Synthesis of stabilized zirconia without dopants

(Sintese de zircônia estabilizada sem dopantes)

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Abstract

ZrO_2-SiO_2 powders were synthesized through Pechini's method starting with D_4Vi, PMS and zirconium citrate. The complex polymer was decomposed to form different phases at high temperatures. During the resin decomposition, the phase transformation from monoclinic to tetragonal zirconia was detected by thermal analysis. The crystallization and the diffusion process of Si and Zr were analyzed by X-ray diffraction, XRD, scanning electron microscopy and microanalysis by EDS. Tetragonal zirconia at 1000 ºC, monoclinic zirconia at 1200 ºC and monoclinic zirconia with cristobalite silica from 1300 º to 1400 ºC were formed. From 1000 ºC to 1300 ºC a diffuse amorphous band was related to the silica phase. The mapping of K_α line of Zr and Si showed low diffusion of Si into the ZrO_2 structure. The kinetics of crystallization formed macroparticles of silica and small particles of zirconia. A diffusion interface between SiO_2 and ZrO_2 to form $ZrSiO_4$ phase was not observed, confirmed by XRD.
Keywords: Pechini method, zirconia stabilization, EDS microanalysis.

Resumo

Foram sintetizados através do método Pechini pós de ZrO_2-SiO_2 iniciando com D_4Vi, PMS e citrato de zircônio. O polímero complexo foi decomposto para formar diferentes fases em altas temperaturas. Durante a decomposição da resina foi detectado a transformação de fase monoclínica tetragonal por análise térmica. A cristalização e o processo de difusão do Si e do Zr foi analisado por difração de raios X, microscopia eletrônica de varredura e microanálise por EDS. Foi formada zircônia tetragonal em 1000 °C, zircônia monoclínica em 1200 °C e zircônia monoclínica com sílica cristobalita de 1300 °C até 1400 °C. Entre 1000 e 1300 °C foi relacionada uma banda amorfa difusa de fase sílica. O mapeamento das linhas K_α do Zr e do Si demonstraram baixa difusão de Si na estrutura do ZrO_2. A cinética de cristalização formou macro-partículas de sílica e pequenas partículas de zircônia. Não foi observada a interface de difusão entre SiO_2 e ZrO_2 confirmada por difração de raios X.
Palavras-chave: método de Pechini, estabilização da zircônia, microanálise por EDS.

INTRODUCTION

Considerable research has been done on the synthesis of ceramic materials based on zirconia. Different synthesis methods such as co-precipitation, sol-gel process and organic precursor have been developed for zirconia stabilization. The stabilization effect occurs with additions of dopants like MgO, CaO, CeO_2, Y_2O_3 and oxides based on rare earths.

According to several authors the mixture of precursors of ZrO_2 and SiO_2 led to $ZrSiO_4$ (zircon) phase formation [1-3]. Although difficult, the preparation of the homogeneous zircon phase has already been the subject of several research papers [4-6]. Veytizou *et alii* [7] synthesized zircon starting from amorphous precursors powder by the sol-gel method. The powder was prepared with tetraethoxysilane (TEOS), $Si(OC_2H_5)_4$ and zirconyl nitrate hydrate, $ZrO(NO_3)_2.6H_2O$. Aguilar *et alii* [8] studied the crystallization of zircon with a synthesis with TEOS and zirconium propoxide. Below 1200 ºC tetragonal zirconia and amorphous silica and zircon were formed for several compositions. Shi *et alii* [9] synthesized ultrafine zircon powder with high purity

starting with a $ZrOCl_2$ solution and fumed silica. The zircon precursor gels were prepared by a wet chemical precipitation and the gel were seeded with zircon sand powder. High chemical homogeneity and particle size from 0.2 to 0.3 µm were obtained at high calcination temperature. The use of conventional technique for $ZrSiO_4$ synthesis does not led to homogeneous phase and favors an abnormal grain growth during the calcination or the sintering process.

