortunately, the values of some parameters for these materials, such as toughness and fracture strength, necessitate further increases if failure risks are to be reduced [1]. One can easily forecast that these insufficiencies could be overcome by developing biomedical components on the basis of ceramic composites [2, 3]. However, it is well known that forming and densification of multiphase ceramics has serious processing difficulties due to the deleterious influences of hard agglomerates, inhomogeneities, low packing levels and inadequate adherence between single components of powder–powder and/or powder–fibre systems.

This paper describes the pretreatments of raw materials, forming by pressure slip casting, and final densification of femoral heads starting with different acqueous suspensions of zirconia, alumina and their mixtures [4]. This innovative technique allows a closer control of chemistry and particle size distribution of the starting materials and avoids the drying step that results in hard agglomerates of different sizes. Here, the raw material is directly transformed into a green/sintered near-net-shape body with high microstructural homogeneity and improved mechanical properties.

2. Experimental procedures and discussion
2.1. Starting powders
The studied powders were single oxides, alumina and 3 mol % yttria-stabilized zirconia, and mixed oxides, homogeneous mixtures of alumina and 3 mol % yttria-stabilized zirconia. Their characteristic properties are given in Table I. The powders belong to the class of pure and highly sinterable materials. From the technological point of view some difficulties in powders manipulation and considerable sintering shrinkages were forecast. The examinations made by scanning electron microscopy (SEM) (Model T330, Jeol, Japan) revealed that all of the starting powders are characterized by the presence of spherical and fairly compact agglomerates ranging from 10 to 100 μm in size; the unit particles of spherical form are submicronic and show narrow size distributions. The powders 8Z2A and 2Z8A demonstrate bimodal particle size distributions since the zirconia and alumina unit particles have different sizes: zirconia particles are much smaller than those of alumina and this fact substantially contributes to the high surface area of zirconia-rich powders.

2.2. Slip preparation
The slips were prepared with "as received" powders, deionized water and an ammonia salt of polycarbonic acid as deflocculant. The so-prepared suspensions were milled in a centrifugal mill with zirconia jar and balls for different periods of time; the first part of the study included relatively short millings only. The solid

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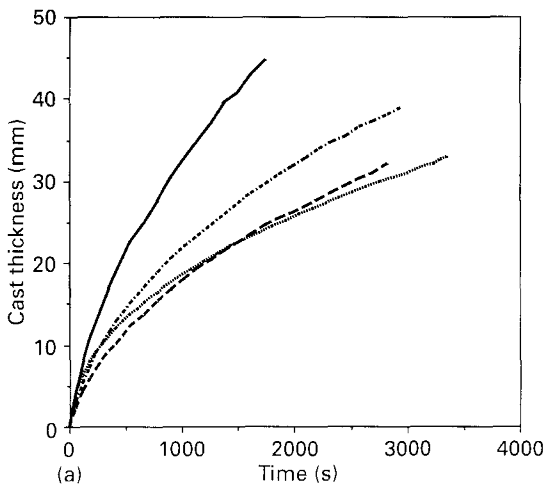
TABLE I Characteristics of starting powders

Powder sample	Composition	Mean crystallite[c] size (nm)	Surface area, (m^2/g)	Mean unit particle (μm)
Z[a]	ZrO_2 stabilized with 3 mol % of Yttria	35·9	6	0·3
8Z2A[a]	80 wt % of ZrO_2 stabilized with 3 mol % of Yttria + 20 wt % Al_2O_3	25·9	16	ZrO_2: 0·1 Al_2O_3: 0·3
2Z8A[a]	20 wt % of ZrO_2 stabilized with 3 mol % of Yttria + 80 wt % Al_2O_3	27·0	9–10	ZrO_2: 0·1 Al_2O_3: 0·4
A[b]	α-Al_2O_3	–	9·5	0·4

[a] Powders produced by TOSOH (Japan)
[b] Powder produced by Alcoa Inc. (USA)
[c] Zirconia phase

concentration was 21 vol % or 33 vol %, while the deflocculant content ranged between 0.5 wt % and 1.8 wt % of the solid.

