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Mechanical properties of HAp–ZrO_2 composites

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Abstract

Hydroxyapatite is a well-known and valuable implant material with bioactive properties. Full utilisation of the unique properties of hydroxyapatite ceramics is, however, possible only after its proper reinforcement, i.e., by preparation of composites. In the present work zirconia reinforced hydroxyapatite composites were obtained by hot pressing method. The reinforcing phase in the form of ZrO_2 particles was selected due to the satisfactory biocompatibility of ZrO_2 and also because of its exceptional mechanical properties.

Our investigations were aimed at assessing the influence of varying ZrO_2 on the phase composition and mechanical properties of HAp–ZrO_2 composites. In order to produce dense sinters, we used three types of initial zirconia powders which differed in morphology and contents of the tetragonal and monoclinic phases. We studied the influence of these oxides on thermal stability of hydroxyapatite matrix as well as on the phase composition and mechanical properties of the composite materials produced.

Keywords: Hot pressing; Composites; Mechanical properties; Apatite; ZrO_2

1. Introduction

Investigations aimed at broadening the medical application potential of implant materials based on hydroxyapatite are carried out in scientific centres across the world. Hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$ shows very high biocompatibility. It is also one of a few bioactive materials capable of creating a direct and firm bond with the bone tissue.[1–3]

Full utilisation of HAp dense ceramics unique properties will be possible only if it is properly reinforced. This can be attained by the preparation of composite materials with a HAp matrix. Amongst a considerable number of reinforcing phases ZrO_2, both in the form of powders and fibres seems to be one of the most interesting. Zirconia-based materials exhibit exceptional toughness[4] due to the martensitic transformation of tetragonal ↔ monoclinic ZrO_2 (T ↔ M).[5] Medical applications of ZrO_2 implants confirmed their satisfactory biocompatibility.[6] In zirconia reinforced hydroxyapatite composites (HAp–ZrO_2) it is possible to combine extremely advantageous properties of both biomaterials, previously applied separately.

The goal of our studies was to determine the influence of the characteristics of the initial ZrO_2 powders on the phase composition and mechanical properties of the HAp–ZrO_2 composites. Three types of ZrO_2 powders obtained by various methods and differing in the phase composition as well as in the shape and size of grains were used for the preparation of the composite materials in the present work.

2. Materials

2.1. Synthesis and properties of HAp and ZrO_2 powders

The synthesis of the hydroxyapatite powder used to obtain monophase HAp sinters constituting the reference material was carried out by the wet method, with CaO and H_3PO_4 as the reagents.[7] The synthesis was carried out at a Ca/P molar ratio equal to 1.69, i.e., with a slight excess of Ca with respect to its stoichiometric amount in HAp. The obtained gelatinous

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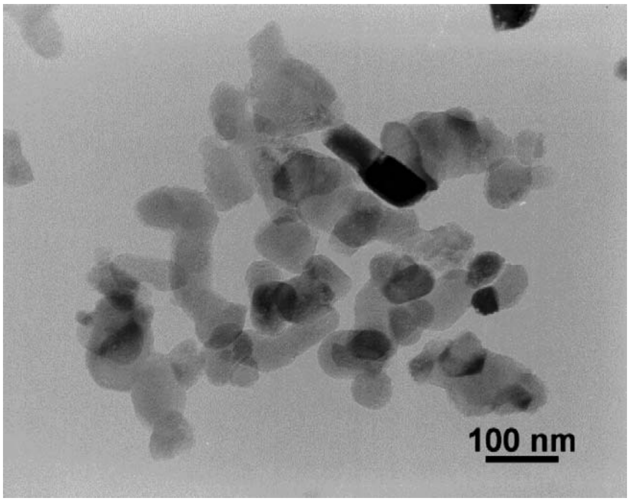

Fig. 1. TEM micrograph of HAp powder.

precipitate was aged, rinsed with distilled water, dried, heated at a temperature of 800 °C for 3 h, and subsequently ground. The calcined hydroxyapatite powder consisted of isometric agglomerated crystallites. Its specific surface area (BET) was equal to $25.7 \pm 0.2\,m^2/g$, while particle size $D_{BET} = 74$ nm. The morphology of the powder, determined by TEM is presented in Fig. 1. X-ray analysis confirmed that the material thus prepared was a pure hydroxyapatite phase (Fig. 2).

Powders of non-stabilised ZrO_2 were produced by the precipitation of hydrated zirconia from aqueous $ZrOCl_2 \cdot 8H_2O$ solution. Depending on the conditions of crystallisation, which strongly influence the size and shape of the crystallites,[8] three types of ZrO_2 powders differing in morphology and phase composition were obtained. Under conditions of hydrothermal crystallisation (temperature 240 °C, time 4 h), performed in an autoclave in distilled water, fine-grained ZrO_2 (FGZ) was prepared. The specific surface area (BET) of this powder was $111.33 \pm 0.5\,m^2/g$, while particle size $D_{BET} = 9$ nm. Its morphology is presented in Fig. 3. X-ray quantitative analysis of this powder showed that it contained 33 vol.% of crystallites with a monoclinic symmetry and 67 vol.% of those with a tetragonal one (Fig. 4).