Additions of silicon into the zirconia structure do not produce vacancies. According to some authors the isovalent substitution of zirconium by silicon caused dispersion of silicon into the zirconia particles and does not favor the stabilization effect of structure. Silicon diffusion caused an interface formation and growth the $ZrSiO_4$ (ZS) phase. However, in any case the tetragonal and/or cubic phase of zirconia takes place without the formation of the SZ phase.

Among several methods of synthesis, the polymeric precursor process led to obtain high powder surface area and chemical homogeneity at molecular level. The objective of the present work was an investigation of the phase formation during decomposition of the polymeric precursors based on

silica and zirconia and to verify the diffusion process of silicon into the zirconia structure. The synthesis method was the polymeric precursor that produced powders with high surface area and homogeneity of phases.

EXPERIMENTAL

Reagents based on Zr and Si were mixed by using the polymeric precursor process, Table I.

Table I - Purity and origin of reagents.
[Tabela I - Pureza e origem dos reagentes.]

Name	Purity (%)	Origin
IV Zirconium Butoxide	99.2	Aldrich
Citric Acid	99.3	Vetec
Ethyleneglicol	99.0	Vetec
Tetrametiltetravinilciclotetrasiloxane (D_4Vi)	99.6	Dow Corning
Polymetilsiloxane (PMS)	99.8	Dow Corning

Citric acid was mixed to IV-zirconium butoxide in water and homogeneized at 90 °C for 6 h. Ethyleneglycol was added to the solution and stirred for 2 h. The zirconium citrate was mixed by stirring to D_4V_i and PMS according to Table II.

Table II - Concentration of reagents in the mixture of compounds.
[Tabela II - Concentração dos reagentes na mistura dos compostos.]

Concentration	Zr Resin (g)	D_4Vi (g)	PMS (g)
C1	30	75	5
C2	40	65	5
C3	50	55	5

The polymeric resin was calcined from 100 to 1400 °C several times. The powder was deagglomerated in agate mortar and sieved at 325 meshes.

The powder was characterized by Fourier transform infrared spectroscopy, FTIR, in a Bomem B100 equipment with KBr pellets, with a resolution of 4 cm^{-1} from 4000 to 400 cm^{-1}. DTA analysis was performed in a TA instruments model 2910 with a heating rate of 10 °C/min under oxygen. The powder was analyzed by X-ray diffraction in a Shimadzu XRD 6000 diffractometer with CuKα radiation, 1.5418 Å, and 2θ from 10º to 80º. The powder was analyzed by scanning electron microscopy, SEM, and energy dispersive spectroscopy, EDS, with a JEOL-JSM T-300 microscope with an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

Fig. 1 shows the DTA curves of C1, C2 and C3 concentrations with an endothermic reaction related to water release near 100 °C (adsorbed water) and an endothermic peak due to release of structural water from 180 to 200 °C. The decomposition of polymer takes place with an endothermic peak from 400 to 800 °C. Near 1200 °C an endothermic peak is related to monoclinic to tetragonal phase transformation. It is not clear whether the peak of the zirconia crystallization occurs close to 700-800 °C. Transformations related to silica formation and $ZrSiO_4$ were not observed. This indicated that the amorphous phase of silica appears in a wide temperature range.

The X-ray diffraction pattern of powder of C3 concentration, Fig. 2, shows the tetragonal zirconia phase
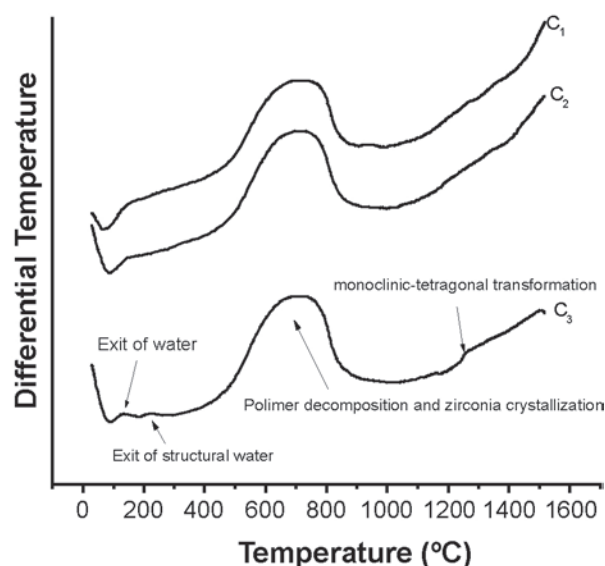

