

Wear behaviour, fluorescence and SEM investigations on nanocomposite zirconia-toughened alumina

P. Taddei · S. Affatato · R. Torrecillas ·
C. Fagnano · P. Ferrieri · A. Toni

Received: 14 July 2005 / Accepted: 31 October 2005 / Published online: 6 June 2006
© Springer Science+Business Media, LLC 2006

Abstract The need to improve the reliability of alumina and zirconia hip prostheses has led to the development of zirconia-toughened alumina (ZTA) ceramics. The set-up of new colloidal processing routes brought about new ZTA nanocomposites (NZTA) with a significantly smaller and narrower particle size distribution of zirconia than conventional powder mixing methods. These nanocomposites present reinforcement mechanisms other than transformation toughening, mainly based on residual thermal stresses. In this study, the wear behaviour of NZTA–NZTA couplings was evaluated in a hip joint simulator run for seven million cycles, in comparison with commercial and experimental alumina couplings. From a statistical point of view, the three sets of specimens did not show significant differences in wear behaviour. However, from a gravimetric point of view, the weight loss decreased along the series: experimental alumina > NZTA > commercial alumina. The R_1 and R_2 fluorescence bands (due to the Cr^{3+}

ions naturally present in alumina ceramics as trace impurities) increased in intensity along the series: experimental alumina < NZTA < commercial alumina, indicating a progressive improvement of the surface quality. SEM analysis confirmed that the better the sample finishing, the better was the wear behaviour. By taking into account that the tested NZTA samples were prototypes (thus with a surface finishing worse than for a production type), it can be stated that NZTA can offer the option of improving the lifetime and reliability of ceramics.

Introduction

Alumina and zirconia couplings are widely used in total hip arthroplasty (THR) [1–4], since they were found to produce lower wear rates than other combinations (i.e. metal-on-polyethylene and ceramic-on-polyethylene) [5–14]. However, also ceramic materials present some limitations: high fracture rates in the case of alumina components [15, 16] and hydrothermal degradation for zirconia [17–21].

The development of mixed oxides ceramic materials may be the key for good alternative bearing surfaces. The addition of zirconia into an alumina matrix (zirconia-toughened alumina, ZTA) has been reported to result in an enhancement of flexural strength, fracture toughness and fatigue resistance [22–27], mainly attributed to the stress-induced phase transformation that tetragonal zirconia undergoes into the more stable monoclinic phase. This phase transformation is accompanied by a volume increase (about 4%) that induces compressive stresses around a propagating crack and develops the toughening effect [22].

P. Taddei · C. Fagnano
Centro di Studio sulla Spettroscopia Raman, Dipartimento di
Biochimica “G. Moruzzi”, Sezione di Chimica e Propedeutica
Biochimica, Università di Bologna, Bologna, Italy

S. Affatato (✉) · A. Toni
Laboratorio di Tecnologia Medica, Istituti Ortopedici Rizzoli,
Via di Barbiano 1/10, 40136 Bologna, Italy
e-mail: affatato@tecno.ior.it

R. Torrecillas
INCAR, Spanish Research Council (CSIC), Oviedo, Spain

P. Ferrieri
Dipartimento di Scienze della Terra e Geologico-Ambientali,
Università di Bologna, Bologna, Italy

A. Toni
I° Divisione di Ortopedia e Traumatologia, Bologna, Italy

ZTA composites can be obtained by many methods of synthesis. Conventional ones include the mechanical mixing of the powder and/or attrition milling, followed by freeze-drying and/or hot pressing; another method involves the hydrolysis of zirconium alkoxides in a dispersed alumina slurry [28–30]. However, by following these processing routes, the obtainment of a fine and homogeneous microstructure is an almost impossible target. The development of new processing protocols in non-aqueous media [31] has allowed preparation of nanocomposite ZTA (NZTA) with a significantly smaller and narrower particle size distribution of zirconia than conventional methods [31, 32]. These nanocomposites have proved a very homogeneous microstructure [31, 32], nearly the same hardness as alumina (1700 Hv vs. 1800 Hv), a higher toughness ($10 \text{ MPa m}^{1/2}$ vs. $4 \text{ MPa m}^{1/2}$), a higher fatigue limit ($7 \text{ MPa m}^{1/2}$ vs. $2.5 \text{ MPa m}^{1/2}$) and high hydrothermal stability.