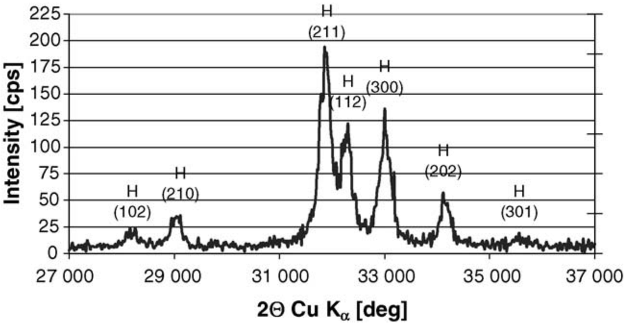

Fig. 2. X-ray diffraction pattern of pure HAp powder (after sintering at a temperature of 800 °C).

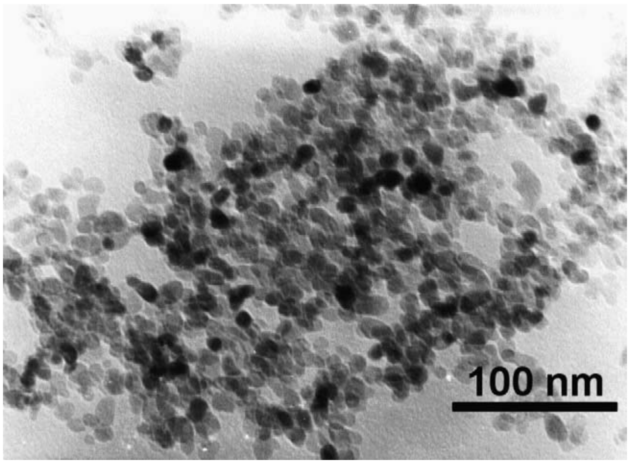

Fig. 3. TEM micrograph of fine-grained ZrO_2 powder.

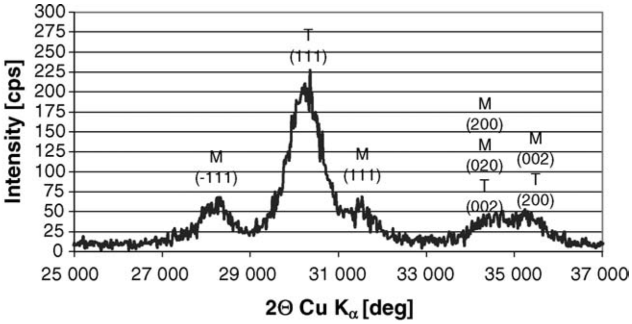

Fig. 4. X-ray diffraction pattern of fine-grained ZrO_2 powder.

The coarse-grained ZrO_2 (CGZ) powder was obtained by heat treatment (temperature 1050 °C, 1 h soaking time, heating rate 10 °C/min) of the precipitated deposit. The specific surface area of this powder (BET) was $1.19 \pm 0.4\,m^2/g$. Particle size D_{BET} was equal to 864 nm. The morphology of this powder is presented in Fig. 5. X-ray quantitative analysis of the CGZ powder showed that it contained exclusively crystallites with a monoclinic symmetry (Fig. 6).

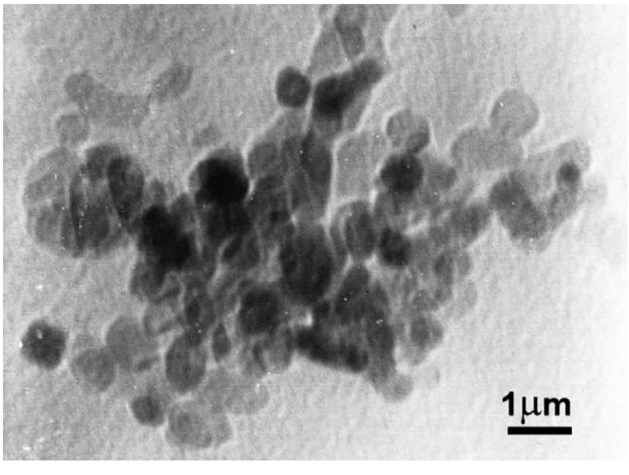

Fig. 5. TEM micrograph of coarse-grained ZrO_2 powder.