Figure 1: DTA curves of sample C1, C2 and C3.
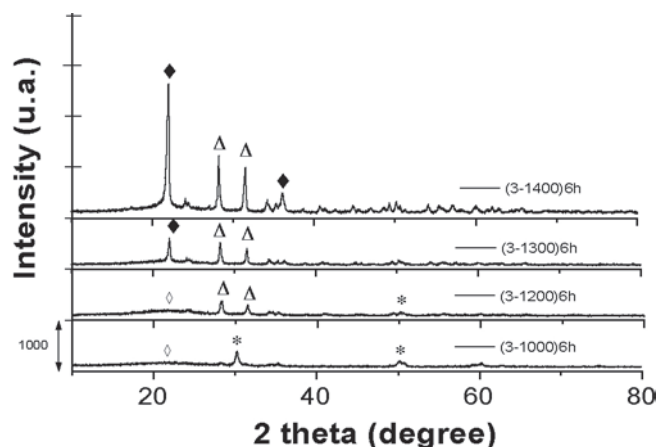*[Figura 1: Curvas de DTA das amostras de composições C1, C2 e C3.]*

Figure 2: X-ray diffraction patterns of C3 powder.
[Figura 2: Difratogramas de raios X do pó de concentração C3.]

formation at 1000 ºC/6 h. The increase of temperature from 1200 ºC to 1300 ºC shows the formation of the monoclinic phase of the zirconia at 1200 ºC and the monoclinic phase with a crystalline phase of crystobalite silica at 1300 ºC/6 h. The powder calcined at 1400 ºC/6 h shows the same pattern observed at 1300 ºC/6 h with intense peaks. According to the phase diagram [8], above 1250 ºC a phase based on ZrO_2. SiO_2 ($ZrSiO_4$) is formed for all stoichiometric compositions. However the zircon phase was not observed showing separated phases for ZrO_2 and SiO_2.

Fig. 3 shows X-ray diffraction patterns of different compositions calcined at various times. The phase analysis of C1 and C2 compositions shows 100% of the tetragonal zirconia in the powder calcined at 1000 ºC. Intense peaks of stabilized zirconia phase were observed with formation of two different phases, tetragonal and cubic. A diffuse band of amorphous material related to silica shows that the crystalline phase was formed at temperatures above 1000 ºC.

Analysis by mapping the K_α line of Zr, Si and O of powder of C2 composition, Fig. 4, shows broad Si peaks and weak Zr peaks for all compositions. The Zr peak increases from C1 to C3 composition. The poor traces of Zr could indicate the presence of small concentration of ZrO_2 particle in the powder. The spectra show a peak of carbon related to sample powder substrate in the three compositions.

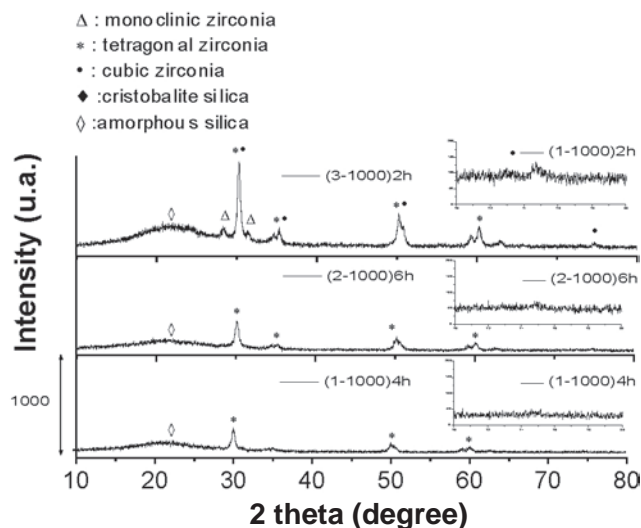Fig. 5 shows the scanning electron microscopy micrograph of the C3 concentration powder calcined at

