PREPARATION AND CHARACTERISTICS OF NANOSIZED ZIRCONIA-MULLITE POWDERS

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Abstract

Nanosized spherical Al_2O_3-SiO_2-ZrO_2 particulate composites with average particle size in the range of 45-62 nm were prepared by evaporation of commercial oxides in inductively coupled plasma. The as-prepared powders contain m-, t-ZrO_2 phases and a small amount of crystalline mullite. The crystallisation of mullite occurs at 945-995^oC depending on the ratio Al_2O_3/SiO_2 and content of ZrO_2. The presence of mullite hinders growth of zirconia crystallites and it prevents, characteristic for the nanosized zirconia tetragonal phase, transition to monoclinic at high temperatures.

Keywords: nanosized mullite, zirconia, plasma technique, phase composition, crystallite size

INTRODUCTION

Mullite is promising material for engineering applications because it exhibits high stability, low thermal expansion and high resistance at elevated temperatures [1,2]. However, commonly the densification of mullite ceramics proceeds above the eutectic point (1587^{o}C) of the alumina-silica binary system resulting in the presence of a residual glassy phase after sintering which impairs mechanical parameters of ceramics [1,3]. This problem can be solved by sintering active nanosized powders below 1587^{o}C. Besides this, the strength and the fracture toughness of mullite can be enhanced by the addition of zirconia [4] but the characteristics of the produced ceramic strongly depend on distribution of components, particle size and phase composition of raw powders used.

The aim of the present work is to develop a thermal plasma method for producing highly homogeneous particulate nanocomposites in the Al_3O_3-SiO_2-ZrO_2 system and to determine their characteristics.

EXPERIMENTAL

The thermal plasma technique is based on evaporation of coarse-grained commercially available powders in inductively coupled air plasma using technological equipment described in [5]. The Al_2O_3 (H.C.Stark, 99.8), ZrO_2 (Auer-Remy, 99.8) and SiO_2 (Reahim, 99.7) were used as raw powders. The oxide powders with a particle size in the range of 10-30 μm are mixed and injected into the plasma flame by carrier gas. Evaporation of raw oxides is achieved by varying the power of the RF oscillator, the flow rate of the plasma forming gas, feeding rate of powder, and their injection velocity. The formation of particles from vapours and their growth are controlled by introducing cold air into the reaction chamber.

Chemical and phase composition of the prepared oxides are determined by chemical spectrophotometric and X-ray diffraction analysis. The specific surface area is

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determined by the argon adsorption-desorption method and the average particle size is calculated from these data. The crystallite size of zirconia phases and mullite is determined by the X-ray line broadening method using the Scherrer equation. The particle size and shape are studied by transmission electronic microscopy.

RESULTS AND DISCUSSION

The characteristics of as-prepared powders in the Al_2O_3-SiO_2-ZrO_2 system and influence of calcination temperature on phase composition are shown in Tab.1.

Tab.1. Characteristics of the as-prepared and calcinated nanoparticles in Al_2O_3-SiO_2-ZrO_2 system; SSA – specific surface are, d – calculated average particle size.