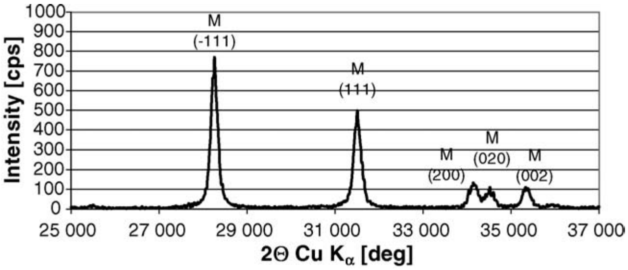

Fig. 6. X-ray diffraction pattern of coarse-grained ZrO_2 powder.

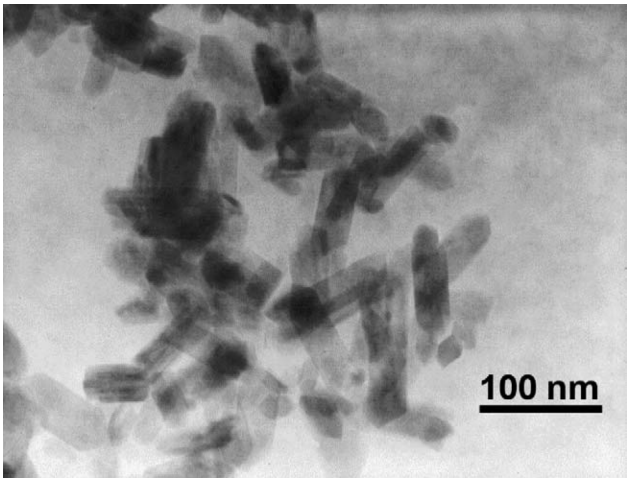

Fig. 7. TEM micrograph of ZrO_2 powder with needle-like particles.

The third type of powder was manufactured by autoclaving (temperature 240 °C, time 15 h) of the precipitate in the presence of a NaOH solution. It was composed of elongated "needle"-shaped grains. It will be denoted as a needle-grained zirconia, NGZ. Specific surface area (BET) of this powder was $43.0 \pm 0.5\,m^2/g$. In this case it is difficult to discuss the particle size, the calculated $D_{BET} = 24$ nm should be treated merely as one of the geometric parameters (width or length). As can be seen in the TEM micrograph the length of elongated, needle-shaped grains is approximately 100 nm. The morphology of this ZrO_2 is presented in Fig. 7. The initial NGZ powder consisted of crystallites with a monoclinic symmetry (Fig. 8).

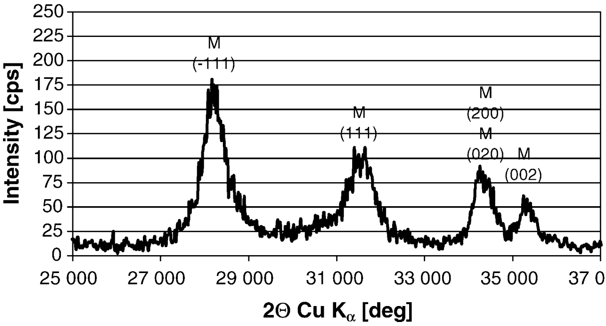

Fig. 8. X-ray diffraction pattern of ZrO_2 powder with needle-like crystallites.

The ZrO_2 powders thus obtained were used in the present work as the reinforcing phase in dense composites with a hydroxyapatite matrix produced by hot pressing method.

2.2. *Preparation of the initial HAp–ZrO_2 composite powders*

Content of ZrO_2 reinforcing phase in all composites was equal to 20 wt.%.

The HAp–ZrO_2 composite powders were obtained by the precipitation of hydroxyapatite in the presence of zirconia. ZrO_2 powder was added to the appropriate amount of an intensively stirred aqueous suspension of $Ca(OH)_2$ resulting from the reaction of CaO with H_2O. HAp was precipitated in the presence of ZrO_2 particles by addition of H_3PO_4 solution.[9,10] The precipitates thus obtained were several times rinsed with distilled water, dried at temperature 90 °C during 48 h, heat treated at a temperature of 800 °C with 3 h soaking time in air atmosphere and ground. Powders were milled in a "attritor"—type mill in ethyl alcohol, using grinding balls made of ZrO_2. After 3 h milling time the suspension together with the zirconia balls were dried at 90 °C and then sieved in order to separate the powder. The powders thus fabricated were used as the starting material for the production of dense HAp–ZrO_2 sinters.

2.3. *Preparation of dense sinters*

In the preliminary studies of the dense HAp–ZrO_2 and HAp sinters preparation two methods were tested: pressureless sintering of uniaxial pressed samples and hot pressing.

The samples were uniaxially pressed under the pressure of ca. 100 MPa and then pressureless sintered in air atmosphere at the temperatures: 1150, 1200, 1250, and 1300 °C with 2 h soaking time. The obtained materials exhibited high open porosity (ca. 50%) and their bending strength was low (10 MPa).