Figure 3: X-ray diffraction patterns of C1, C2 and C3 compositions with different times of calcination.
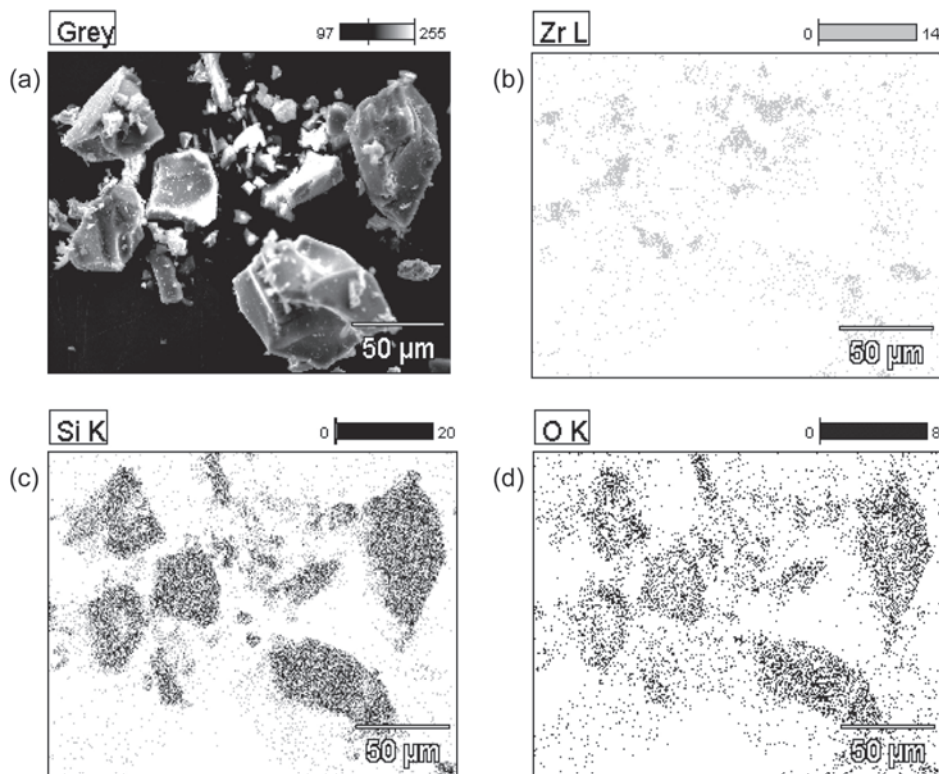*[Figura 3: Difratogramas de raios X das composições C1, C2 e C3 com diferentes tempos de calcinação.]*