These properties make NZTA couplings promising for THR. Therefore, in the present study, the wear behaviour of NZTA–NZTA couplings was evaluated in a hip joint simulator; commercial and experimental alumina couplings were tested for comparison.

The wear trend of the three sets of specimens was evaluated in terms of weight loss. Some preliminary SEM results are here reported together with fluorescence measurements. The latter were used to investigate the surface quality of the acetabular cups and their residual stress, according to a piezospectroscopic technique proposed in the late 1970s [33] and widely applied to the study of alumina and alumina–zirconia composites [34–44]. The piezospectroscopic effect may be defined as the shift of the characteristic frequencies of spectral bands—be they Raman, IR or fluorescence bands—in response to an applied strain or stress. Alumina is characterised by two strong and sharp fluorescence bands at about $14,400$ and $14,430 \text{ cm}^{-1}$, which have a well-defined stress dependence [39]. These bands are due to the radiative transitions of the Cr^{3+} ions, present as natural substitution impurities in alumina.

Materials and methods

Materials

The following couplings (femoral ball 28 mm in diameter, acetabular cup 28 mm in inner diameter and 44 mm in outer diameter) were tested:

- four commercial alumina heads and acetabular cups (Biolog Forte, CeramTec, Germany);
- four experimental alumina heads and acetabular cups;
- four experimental NZTA heads and acetabular cups.

The experimental alumina and NZTA couplings were manufactured using a new colloidal processing route, which was described in detail elsewhere [31]. It consists in doping a stable suspension of a high purity alumina powder (Condea HPA 0.5, with an average particle size of $0.45 \mu\text{m}$ and a surface area of $10 \text{ m}^2/\text{g}$) in absolute ethanol (99.97%) by dropwise addition of diluted ($2/3 \text{ vol\%}$ Zr alkoxide, $1/3 \text{ vol\%}$ absolute ethanol) zirconium alkoxide (Aldrich Zirconium-IV-propoxide 70 wt% solution in 1-propanol). A very low amount of zirconia precursor was added, in order to obtain NZTA with only 1.7 vol% (2.5 wt%) zirconia nano-particles. After drying under magnetic stirring at $70 \text{ }^\circ\text{C}$, the powders were thermally treated at $850 \text{ }^\circ\text{C}$ for 2 h in order to remove organic residuals and were subsequently attrition milled with alumina balls for 1 h. Green compacts were obtained by a pressure casting method. The optimum sintering to obtain the desired nano-structural network of zirconia particles consisted of a thermal treatment at $1600 \text{ }^\circ\text{C}$ for 2 h.

Wear tests

The wear tests were carried out using a twelve-station hip joint simulator (Shore Western, USA). The stations were filled with 25% sterile bovine calf serum (SIGMA, St. Louis, USA) balanced with deionised water, plus 0.2% sodium azide (E. Merck, Darmstadt, Germany) to retard bacterial degradation during the wear test. EDTA (ethylenediaminetetraacetic acid) was also added in a concentration of 20 mmol in order to minimise precipitation of calcium phosphate on the bearing surfaces; the latter which has been shown to strongly affect friction and wear properties [45]. The test was carried out under ambient conditions. The load profile was sinusoidal with a peak magnitude of 2030 N and a frequency of 1 Hz.

Weight loss was calculated using a microbalance (SARTORIUS AG, Germany) with a sensitivity of 0.01 mg and an uncertainty of about $\pm 0.03 \text{ mg}$. Each weight measurement was repeated three times and the average weight was used for calculations.