Dense monophase HAp ceramics and HAp–ZrO_2 composites were also prepared by hot pressing method within a temperature range of 1150–1300 °C using a Thermal Technology Inc. furnace which made it possible to carry out sintering in oxygen-free conditions. Pressing was performed in an argon atmosphere at a pressure of 25 MPa and over a period of 0.5 h (soaking time at the maximum temperature). All samples were sintered in a cylindrical graphite mould with the diameter $\phi = 25$ mm.

The hot pressing method was found to be much more useful for the preparation of dense HAp and HAp–ZrO_2 sinters. Therefore, this method was applied in the manufacturing of the composite samples for further studies.

3. Methods

Elasticity, hardness, toughness and bending strength tests were carried out for the prepared HAp and HAp–ZrO_2 dense

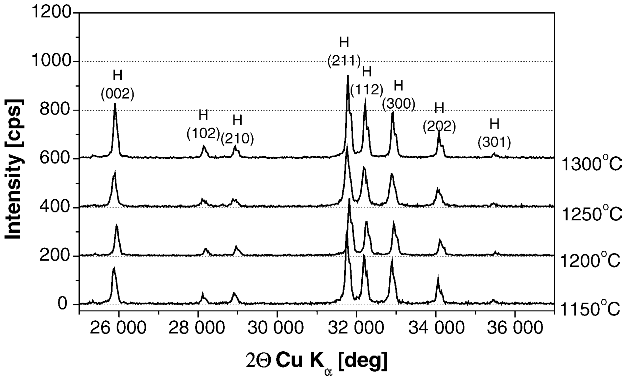

Fig. 9. X-ray diffraction patterns of HAp sinters obtained at various sintering temperatures.

samples. Measurements of modulus of elasticity were performed in non-destructive ultrasonic investigations using the UZP (INCO-VERITAS, Poland) apparatus. The material constants: Young's modulus E, modulus of rigidity G and Poisson ratio μ, were determined by the propagation velocity of the longitudinal ($f = 10$ MHz) and transverse ($f = 2$ MHz) waves within samples. Hardness and fracture toughness were measured using a FV-700 hardness and microhardness tester manufactured by Future-Tech of Japan. Bending strength was checked by the three-point bending method on a span of 14 mm at a crosshead speed of 2 mm/min in a Zwick 1435 tester. Measurements were carried out using 22 rectangular shape samples of each material with the size of 25 mm × 6 mm × 2 mm.

The results of bending strength tests were analysed statistically using Weibull's distribution.[11] This made if possible to identify the Weibull (m) modulus which determines the degree of reliability of materials.

X-ray diffraction analysis in the range of 2θ from 25.000 to 37.000° was used to determine the qualitative phase composition of the investigated powders and materials (XRD7 Rich. Seifert & Co. diffractometer).

4. Results and discussion

During heating of HAp–ZrO_2 materials desirable effects, such as the $T \leftrightarrow M$ transition of the monoclinic ZrO_2 into the tetragonal polymorphic form and its stabilisation by CaO originating from hydroxyapatite, as well as the formation of a solid solution of CaO in ZrO_2 appear. It has been reported, however, that the addition of ZrO_2 to the HAp matrix decreases the temperature of hydroxyapatite decomposition.[12] This leads to uncontrolled and not always desirable changes of physico-chemical and biological properties of the materials. In our studies in the analysed X-ray diffraction patterns (Figs. 9–12) no sign of hydroxyapatite decomposition, nor the appearance of new crystalline phases resulting from the reactions of the compounds co-existing in the systems were detected.

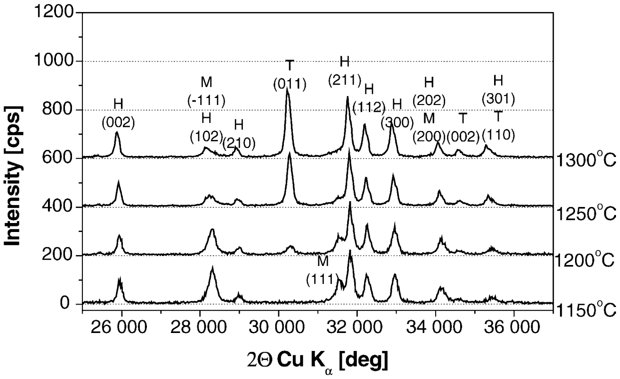

Fig. 10. X-ray diffraction patterns of HAp–CGZ composites obtained at various sintering temperatures (H, hydroxyapatite; T, tetragonal ZrO_2; M, monoclinic ZrO_2).