Figure 4: Scanning electron microscopy micrograph and microanalysis of C1 composition. a) SEM of powder, b) Zr mapping, c) Si mapping, d) O mapping.
[Figura 4: Microscopia eletrônica de varredura e microanálise da composição C1. a) MEV do pó, b) mapeamento do Zr, c) mapeamento do Si, d) mapeamento do O.]
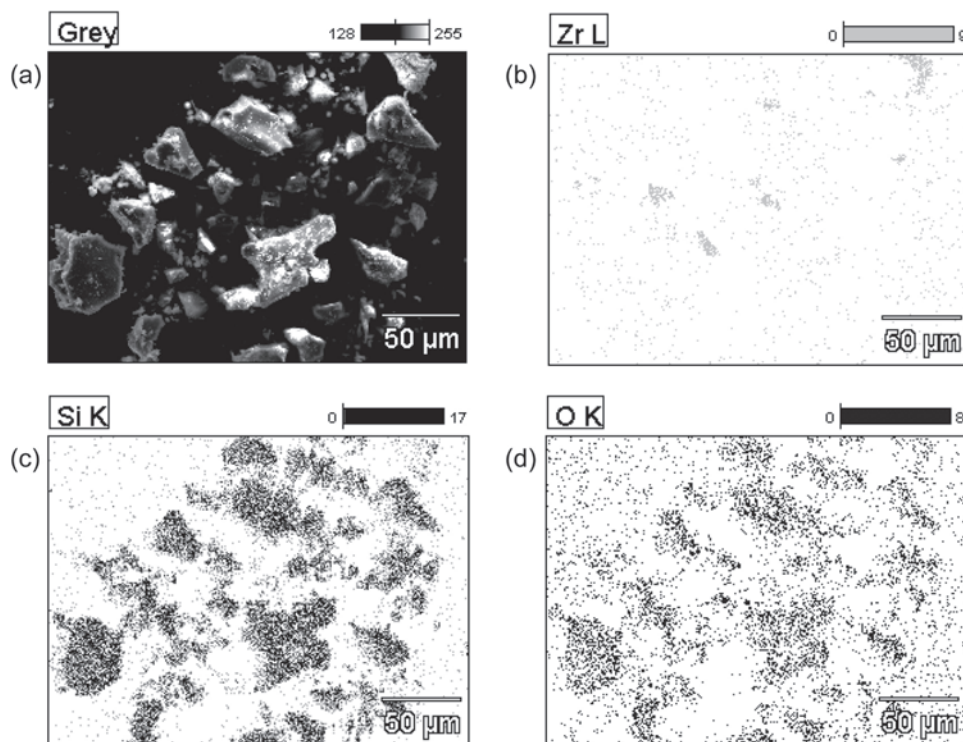
Figure 5: Scanning electron microscopy micrograph and microanalysis of C2 composition. a) SEM of powder, b) Zr mapping, c) Si mapping, d) O mapping.
[Figura 5: Microscopia eletrônica de varredura e microanálise da composição C2. a) MEV do pó, b) mapeamento do Zr, c) mapeamento do Si, d) mapeamento do O.]
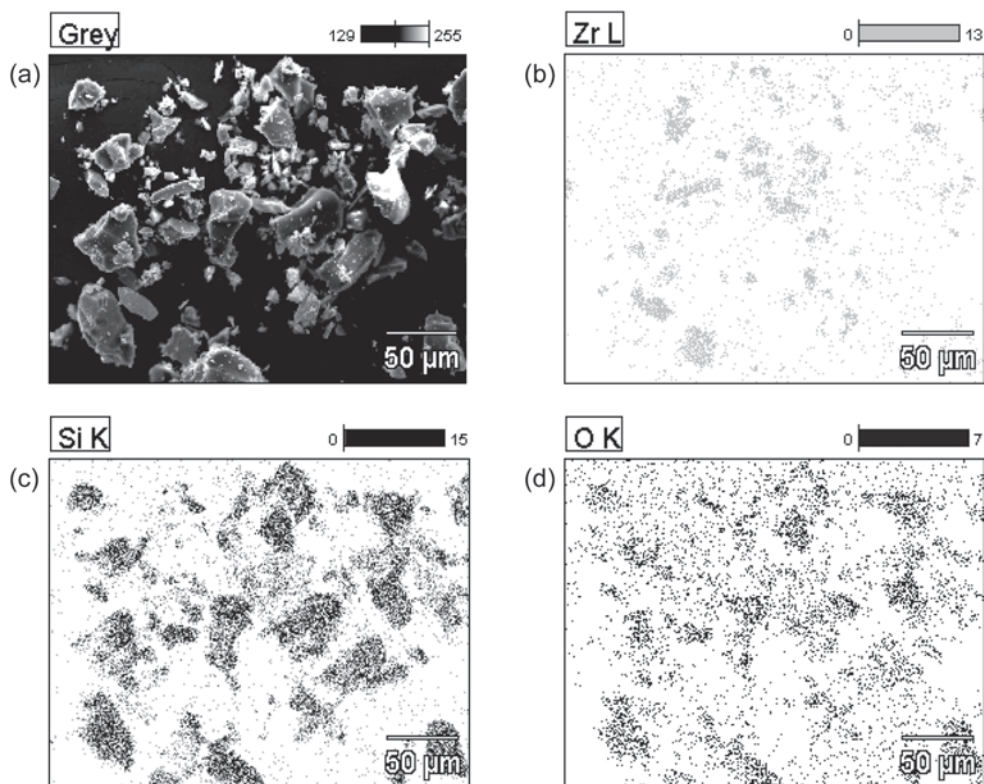