The wear trend was evaluated in terms of weight loss. The wear rates, calculated from the slopes of weight loss versus number of cycles, were obtained using least squares linear regression.

The gravimetric data were statistically analysed (Kruskal–Wallis test).

Fluorescence measurements

The fluorescence spectra were obtained using an argon–krypton laser (Innova Coherent 70) operating at 488 nm to excite the fluorescence and a Jasco NRS-2000C micro-

Raman spectrometer equipped with a 160 K frozen digital CCD detector (Spec-10: 100B, Roper Scientific Inc.) to collect the excited fluorescence. To ensure that no laser heating occurred and contributed to the observed frequency shifts, all measurements were performed at a low laser power (i.e. 1 mW). Instrumental fluctuations represent another source of possible variation in the measured frequency. In order to correct for this, a characteristic neon line at $14,431\text{ cm}^{-1}$ was used as a frequency calibration standard.

The spectra were recorded in back-scattering conditions with 1 cm^{-1} spectral resolution using an objective lens of $10\times$ magnification; the laser spot size was larger than the grain size of the ceramics, assuring that the fluorescence was being averaged over a large number of grains. Moreover, to obtain a good representation of the stress distribution, 10 spectra were collected in 10 different points of each sample.

The spectra were recorded in a non-destructive way on all the worn acetabular cups in the inner surface near the centre (in a spatial range of about 1.5 mm from the centre). A soaked unworn cup of each set of specimens was analysed as control.

The bands monitored were at about $14,396\text{ cm}^{-1}$ (R_1) and $14,424\text{ cm}^{-1}$ (R_2). Their width (expressed as full width at half maximum, FWHM), intensity and frequency were determined by fitting the experimental spectra with mixtures of Lorentzian and Gaussian functions. The fitting was done using a commercial software (OPUS 5.0, Bruker Optik GmbH, Germany).

Scanning electron microscopy analysis

SEM micrographs were obtained on gold-coated unworn acetabular cups using a Philips XL20 with an accelerating tension of 20 kV.

Results

Wear behaviour

All specimens completed the test up to seven million cycles. After seven million cycles, the surface of all femoral heads and acetabular cups was examined with an optical microscope. No macroscopic damage, scratches, or failures were observed on the ceramic specimens.

The weight loss of the three types of ceramic specimens is plotted in Fig. 1 versus the number of cycles. Table 1 shows the experimental values (weight loss versus number of cycles) and the wear rates by type of material (slopes of the regression lines). No significant differences were observed among the wear behaviours of the three types of ceramics.

As regards the photoluminescence measurements, all the samples contained an adequate Cr^{3+} impurity level for the R_1 and R_2 bands to be recorded with a high signal-to-noise ratio, so that precise measurements of band frequency, intensity and FWHM were assured. As an example, Fig. 2 reports a fluorescence spectrum recorded on the unworn control commercial alumina acetabular cup, fitted into the two R_1 and R_2 components.

The data obtained from the fitting of the experimental spectra are reported in Table 2. It can easily be seen that after the test, irrespectively of the sample composition, the R_1 and R_2 bands did not show any significant change in frequency, intensity or FWHM. By comparing the three sets of samples, the only significant observable change regarded the intensity of both R_1 and R_2 bands. As can be easily seen from Fig. 3, the intensity of the fluorescence bands was decreasing along the series: commercial alumina > experimental NZTA > experimental alumina. These results give information on the surface quality of the specimens, according to other authors [46, 47]: the

Fig. 1 Weight loss versus number of cycles for the three sets of ceramic acetabular cups (mean values obtained on three specimens of each set)