No.	As-prepared						Phase composition after calcinations	
	Al_2O_3 [wt.%]	SiO_2 [wt.%]	ZrO_2 [wt.%]	SSA [m^2/g]	$\bar{d}$ [nm]	phase composition	1000°C	1300°C
1	99.8	-	-	34.2	44	δ-, θ-Al_2O_3	δ-, θ-Al_2O_3	α-Al_2O_3
2	89.7	10.1	-	39.1	41	δ-Al_2O_3	δ-, θ-Al_2O_3 $3Al_2O_3.2SiO_2$	δ-, θ-Al_2O_3 $Al_2O_3.2SiO_2$
3	71.9	28.0	-	32.7	53	$3Al_2O_3.2SiO_2$(tr.)	$3Al_2O_3.2SiO_2$	$3Al_2O_3.2SiO_2$
4	49.7	50.1	-	31.5	62	$3Al_2O_3.2SiO_2$(tr.)	$3Al_2O_3.2SiO_2$	$3Al_2O_3.2SiO_2$ - SiO_2
5	-	99.7	-	32.8	83	amorphous	amorphous	α- SiO_2
6	68.3	26.6	5.0	34.1	54	m-, t- ZrO_2 $Al_2O_3.2SiO_2$(tr.)	m-, t- ZrO_2 $Al_2O_3.2SiO_2$	m-, t-ZrO_2 $Al_2O_3.2SiO_2$
7	57.6	28.3	20.0	34.1	48	m-, t-ZrO_2	m-, t- ZrO_2 $Al_2O_3.2SiO_2$	m-, t-ZrO2 $Al_2O_3.2SiO_2$
8	50	19.16	30.0	33.5	45	m-, t-ZrO_2	m-, t-ZrO_2 $Al_2O_3.2SiO_2$	m-, t-ZrO_2 $Al_2O_3.2SiO_2$
9	-	-	99.6	32.0	33	m-, t-ZrO_2	m-, t-ZrO_2	m-ZrO_2

The specific surface areas of the prepared powders are quite identical but calculated average particle size increases from 33 nm of pure ZrO_2 to 45-54 nm of mullite-zirconia and to 83 nm of pure silica particles. Obviously, different boiling and melting temperatures of compounds influence the growth conditions of particles. In general the average size of particles can be influenced by altering the parameters of plasma synthesis – by varying the feeding rate of raw powder and cooling rate of growing particles [6].

As-prepared SiO_2 nanoparticles are X-ray amorphous. X-ray diffraction patterns of Al_2O_3 and Al_2O_3-SiO_2 powders showing weak δ-, θ-Al_2O_3 maxima and traces of mullite accordingly indicate low crystallinity of the prepared nanoparticles. Introduction of zirconia in Al_2O_3-SiO_2 powders promotes formation of X-ray amorphous Al_2O_3-SiO_2 and m-, t-ZrO_2 phases. The X-ray diffraction patterns of Al_2O_3-SiO_2-ZrO_2 show traces of crystalline mullite only at content of ZrO_2 5 wt.%.

Additional calcination of the prepared powders yields crystalline particles whose phase composition depends on the ratio of components and on temperature. The results indicate that the presence of mullite in the Al_2O_3-SiO_2 system hinders formation of α-Al_2O_3 in the case of Al_2O_3 excess at 1300°C high temperature. Similary the presence of alumina, silica or mullite limits phase transition of tetragonal zirconia to monoclinic in Al_2O_3-SiO_2-ZrO_2 system during calcinations, that is characteristic for pure ZrO_2. Detailed studies show

that crystallization of mullite occurs at a temperature range of 945-995°C depending on the ratio of Al_2O_3/SiO_2 and the content of ZrO_2. The low crystallization temperature of mullite could be explained by its small particle size, uniform distribution of components obtained from vapour phase as well as by the presence of crystalline mullite seeds in the as-prepared Al_2O_3-SiO_2 and Al_2O_3-SiO_2-ZrO_2 powders with a low content of ZrO_2.

The prepared Al_2O_3-SiO_2, Al_2O_3-SiO_2-ZrO_2 particles have a spherical form (Fig.1) but their size differs strongly. Such wide particle size distribution is characteristic for powders produced by plasma technique and could be explained by different growth conditions of particles due to temperature gradients of plasma flow, and by collisions of liquid particles.