Figure 6: Scanning electron microscopy micrographs and microanalysis of C3 composition. a) SEM of powder, b) Zr mapping, c) Si mapping, d) O mapping.
[Figura 6: Microscopia eletrônica de varredura e microanálise da composição C3. a) MEV do pó, b) mapeamento do Zr, c) mapeamento do Si, d) mapeamento do O.]
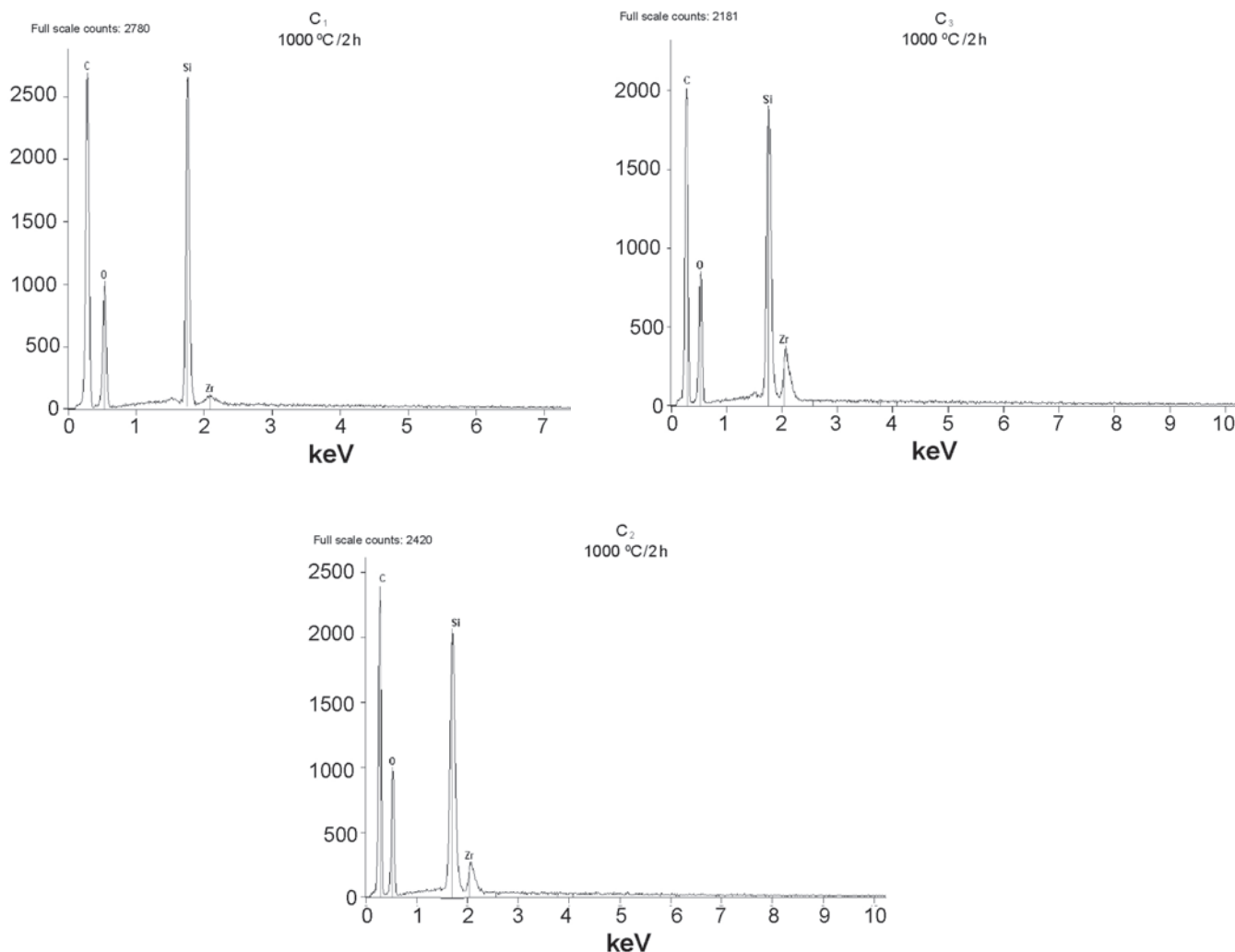
Figure 7: Spectra of mapping of K_α line of Zr, Si, O and C. a) C1 composition, b) C2 composition, c) C3 composition. Powder calcined at 1000 °C/2 h.