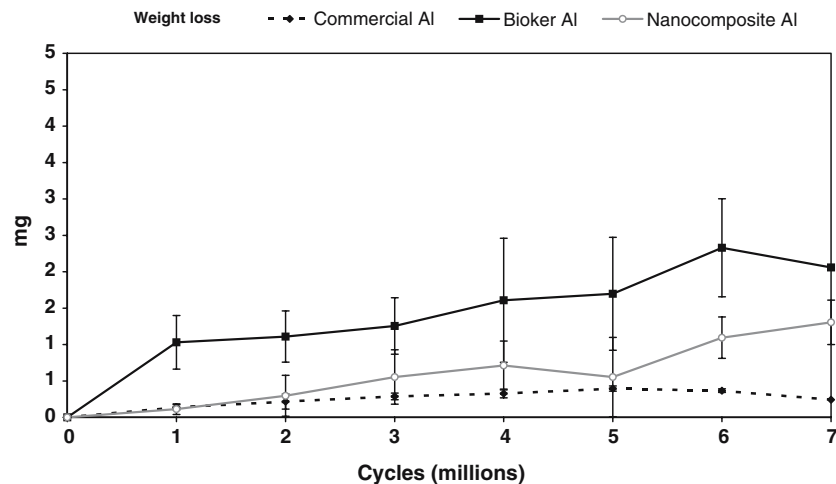


Table 1 Experimental weight losses and wear rates (calculated as slopes of the regression lines) for the three sets of specimens

Ceramic acetabular cups weight loss: Mean ± Standard Deviation (mg)			
Cycles	Commercial alumina	Experimental alumina	Experimental NZTA
1	0.14 ± 0.04	1.03 ± 0.37	0.11 ± 0.07
2	0.22 ± 0.10	1.11 ± 0.35	0.30 ± 0.28
3	0.29 ± 0.05	1.25 ± 0.39	0.55 ± 0.37
4	0.33 ± 0.06	1.61 ± 0.85	0.71 ± 0.34
5	0.39 ± 0.04	1.70 ± 0.78	0.55 ± 0.55
6	0.37 ± 0.03	2.33 ± 0.67	1.09 ± 0.28
7	0.24 ± 0.11	2.06 ± 1.46	1.30 ± 0.31
Wear Rate (slopes of the regression lines)	0.04	0.27	0.18

strongest fluorescence corresponds to the sample with the best surface finishing (i.e. commercial alumina).

These findings were confirmed by the SEM analysis of the three sets of unworn acetabular cups.

Figure 4a shows the SEM micrograph of an unworn commercial alumina sample. The surface analysis of this specimen highlighted only limited surface defects: some pits ranging in size from sub-granular (i.e. less than 1 μm, as in the Figure) to approximately 7 μm were visible.

Figure 4b shows the SEM micrograph of an unworn experimental alumina sample. The polishing marks due to manufacturing were clearly observable together with several pits of larger size than in commercial alumina samples. The microstructure of the unworn NZTA acetabular cup (Figure 4c) showed less defects than the latter, although the line marks due to manufacturing were clearly visible. A fine and homogeneous dispersion of zirconia grains within the alumina matrix can be observed. Zirconia particles had a grain size ranging between 30 and 150 nm (i.e. several times smaller than alumina grains) and were found to be mainly (>70%) intragranular, with almost perfect spherical shape. The alumina grains exhibited a relatively broad grain size distribution, and many grains were tabular or elongated.

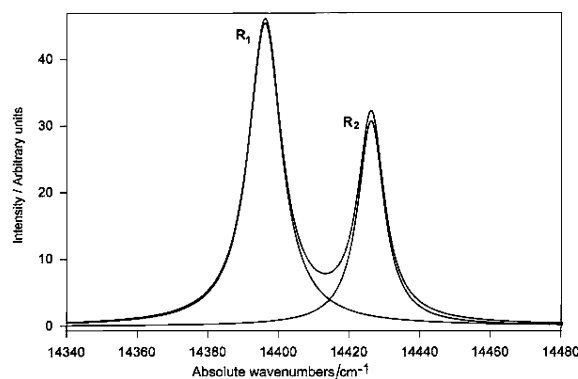


Fig. 2 Fluorescence spectrum recorded on the unworn commercial alumina acetabular cup, fitted into the two R_1 and R_2 components

Discussion and conclusions

The NZTA materials tested in the present study were synthesised by using a new colloidal processing route, producing nano-sized zirconia grains with a narrow grain-size distribution [30, 31]. More in details, the present paper reports the results obtained on a NZTA with a particularly low amount of zirconia precursor (1.7 vol%, i.e. 2.5 wt%).