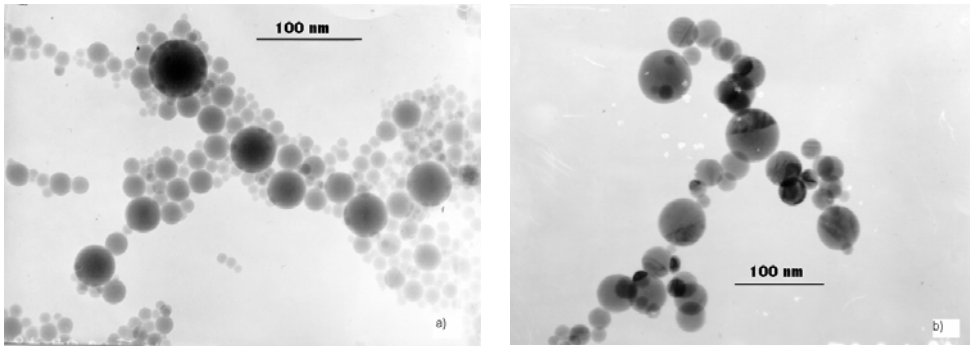

Fig.1. Micrographs of Al_2O_3-SiO_2 (a), and Al_2O_3-SiO_2-ZrO_2 (b) particles.

Additional calcination of Al_2O_3-SiO_2-ZrO_2 powders at temperatures in the range of 800-1400°C decreases their specific surface area and average particle size up to 100 nm. Simultaneously the calcination influences the phase composition of powders and their crystallite size (Fig.2,3).

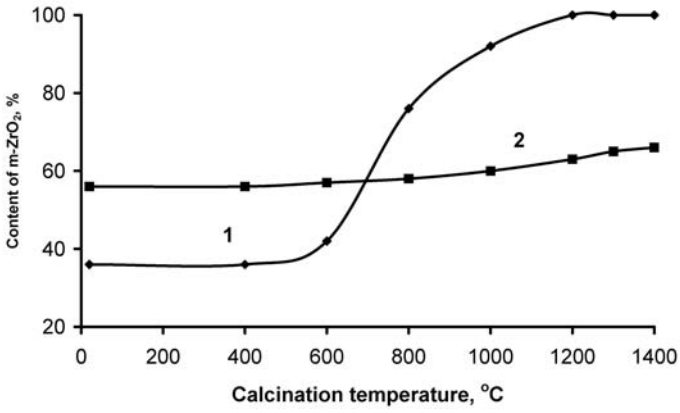

Fig.2. Dependence of the content of m-ZrO_2 phase on the calcination temperature of ZrO_2 (1) and Al_2O_3-SiO_2-30 wt.% ZrO_2 (2) samples.

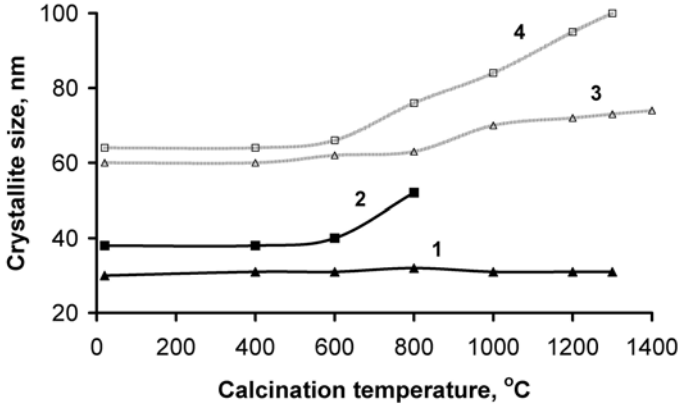

Fig.3. Dependence of the content of crystallite size of t-ZrO_2 (1,2) and m-ZrO_2 (3,4) phase on the calcination temperature of ZrO_2 (4, 2) and mullite-30 wt.% ZrO_2 (1,3) samples.

The data testify that combining synthesis of mullite and zirconia from the vapour phase increases the content of m-ZrO_2 and reduces the crystallite size of both zirconia phases in as-prepared powders with respect to pure nanosized ZrO_2. Calcination of Al_2O_3-SiO_2-ZrO_2 samples results in insignificant increase of m-ZrO_2 phase content and the crystallite size of t-ZrO_2 retains its initial size up to 1300°C.