The viscosity measurements were performed by viscometer (Haake Model RV 20): the shear rates changed up to $1000\ s^{-1}$. The viscosity of the slips studied strongly depends on powder type, pretreatment procedure and deflocculant content; slips of lowest viscosity were obtained with the following deflocculant content: (i) 0.3 wt % for powders Z and A; (ii) 0.4 wt % for powder 2Z8A; (iii) 1.8 wt % for powder 8Z2A.



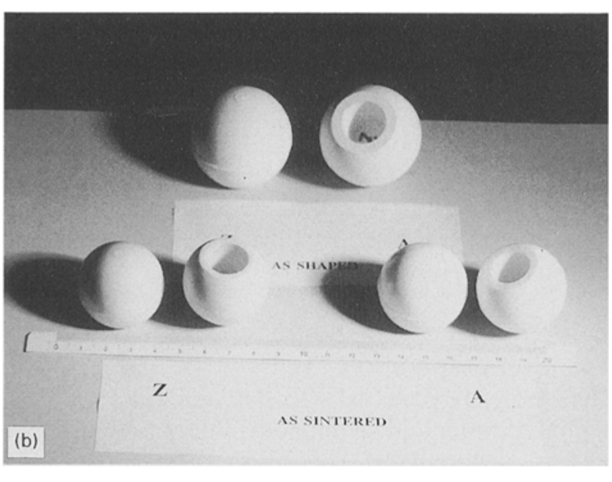


Figure 1(a) Casting curves of different slips (—— Z; ··· ··· 8Z2A; - - - 2Z8A; –·–·– A). (b) "As-formed" (upper row) and "as-sintered" zirconia and alumina femoral heads.

2.3. Forming

The forming procedures were carried out using in-house developed laboratory equipment able to produce greens of two geometrical shapes: discs with a diameter of 50 mm and femoral heads of near-net-shape.

The casting curves of slips with the lowest viscosity were obtained at different casting pressures. Some of the casting curves are shown in Fig. 1a: the slips prepared with the powders A, 2Z8A and Z were cast at 10 MPa, while that of powder 8Z2A, having rather low casting rates, was obtained at 15 MPa in order to have similar casting kinetics.

The green densities of different samples were 51% TD for Z, 45% TD for 8Z2A, 53% TD for 2Z8A and 59% TD for A. The relatively low green densities for 8Z2A specimens correlate with the characteristics of the powder: the fluffy character of the aggregated unit particles does not permit high packing levels. It may be that more intensive deagglomeration would partially solve this problem.

Femoral heads were produced with all of the powders studied: their characteristic properties are in full accordance with those of discs prepared under the same conditions. The femoral heads produced with powders A and Z are shown in Fig. 1b.

2.4. Microstructure and mechanical properties of sintered samples

The Z, 8Z2A and A green samples were sintered in air at 1500 °C and soaked for 2 h at this temperature; 2Z8A was sintered at 1550 °C and soaked for 2 h at this temperature. The properties of the sintered bodies are given in Table IIa.

SEM observations revealed that A and Z samples are highly homogeneous and made up of predominantly submicrometre-sized grains with a narrow size

TABLE II Properties of sintered samples (a) Physical and mechanical properties

Sample	Z	8Z2A	2Z8A	A
Density (% TD)	100	99·6	99·3	100
Linear shrinkage (%)	20·5	21·5	18·3	15·5
Average grain size[a] (μm)	0·57	zirconia: 0·49 alumina: 0·59	zirconia: 0·35 alumina: 0·87	0·96
H_{v20} (GPa)	13·1	14·3	17·8	16·7
K_{IC} (MPa·m$^{1/2}$) (Niihara)	5·9	6·1	4·6	5·2
Flexural strength (MPa)	1056	1057	–	324