Table 2 Frequency, intensity and full width at half maximum (FWHM) of the R_1 and R_2 bands as obtained by fitting the experimental fluorescence spectra of the acetabular cups analysed. The data reported are mean values referring each to ten spectra

Sample		R_1 band			R_2 band		
		Frequency (±SD)	Intensity (±SD)	FWHM (±SD)	Frequency (±SD)	Intensity (±SD)	FWHM (±SD)
Commercial alumina	Control	14396.2 ± 0.1	45 ± 2	11.63 ± 0.05	14424.2 ± 0.1	30 ± 1	9.59 ± 0.02
	Worn, 1	14396.0 ± 0.1	43 ± 2	11.51 ± 0.09	14424.0 ± 0.1	29 ± 1	9.54 ± 0.03
	Worn, 2	14396.2 ± 0.1	46 ± 1	11.59 ± 0.07	14424.3 ± 0.1	31 ± 1	9.52 ± 0.01
	Worn, 3	14396.1 ± 0.1	46 ± 3	11.62 ± 0.06	14424.0 ± 0.1	31 ± 2	9.56 ± 0.02
Experimental alumina	Control	14396.0 ± 0.1	18 ± 1	11.52 ± 0.02	14424.0 ± 0.1	12 ± 1	9.31 ± 0.01
	Worn, 4	14396.2 ± 0.2	19 ± 1	11.55 ± 0.05	14424.2 ± 0.1	13 ± 1	9.34 ± 0.02
	Worn, 5	14396.2 ± 0.1	18 ± 1	11.47 ± 0.02	14424.2 ± 0.1	12 ± 1	9.25 ± 0.02
	Worn, 6	14396.1 ± 0.1	17 ± 1	11.49 ± 0.02	14424.1 ± 0.1	12 ± 1	9.28 ± 0.02
Experimental NZTA	Control	14395.8 ± 0.1	25 ± 1	11.39 ± 0.01	14423.7 ± 0.1	16 ± 1	9.35 ± 0.01
	Worn, 7	14395.8 ± 0.1	27 ± 3	11.42 ± 0.04	14423.8 ± 0.1	17 ± 2	9.35 ± 0.04
	Worn, 8	14396.0 ± 0.1	23 ± 1	11.36 ± 0.02	14423.9 ± 0.1	14 ± 1	9.30 ± 0.03
	Worn, 9	14395.7 ± 0.2	25 ± 2	11.36 ± 0.05	14423.7 ± 0.2	16 ± 1	9.27 ± 0.08