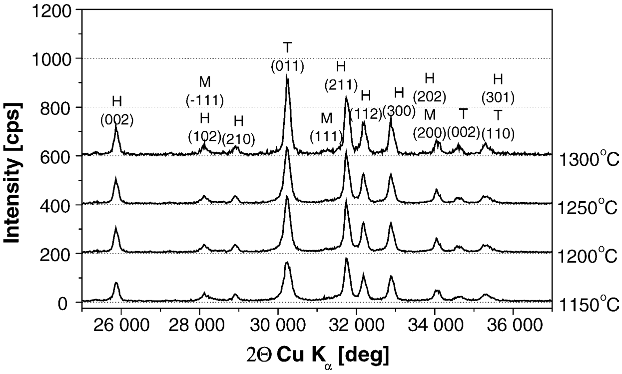

Fig. 11. X-ray diffraction patterns of HAp–FGZ composites obtained at various sintering temperatures (H, hydroxyapatite, T; tetragonal ZrO_2; M, monoclinic ZrO_2).

Volume and weight fractions of tetragonal and monoclinic ZrO_2 forms as well as the share of HAp in the prepared composites were determined by Rietveld's method. The results are given in Table 1.

Fig. 9 presents the results of the qualitative X-ray analysis of hydroxyapatite ceramics obtained at different temperatures of the hot pressing process. The diffraction patterns show only sharp, clear peaks at positions typical for hydrox-

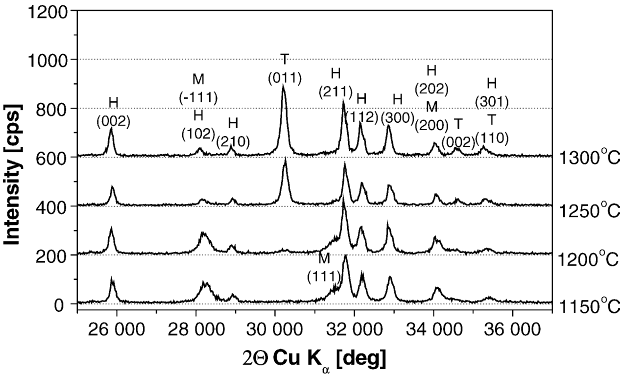

Fig. 12. X-ray diffraction patterns of HAp–NGZ composites obtained at various sintering temperatures (H, hydroxyapatite, T, tetragonal ZrO_2, M, monoclinic ZrO_2).

Table 1
Shares of tetragonal and monoclinic ZrO_2 forms as well as the proportions of HAp in the HAp–ZrO_2 composites as the function of sintering temperature

Type of material	Sintering temperature (°C)	HAp		Monoclinic ZrO_2		Tetragonal ZrO_2	
		wt.%	vol.%	wt.%	vol.%	wt.%	vol.%
HAp–CGZ composite	1150	82.09	86.66	17.43	12.63	0.48	0.70
	1200	82.01	84.37	13.82	9.73	4.17	5.89
	1250	79.15	76.29	6.17	4.10	14.68	19.61
	1300	78.54	75.12	5.07	3.32	16.39	21.56
HAp–FGZ composite	1150	80.37	75.47	1.67	1.08	17.96	23.44
	1200	79.90	74.60	1.23	0.80	18.87	24.66
	1250	81.10	76.22	1.37	0.89	17.53	22.89
	1300	80.62	75.66	1.16	0.75	18.22	23.59
HAp–NGZ composite	1150	82.01	86.52	17.32	12.51	0.67	0.98
	1200	81.44	85.11	16.32	11.67	2.25	3.22
	1250	78.94	74.48	3.06	1.99	18.00	23.53
	1300	77.42	72.36	2.71	1.76	19.87	25.88

yapatite, which proves phase purity and high crystallinity of the material obtained. At none of the sintering temperatures (from 1150 to 1300 °C) were reflections indicating the thermal decomposition of hydroxyapatite to α-TCP and TTCP observed.

Fig. 10 presents the X-ray diffraction patterns of the HAp–ZrO_2 composite material toughened with CGZ particles. At temperatures higher than 1200 °C the process of phase transition of the monoclinic ZrO_2 into the tetragonal form can be observed. This is manifested by the disappearance of the reflections originating from the monoclinic ZrO_2 at $2\Theta = 28.300$ and $31.500°$, and the appearance of peaks at $2\Theta = 30.300$ and $34.660°$, corresponding to the tetragonal ZrO_2. Such changes are presumably due to the formation of CaO–ZrO_2 solid solution. It can be postulated that hydroxyapatite is the possible source of calcium.[13] These results agree with those obtained by Heimann and Vu.[14] In contrast to their HAp–ZrO_2 composites, however, our materials did not contain the $CaZrO_3$ phase.