[a] On the basis of SEM examinations

(b) Tribological characteristics

Sample	Sliding rate 0·7 m/s		Sliding rate 1·0 m/s	
	Friction coefficient	Wear rate (m^3/N·m)	Friction coefficient	Wear rate (m^3/N·m)
8Z2A	0·03	$9{\cdot}14 \times 10^{-5}$	0·06	$6{\cdot}80 \times 10^{-5}$
Commercial alumina	0·20	$1{\cdot}10 \times 10^{-5}$	0·22	$2{\cdot}67 \times 10^{-5}$

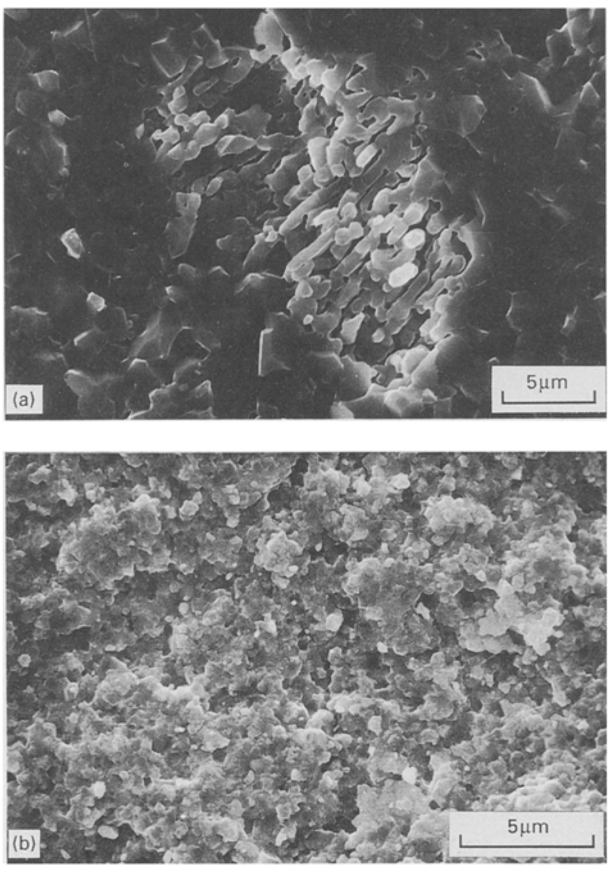


Figure 2 SEM micrographs of sintered samples: (a) zirconia Z; (b) zirconia–alumina 8Z2A.

range. In the samples in which milling pretreatments were short, clusters of micropores were noticed, (Fig. 2a): this could be explained as an internal porosity effect of the sintered agglomerates. The sintered 8Z2A and 2Z8A samples show highly homogeneous microstructures (Fig. 2b). All sintered samples reach almost full theoretical densities and do not present macroscopical deformations. The grains remain of submicrometre size, but some abnormally grown alumina grains can be noticed: further optimization of raw material composition and sintering cycle is under investigation. The tribological characteristics were determined by a pin-on-disc apparatus. The friction and wear behaviour of 82ZA discs against a commercial alumina pin, was studied in air at room temperature in unlubricated conditions, at two different sliding rates, 0.7 and 1.0 m/s, with a normal load of 33 N and at a sliding distance of 3000 m. The experimental results, reported in Table IIb, are compared with those obtained, under the same conditions, with a commercial alumina [5]. For both chosen sliding rates, the coefficients of friction of the 8Z2A/Al_2O_3 system are lower than the values registered for the Al_2O_3/Al_2O_3 system, while the corresponding wear rates are slightly higher.

3. Conclusions

The forming technique studied allows the processing of different powders, single or mixed oxides, and produces highly densified samples of complex geometry (such as femoral heads) with reduced machining labour.

The properties of the tested materials, alumina A, zirconia Z and their mixtures 8Z2A and 2Z8A are comparable, if not superior, to those of similar materials actually on the market.

For biomedical applications the 8Z2A sample seems to have the best performance of the systems studied showing: (i) the highest K_{IC} and flexural strength values; (ii) hardness and tribological behaviour slightly lower than those of alumina.

Further studies of the ZrO_2/Al_2O_3 system are in progress.

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