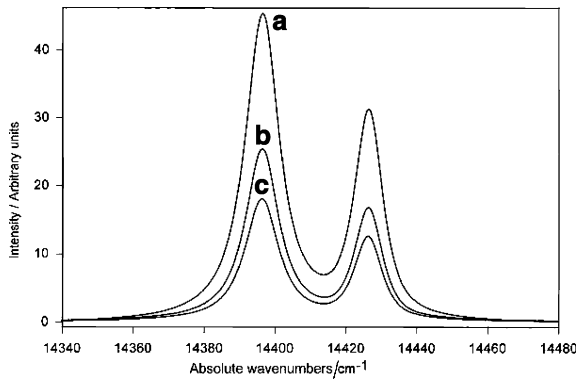
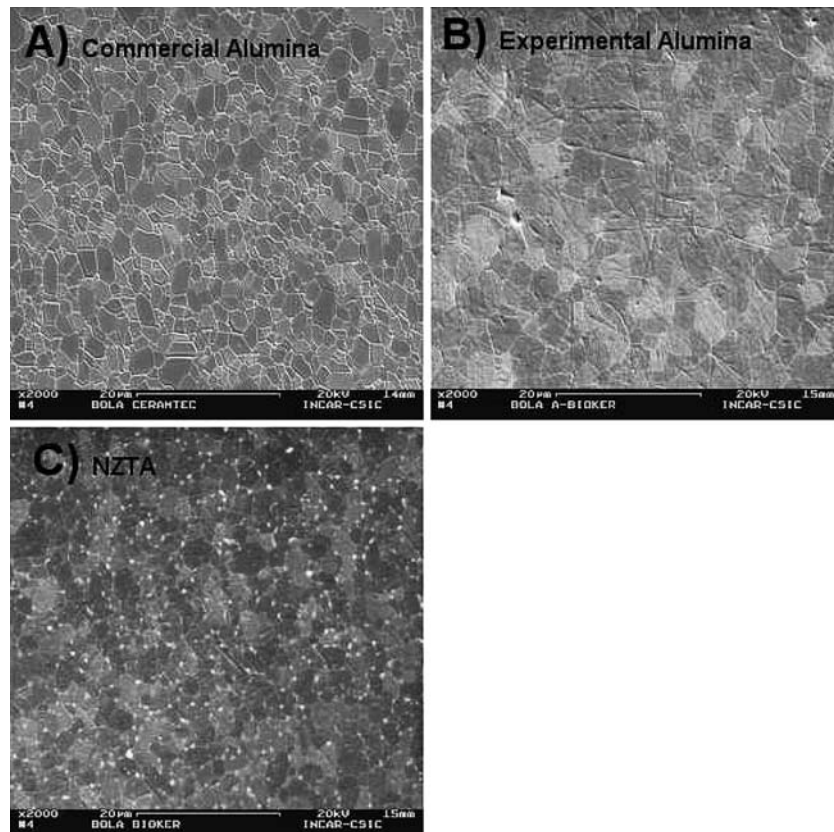


Fig. 3 Fluorescence spectra recorded on unworn acetabular cups: commercial alumina (a), experimental NZTA (b) and experimental alumina (c)

It is well known that the lowering of the ZrO_2 content down to 2.5 wt% leads to a particularly low monoclinic zirconia volume fraction [48] and a slow crack growth resistance, never reached before [49]. Therefore, the new colloidal processing route avoids the use of any stabilising oxide of the tetragonal zirconia phase and allows obtainment of ceramic materials resistant versus ageing degradation [48]. On the other hand, the small grain size of zirconia nano-particles reduces their ability to transform under applied stress: actually, these particles are well below the critical size for phase transformation [50].

Fig. 4 SEM micrographs of unworn commercial alumina (A), experimental alumina (B) and NZTA acetabular cups



Therefore, the transformation toughening mechanism does not seem to work for these NZTA composites.

In the light of their attractive properties, the NZTA–NZTA couplings were tested in a hip joint wear simulator in comparison with commercial and experimental alumina components.

From a statistical point of view, the three sets of specimens did not show significant differences in wear behaviour. However, it can be observed that, from a gravimetric point of view, the commercial alumina acetabular cups showed a better behaviour than the NZTA ones; the experimental alumina couplings displayed the highest weight loss.

This result did not appear surprising in the light of the fluorescence measurements: the intensity of the R_1 and R_2 bands followed a complementary trend, i.e. reached the highest and lowest values for commercial and experimental alumina samples, respectively. These differences can be interpreted according to other authors [46, 47, 51]. To evaluate the density of sintered alumina components, Schilling et al. [51] have developed a method based on luminescence intensity measurements as an alternative tool to Archimedes immersion method. A high fluorescence intensity is indicative of a material with low porosity; in fact, pores act as scattering centres of the incident laser beam and are responsible for a lower fluorescence

intensity. On the other hand, in a material with low porosity the volumetric concentration of the Cr^{3+} ions is higher and thus the fluorescence intensity as well. On this basis, it can be affirmed that the surface quality of the acetabular cups improves going from experimental alumina to experimental NZTA and even more to commercial alumina. Accordingly, SEM analysis showed a better surface finishing for the former specimens.