The X-ray diffraction pattern of the composite material reinforced with FGZ presented in Fig. 11 does not show a clear range in which transition from the monoclinic to the tetragonal phase occurs. This is typical for the temperature range studied and different from the previously discussed CGZ reinforced composites. The tetragonal ZrO_2 predominates, while peaks originating from the monoclinic ZrO_2 exhibit low intensity. This implies significantly lower content of this phase in the material. From the point of view of fracture mechanics, this is an advantageous effect since it is well known that an increase in fracture toughness (K_{IC}) is possible only for materials containing the tetragonal ZrO_2.[15] As it was confirmed by mechanical tests the composites reinforced with FGZ exhibit the $K_{IC} \sim 1.4\,\mathrm{MPa\,m^{1/2}}$ after sintering in all applied temperatures (K_{IC} of HAp matrix was $\sim 1.0\,\mathrm{MPa\,m^{1/2}}$). Only the initial FGZ powder present in these composites contained crystallites with a tetragonal symmetry. The results of X-ray quantitative analysis confirmed that independently of the sintering temperature these HAp–ZrO_2 materials contained similar amounts of the monoclinic and tetragonal ZrO_2 (Table 1). Therefore, in the case of these materials formation of CaO solid solution in ZrO_2 and stabilisation of its tetragonal phase are the only processes which may be expected in the temperature range studied.

Fig. 12 presents X-ray diffraction patterns for the HAp–NGZ composite materials. The spectra resemble patterns obtained for the HAp–CGZ composites, i.e., as the sintering temperature increases from 1150 to 1300 °C, the amount of the ZrO_2 monoclinic phase significantly decreases, while that of the tetragonal phase increases (Table 1). This is due to the fact that both CGZ and NGZ zirconia powders applied as the reinforcing phases for composites with a HAp matrix, contained exclusively monoclinic ZrO_2 crystallites. Both powders differed only in the method of preparation, and consequently in morphology.

Based on the X-ray quantitative analysis and determination of the grain size distribution it can be concluded that only the phase composition of the initial ZrO_2 powder influences the type and content of the polymorphic modification of ZrO_2 occurring in HAp–ZrO_2 composites at any given temperature. The results unequivocally show the occurrence of the T ↔ M transition of the monoclinic ZrO_2 into its tetragonal form in composites containing CGZ and NGZ in the temperature range studied. In the case of composites reinforced with the FGZ this transition did not take place since the initial ZrO_2 powder introduced into the HAp matrix already contained the tetragonal phase. Hence, for this material only the stabilising effect of CaO on the structure of the tetragonal phase may be expected, which in practice means the formation of a solid solution of CaO in ZrO_2. The high thermal stability of hydroxyapatite matrix and lack of $CaZrO_3$ in our composites is probably due to the characteristics of the initial ZrO_2 powders as well as a selection of appropriate conditions of hot pressing process, different from those applied in other studies.

The relative density of the investigated materials ranged from 97.1 to 99.9%.

Mechanical properties of ceramic materials are governed by the laws of probability. As a result of the random loca-

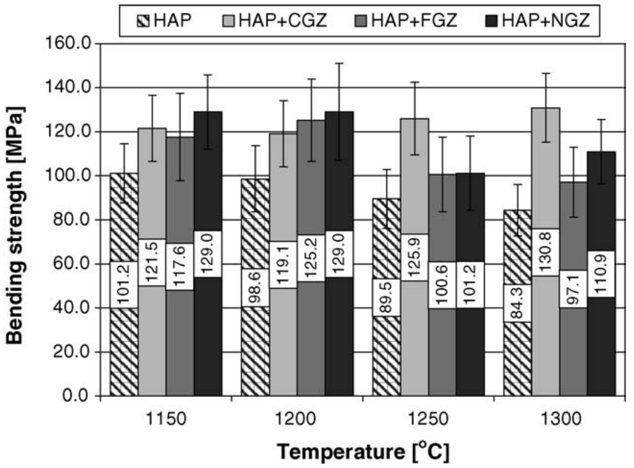

Fig. 13. Bending strength of HAp and HAp–ZrO_2 sinters as a function of the sintering temperature.

tion of defects in these materials, the samples show some distribution in mechanical strength. In consequence, from a mathematical point of view mechanical strength should be assumed as a random variable.[16]

Similarly to other ceramic materials, the materials studied in the present work showed a significant distribution of bending strength values (Fig. 13). This is directly connected with the limited reliability of ceramic materials due to – as was previously mentioned – non-uniform location of defects in the material. Thus, proper analysis of determined strength values as well as their distribution requires a probabilistic approach and the determination of Weibull modulus for the investigated sinters. Table 2 presents the average values of bending strength together with standard deviation, the values of characteristic strength σ_0 and the Weibull modulus for the materials studied hot pressed in the temperature range of 1150– 1300 °C. Based on the results obtained, it can be concluded that the incorporation of 20 wt.% of FGZ, CGZ and NGZ into HAp considerably improves the bending strength of the dense monophase HAp ceramics. The increase was approximately 30%. It should be stressed that an increase in the strength by the addition of a reinforcing phase does not necessarily improve the reliability of the material. The determined values of the Weibull modulus, which precisely describe the level of this reliability, indicate its small increase (with respect to pure HAp material) for composites strengthened with CGZ and for some materials reinforced with NGZ. This may imply higher efficiency of ZrO_2 with a greater grain size in increasing the strength of composites. However, the reliability of composites reinforced with FGZ was not improved after hot pressing at temperatures of 1250 and 1300 °C. On the contrary, it decreased by approximately 15% in comparison to pure hydroxyapatite sinters. A similar drop in reliability was observed for materials reinforced with NGZ sintered at temperatures of 1200 and 1250 °C. It is not surprising that the lowest Weibull modulus values were obtained for composites reinforced with FGZ, for which the best efficiency in increasing the fracture toughness was also observed. It is probably caused by the presence in the material of inclusions of the reinforcing phase which increased its crack resistance. On the other hand, however, they served as the source of residual stresses and constituted the areas of their highest concentration which reduced the strength.