At similar calcination conditions the growth of crystallite size of pure zirconia phases starts at 500-550°C and at 1000°C, the crystallite size of t-ZrO_2 and m-ZrO_2 reaches 54 nm and 86 nm, respectively. The growth of the crystallite size causes a phase transition of tetragonal modification of zirconia to monoclinic and content of the later one reaches 100% at 1200°C. Therefore the results testify that the presence of mullite stabilizes the crystallite size and phase content of zirconia at a high temperature.

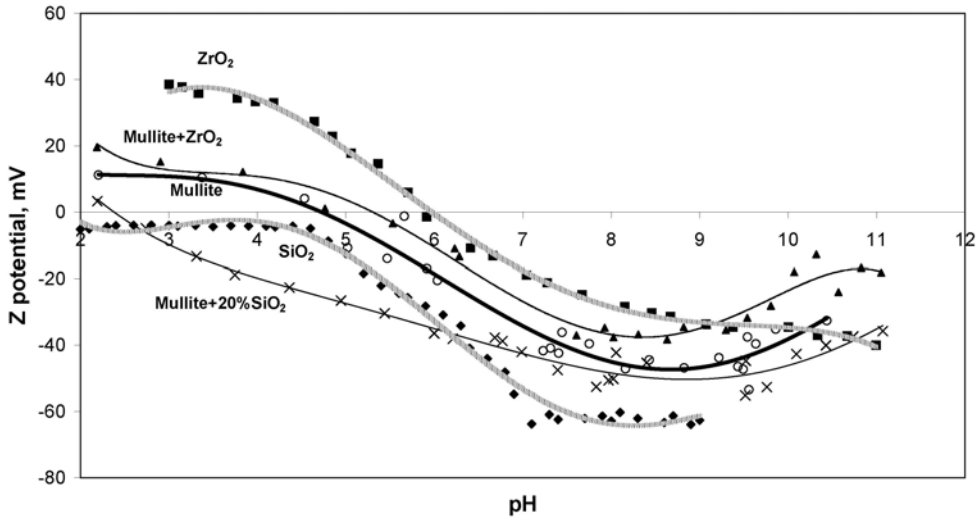

Fig.4. Z-potential curves of mullite, mullite-SiO_2 and mullite-ZrO_2.

This feature of Al_2O_3-SiO_2-ZrO_2 particulate nanocomposites can be explained on the basis of studies of particle surface characteristics by means of electrokinetic titration (Fig.4). The titration curves show that the surface of ZrO_2 in the presence of mullite is thoroughly transformed. The titration curves of Al_2O_3-SiO_2-ZrO_2 powders are shifted to the side of lower pH with respect to pure ZrO_2, and they are close to titration curve of mullite.

Similarity of the titration curves for Al_2O_3-SiO_2-ZrO_2 and mullite samples indicates that surface characteristics of Al_2O_3-SiO_2-ZrO_2 particles are similar to those of mullite. This indicates that the surface of zirconia is at least partially covered with mullite. Formation of such particles from the vapour phase is connected with different boiling and formation temperatures of various phases. The zirconia particles formed at higher temperature can act as nuclei for deposition of mullite. Complex microstructure of the prepared Al_2O_3-SiO_2-ZrO_2 particles limits contacts among ZrO_2 particles, and therefore hinders crystallite growth during calcination.

CONCLUSIONS

The developed thermal plasma technique provides the production of spherical nanosized Al_2O_3-SiO_2, Al_2O_3-SiO_2-ZrO_2 powders with average particle size in the range of 45-62 nm containing m-, t-ZrO_2, δ-, θ-Al_2O_3 phases and a small amount of crystalline mullite depending on the ratio of compounds.

High homogeneity, small particle size and the presence of a small amount of crystalline mullite phase in the as-prepared powders at least in the Al_2O_3-SiO_2-ZrO_2 system with low content of zirconia facilitate crystallisation of mullite at 945-990°C depending on the content of SiO_2 and ZrO_2.

The presence of mullite in the system prevents the growth of crystallites of zirconia and suppresses the phase transition t→m-ZrO_2.

Electrokinetic titration curves testify zirconia particles are covered at least partially by mullite phase due to the different condensation and formation temperatures of components from the vapour phase.

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