[Figura 7: Mapeamento dos espectros das linhas K_α do Zr, Si, O e C. a) composição C1, b) composição C2, c) composição C3. Pó calcinado em 1000°C/2 h.]

1000 °C. Particles in the 10-50 μm range were observed indicating powder agglomeration. A mapping of the K_α line of the powder indicated that there is a zirconia phase growth with the formation of microparticles and low frequency of distribution of particles. The analysis of the Si concentration shows a high frequency of particles forming macroparticles. According to the mapping data, low diffusion of zirconium and silicon ions takes place in SiO_2 and ZrO_2 particles, respectively. The Si distribution indicated low propagation into the zirconia particles without solid solution formation and $ZrSiO_4$ phase formation. During decomposition of the polymeric resin individual nuclei of phases grows forming the crystalline phase of zirconia and the amorphous phase of silica. The cause of the different phase formation is the poor mixing between the precursors resin at molecular level. Several works indicated that the ZrO_2-SiO_2 mixture led to zircon phase formation.

Analysis by SEM of C1 powder, Fig. 6, shows

macroparticle with size in the 5-60 μm range. The mapping of K_α line shows an increase of ZrO_2 particle frequency and a growth of particles relative to the powder of C1 concentration. The growth of zirconia particle does not led to dispersion of silicon into the ZrO_2 structure. Substitution of silicon for zirconium positions into the lattice does not cause vacancies formation according to the reaction:

Silicon is isovalent relative to zirconium ion and has low diffusivity into the zirconia structure, the phase nucleates and grows in amorphous silica.

Analysis by scanning electron microscopy of powder with C3 concentration of zirconium, Fig. 7, shows a decrease of particle size of amorphous silica and an increase of particle frequency of zirconia demonstrating a particle growth relative to the powder of C1 and C2 concentrations. The X-ray diffraction pattern of the powder calcined at 1000 °C shows a decrease of the stabilized phase with formation of the monoclinic phase. This could indicate a limit of zirconia

particle size for stabilization. The K_α line mapping shows an increase of Si diffusion into the zirconia particle causing a decrease of zirconia stabilization considering that Si does not contribute to vacancy formation.

CONCLUSIONS

A complex polymer synthesized by using the Pechini method decomposes at different temperatures and times. Tetragonal zirconia was formed at 1000 ºC, monoclinic zirconia at 1200 ºC and monoclinic zirconia and cristobalite silica in the 1300-1400 ºC range. A diffuse amorphous band observed by X-Ray diffraction was formed from 1000 to 1300 ºC relative to the silica phase. The increase of zirconia concentration led to the formation of fully tetragonal zirconia, TZP. A mapping of Zr and Si K_α line by EDS indicated the formation of small silica particles. The mapping of K_α line of Si shows low propagation into the zirconia particles without solid solution formation. Such results demonstrated that the zirconia stabilization occurs without the influence of Si ions into the zirconia structure.

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