Hardness and fracture toughness were measured in order to determine the influence of the ZrO_2 reinforcing phase on the mechanical characteristics of composite materials with respect to pure hydroxyapatite. Hardness, and particularly K_{IC}, belong to the most important parameters used in the characterization of ceramic materials, for which toughness is of primary importance. For dense hydroxyapatite ceramics the Vickers hardness fell within the range of 5.7–6.6 GPa, while for HAp–ZrO_2 composites – within the range of 6.1–7.6 GPa (Table 2).

Table 2
Mechanical properties of monophase HAp ceramics and HAp–ZrO_2 composites

Type of material	Sintering temperature (°C)	Vickers hardness (GPa)	Bending strength, σ (MPa)	Weibull modulus, m	Characteristic value, σ_0 (MPa)	Correlation coefficient, r
HAp	1150	5.8	101.2 ± 13.4	8.8	108	0.99
	1200	6.4	98.6 ± 15.1	7.9	106	0.94
	1250	6.6	89.5 ± 13.4	8.2	93	0.94
	1300	5.7	84.3 ± 11.6	8.3	89	0.98
HAp–CGZ composite	1150	6.8	121.6 ± 15.0	9.9	126	0.94
	1200	6.4	119.1 ± 15.0	9.1	128	0.98
	1250	6.7	125.9 ± 16.5	9.3	130	0.94
	1300	6.5	130.8 ± 15.6	9.9	134	0.91
HAp–FGZ composite	1150	7.4	120.4 ± 19.8	7.3	122	0.95
	1200	7.6	125.2 ± 18.7	7.8	133	0.97
	1250	6.5	100.6 ± 17.0	6.7	108	0.98
	1300	6.1	97.1 ± 15.9	7.2	103	0.97
HAp–NGZ composite	1150	7.1	129.0 ± 16.9	9.1	134	0.96
	1200	7.3	123.9 ± 22.0	7.0	131	0.92
	1250	7.1	101.2 ± 16.8	7.0	104	0.97
	1300	6.9	110.9 ± 14.6	9.2	113	0.90

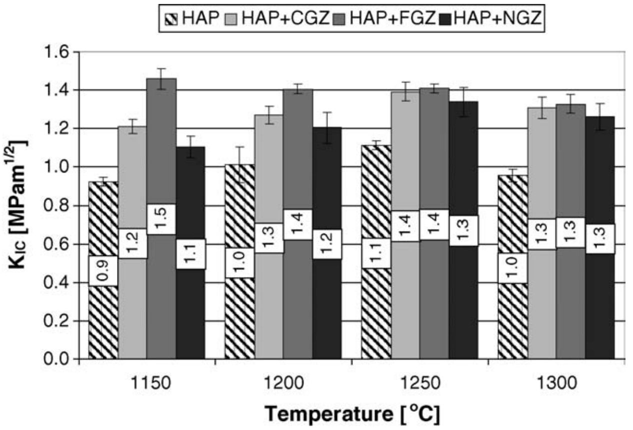

Fig. 14. K_{IC} values for HAp and HAp–ZrO_2 sinters as a function of the sintering temperature.

Based on the results obtained it is possible to distinguish a group of materials whose hardness depends on sintering temperature only to a small degree. This group includes composites reinforced with CGZ and NGZ. In the case of pure HAp and composites reinforced with FGZ, a more significant effect of sintering temperature on this parameter can be observed.

Results of the K_{IC} measurements are presented in Fig. 14. For dense HAp ceramics, the K_{IC} values fell within the range of 0.9–1.1 MPa m$^{1/2}$ and for HAp–ZrO_2 composites – of 1.1–1.5 MPa m$^{1/2}$. Hence, an increase in K_{IC} value for HAp–ZrO_2 composite materials with respect to the monophase HAp ceramics was noted. It ranged from 27 to 58% depending on the sintering temperature.