These findings suggest that the better the sample finishing, the better was the wear behaviour. At this purpose, it should be remembered that the analysed NZTA specimens were only prototypes and therefore their surface finishing (and thus wear behaviour) can be worse than for a production type, as previously observed for ceramic couplings [52]. This observation is of importance, since it means that full density should be reached in order to limit to the minimum wear in ceramic materials. This is particularly true for the cups, where it is always difficult to obtain excellent forming conditions and surface finishing (concave surface).

In this light, it can be affirmed that NZTA materials can offer the option of improving the lifetime and reliability of ceramic joint prostheses. In any case, it can be observed that their wear behaviour is better than that reported in the literature for ceramic-on-polyethylene [5–7], metal-on-polyethylene [5, 7–12] and metal-on-metal couplings [9, 13, 14].

Acknowledgements Authors would like to thank Barbara Bordini, Manuela De Clerico, and Roberta Fognani for statistical analysis and support during the experiments. The authors would like to acknowledge MIUR for 60% grants and the European Union for the financial support under the GROWTH2000, project Bioker, reference GRD-2000-25039.

References

- Boehler M, Knahr K, Plenk H, Walter A, Salzer M, Schreiber V (1994) *J Bone Joint Surg Br* 76:53
- Garcia-Cimbrello E, Martinez-Sayanes JM, Minuesa A, Munuera L (1996) *J Arthroplasty* 11:773
- Riska E (1993) *Clin Orthop Relat Res* 297:87
- Toni A, Terzi S, Sudanese A, Tabarroni M, Zappoli FA, Stea S, Giunti A (1995) *Chir Organi Mov* 80:13
- Affatato S, Frigo M, Toni A (2000) *J Biomed Mater Res (Appl Biomater)* 53:221
- Affatato S, Testoni M, Cacciari GL, Toni A (1999) *Biomaterials* 20:971
- Saikko V, Ahlroos T, Caloni O, Keränen J (2001) *Biomaterials* 22:1507
- Affatato S, Terzi S, Nardi D, Toni A (1997) *Chir Organi mov* 82:393
- John St KR, Zardiackas LD, Poggio RA (2004) *J Biomed Mater Res (Appl Biomater)* 68:1
- Affatato S, Bersaglia G, Rocchi M, Taddei P, Fagnano C, Toni A (2005) *Biomaterials* 26:3259
- Ingram JE, Stone M, Fisher J, Ingham E (2004) *Biomaterials* 25:3511
- Saikko V, Caloni O, Keränen J (2001) *J Biomed Mater Res* 57:506
- Scholes SC, Green SM, Unsworth A (2001) *Proc Inst Mech Eng [H]* 215:523
- Streicher RM, Semlitsch M, Schon R, Weber H, Rieker C (1996) *Proc Inst Mech Eng [H]* 210:223
- Maccauro G, Piconi C, Burger W, Pilloni L, De Santis E, Muratori F, Learmonth ID (2004) *J Bone Joint Surg Br* 86:1192
- Wolfgang K (2004) In Proceedings of the annual meeting of the American Academy of Orthopaedic Surgeons, San Francisco, CA, March