The fracture toughness behaviour of these sinters depends on the characteristic of initial zirconia powders as well as on the sintering temperature (Fig. 14). For monophase HAp sinters and composites reinforced with CGZ and NGZ the highest values were attained at a temperature of 1250 °C. In the case of the composites containing FGZ, the highest K_{IC} value (1.5 MPa m$^{1/2}$) was observed for materials prepared at 1150 °C. It is also worth noting that the composites with FGZ exhibited the highest K_{IC} values in the entire range of sintering temperatures. This is connected with the fact that of three initial ZrO_2 powders used for the preparation of composites, only the fine-grained one contained not exclusively monoclinic, but also tetragonal crystallites of zirconia. This created the conditions under which the toughening mechanism by the T ↔ M transition during sintering in the whole temperature range used was possible.[15] Therefore, the toughening of the composites containing the FGZ was nearly independent of the sintering temperature. In the case of composites reinforced with CGZ and NGZ, the tetragonal ZrO_2 phase became dominant only when a temperature of 1250 °C was reached. Thus, these materials attained conditions leading to the additional stabilisation of a considerable amount of ZrO_2 grains by calcium originating from HAp only at a temperature of 1200 °C. Hence, the highest toughening efficiency for these materials was obtained at this temperature.

Table 3 presents the calculated values of elasticity for the investigated materials. The non-destructive measurements of the speed of propagation of ultrasonic waves in directions perpendicular and parallel to the axes of the cylindrical samples were carried out. The results of these measurements were also used to estimate the anisotropy of the materials.

All of the samples studied exhibited a negligible difference in the rate of propagation of waves in the directions perpendicular and parallel to their axes, with divergences ranging from 0.44 to 2.50%. Thus, it can be concluded that the density of the sinters in both directions was similar. Since a material is considered anisotropic if the density differences amount to 10% the composites obtained in the present work should be treated as homogenous.

Table 3
Elasticity of HAp and HAp–ZrO_2 sinters

Type of material	Sintering temperature (°C)	Anisotropy (%)	Young's modulus, E (GPa)	Rigidity modulus, G (GPa)	Poisson ratio, μ
HAp	1150	1.52	119.5 ± 2.6	46.5 ± 0.6	0.285 ± 0.006
	1200	2.50	119.3 ± 3.1	46.2 ± 0.4	0.291 ± 0.006
	1250	1.97	119.3 ± 2.0	46.4 ± 0.2	0.287 ± 0.004
	1300	1.63	118.8 ± 1.6	46.2 ± 0.4	0.285 ± 0.004
HAp–CGZ composite	1150	0.79	128.1 ± 1.2	50.0 ± 0.4	0.282 ± 0.003
	1200	0.44	127.7 ± 2.3	49.9 ± 1.0	0.281 ± 0.007
	1250	0.71	125.6 ± 2.0	49.0 ± 0.6	0.282 ± 0.005
	1300	0.55	125.7 ± 1.7	49.0 ± 0.6	0.283 ± 0.004
HAp–FGZ composite	1150	1.50	128.1 ± 2.2	50.0 ± 0.7	0.281 ± 0.005
	1200	1.19	126.9 ± 3.7	49.4 ± 0.7	0.283 ± 0.008
	1250	1.46	126.7 ± 1.5	49.5 ± 0.4	0.279 ± 0.004
	1300	0.98	126.0 ± 4.1	49.2 ± 0.8	0.280 ± 0.009
HAp–NGZ composite	1150	1.16	127.6 ± 4.7	49.7 ± 1.2	0.284 ± 0.011
	1200	0.98	128.1 ± 1.3	50.0 ± 0.5	0.280 ± 0.003
	1250	1.09	126.6 ± 3.1	49.3 ± 0.6	0.283 ± 0.006
	1300	1.59	127.3 ± 2.0	49.5 ± 0.6	0.286 ± 0.005

As expected, the introduction of ZrO_2 to the HAp matrix led to an increase in Young's modulus for composite materials by approximately 7% with respect to pure HAp ceramics.

5. Conclusions

Zirconia, irrespective of its morphology and phase composition, did not induce the decomposition of hydroxyapatite matrix in HAp–ZrO_2 composites produced by hot pressing method. This is of significant importance for implantology since potential products of decomposition can significantly influence the behaviour of a material in a living organism, i.e., they can determine its biocompatibility and bioactivity to a considerable degree.

The use of three ZrO_2 powders differing in morphology and phase composition led to an increase in the bending strength and toughness of HAp–ZrO_2 composites with respect to monophase HAp ceramics. The method of preparation resulting in different phase compositions of initial ZrO_2 powders influenced the mechanical properties of HAp–ZrO_2 sinters hot–pressed in the range of 1150–1300 °C.

Improvements in toughness and strength achieved for HAp–ZrO_2 composites were not accompanied by an increase in the Weibull modulus, and thus by better materials reliability. This phenomenon may be explained by the fact that higher K_{IC} values lead to an increase in the Weibull modulus only below a certain critical length of cracks.[17] Above this critical length, any further increase in K_{IC} is accompanied by the decrease of the Weibull modulus, and thus by lowering of the material reliability.

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