- Piconi C, Burger W, Richter H, Cittadini A, Maccauro G, Covacci V, Bruzzese N, Ricci G, Marmo E (1998) *Biomaterials* 19:1489
- Kim DJ, Lee MH, Lee DY, Han JS (2000) *J Biomed Mater Res* 53:438
- Chevalier J, Deville S, Munch E, Jullian R, Liar F (2004) *Biomaterials* 25:5539
- Burger W, Richter HG, Piconi C, Vatteroni R, Cittadini A, Boccalari M (1997) *J Mater Sci Mater Med* 8:113
- Santos EM (2004) In Proceedings of the annual meeting of the American Academy of Orthopaedic Surgeons, San Francisco, CA, March
- Green DJ, Hannink RHJ, Swain MW (1989) In Transformation toughening of ceramics. CRC Press Inc., Boca Raton FL, p 232
- Claussen N (1976) *J Am Ceram Soc* 61:49
- Lange FF (1982) *J Mater Sci* 17:247
- Hori S, Yoshimura M, Somiya S (1986) *J Am Ceram Soc* 69:169
- Becher PF, Alexander KB, Bleier A, Waters SB, Warwick WH (1993) *J Am Ceram Soc* 76:657
- Casellas D, Ràfols I, Llanes L, Anglada M (1999) *Int J Ref Met Hard Mater* 17:11
- Fegley BJ, White P, Bowen HK (1985) *J Am Ceram Soc* 68:60
- Cortesi P, Bowen HK (1989) *Ceram Int* 137
- Jang HM, Moon JH (1990) In: Messing GI, Hirano SI, Hausner H (ed) *Ceramic Powder Science III*, American Ceramic Society, p 979
- Schehl M, Diaz LA, Torrecillas R (2002) *Acta Mater* 50:1125
- De Aza AH, Chevalier J, Fantozzi G, Schehl M, Torrecillas R (2002) *Biomaterials* 23:937
- Grabner L (1978) *J Appl Phys* 49:580
- Krishnan R, Kesavamoorthy R, Dash S, Tyagi AK, Raj B (2003) *Scripta Mater* 48:1099
- Garcia MA, Paje SE, Llopis J (2002) *Mater Sci Eng A325:302*
- Ma Q, Clarke DR (1994) *J Am Ceram Soc* 77:298
- Merlani E, Schmid C, Sergio V (2001) *J Am Ceram Soc* 84:2962
- Ma Q, Clarke DR (1993) *J Am Ceram Soc* 76:1433
- He J, Clarke DR (1995) *J Am Ceram Soc* 78:1347
- Sergo V, Pezzotti G, Sbaizero O, Nishida T (1998) *Acta Mater* 46:1701
- Selcuk A, Atkinson A (2002) *Mater Sci Eng A335:147*
- Jankowiak R, Roberts K, Tomasik P, Sikora M, Small GJ, Schilling CH (2000) *Mater Sci Eng A281:45*
- Abbasova R, Visintin S, Sergio V (2005) *J Mater Sci* 40:1593
- Taddei P, Affatato S, Fagnano C, Toni A (2006) *J Mater Sci* 41:399–407
- Mckellop H, Lu B, Benya P (1992) In Proceeding of the 38th ORS, Washington D.C, p 402
- Krishnan R, Kesavamoorthy R, Dash S, Tyagi AK, Raj B (2003) *Scripta Mater* 48:1099

47. Garcia MA, Paje SE, Llopis J (2002) *J Mater Sci Eng A* 325:302
48. Deville S, Chevalier J, Fantozzi G, Bartolomé JF, Requena J, Moya JS, Torrecillas R, Diaz LA (2003) *J European Ceram Soc* 23:2975
49. Chevalier J, Deville S, Fantozzi G, Bartolomé JF, Pecharroman C, Moya JS, Diaz LA, Torrecillas R (2005) *Nano Lett* 5(7): 1297–1301
50. Heuer AH, Claussen N, Kriven W, Rühle M (1982) *J Am Ceram Soc* 65:642
51. Schilling CH, Garcia V, Li CP, Jankowiak R (2002) *Am Ceramic Soc Bull* 81:25
52. Affatato S, Goldoni M, Testoni M, Toni A (2001) *Biomaterials* 22:717