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Crystallization behaviour and microstructural development in $ZrSiO_4$ and V-$ZrSiO_4$ solid solutions from colloidal gels

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Abstract

Zircon and vanadium-doped zircon blue pigments were prepared by heat treatment of gel precursors. Gels with nominal compositions V_x-$ZrSiO_4$ with $x = 0.0$, 0.002, 0.004, 0.02 and 0.2 were prepared by formation of a silica coating on zirconia colloidal particles previously obtained. The crystallization behavior and microstructural evolution were studied using X-ray powder diffraction (XRD), energy dispersive X-rays microanalysis (EDX), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). The results indicated that the vanadia loading in the precursor gels speeds up the crystallization of the vanadium-containing tetragonal zirconia solid solutions and their transformation to the monoclinic form. The overall conversion rate of gel precursors to pigmenting powders increased when the vanadia content was higher. Microstructural data revealed that the used procedure for the preparation of vanadium-zircon pigments allowed high-purity and non-agglomerated powders with controlled particle size to be obtained. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ceramic pigments are very important ceramic materials used to introduce color into ceramic glazes. The zircon-vanadium blue ceramic color has been widely used in the ceramic industry for several decades. It is accepted that the origin of the blue color in this pigment is due to the solid solution of V^{+4} in the zircon lattice.[1–5] However, several basic aspects concerning the characterization of the solid solution, such as: the vanadium distribution in dodecahedral and/or tetrahedral sites and the limit of solubility of vanadium into the structure, are still subjects of controversy.[6–8]

Ceramic pigments are used as powdered materials and it is highly desirable for ceramic processing, as for many other powdered ceramic materials, to dispose of non-agglomerated powders with controlled particle size and shape. The use of preparation methods leading to the control of these powder features has been scarcely considered in the literature.

The V-zircon pigment is industrially produced from the reaction of zirconia and silica in near-stoichiometric proportions combined with V_2O_5 (or ammonium metavanadate) and mineralizers. The mineralizers used are generally combination of two or more alkali halides, such as sodium chloride, sodium fluoride and ammonium chloride.[9,10]

From this conventional synthetic approach the powder requirements for any given ceramic pigment may be difficult to achieve because hard agglomerates (and/or aggregates) form on the thermal processing. In order to reach suitable particle characteristics pigments should be ground to a standard fineness before being used.

During the last decade undoped and vanadium-containing zircon powders have been obtained by the sol-gel process with different precursors.[10–16] Results have shown that after thermal processing of either pure or doped zircon gel precursors the resulting yield consists of heterogeneously shaped particles and agglomerated solids. Other techniques of synthesis have been used to produce zircon in order to control the powder morphology and decrease the synthesis temperature. Thus, Tartaj et al.[17] described a procedure for the preparation

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of SiO_2–ZrO_2 spherical particles based on the hydrolysis of liquid aerosols, which yielded zircon after calcination at lower temperatures than those required for other reported synthesized samples. However, the calcination of the powders gave rise to irregular particle morphologies as a consequence of interparticle sintering. Mosset et al.[18] reported the synthesis of submicronic undoped zircon powders, as small disk particles, using a pseudo-hydrothermal aqueous sol-gel route.

Recently a procedure for the preparation of vanadium-doped zircon pigmenting system with different vanadium loadings which enabled their complete formation and further characterization was reported.[8] This method allows preparation and characterization of both the crystalline phases formed during the thermal processing and the final vanadium-zircon solid solution product. Since this sol–gel procedure on the zircon solid solution formation is reasonably well controlled it should be interesting to follow microstructural changes during the reactions taking place and to study the possibility of obtaining suitable microstructures for the end undoped zircon and vanadium-zircon solid solutions products.

In this work, therefore, we have examined the crystallization behavior and the microstructural development during thermal treatment from gels to final zircon-based products. These gel precursors were prepared by using a previously reported more controlled synthetic sol–gel method. The main goal was to determine the effect of the temperature on the microstructural changes up to the end product for samples containing increasing amount of vanadium and to check the possibility of attaining a suitable microstructure in the final zircon-based solid materials, i.e. undoped and vanadium-containing solid solution.

2. Experimental procedure

2.1. Preparation of samples

Gels with nominal compositions V_x-$ZrSiO_4$ with x 0.000, 0.002, 0.004, 0.04 and 0.2 (hereafter referred as A, B, C, D and E, respectively), were prepared by a procedure previously reported.[8] Basically they have been obtained by gelling mixtures of previously prepared either zirconium and vanadium oxide colloids and tetraethylorthosilicate (TEOS). The process involves two steps. First, preparing a suspension of amorphous zirconia particles in which the liquid medium is an ethanol solution and to that, the required amount of TEOS is added. Second, inducing formation of amorphous silica by the addition of previously prepared vanadia colloidal solution in water. The TEOS/H_2O ratio in the mixture is controlled by the concentration of the V_2O_5 solution in water, except for the undoped sample to which no vanadia solution was added. Thus, for the composition without vanadium, i.e. with $x = 0$, the TEOS/H_2O molar ratio is 2 whereas for sample with the highest amount of vanadium, i.e. with $x = 0.2$, it is almost 300. After drying at 120°C the resulting gel precursor powders were ground with mortar and pestle.

In order to examine the structural and microstructural evolution gel powders were heat treated at different temperatures in the range between 400 and 1500°C in air for several periods and then cooled in air in the furnace.

2.2. Techniques of characterization

Structural and microstructural evolution of gels and crystalline specimens were followed by using several techniques.

X-ray diffraction analysis (Model D-500, Siemens, Karlshruhe, Germany) was performed using a graphite monochromatic CuK_α radiation. The diffractometer had two 1° divergence slits, being the scatter and receiving slit 1° and 0.15°, respectively.

The microstructure of the as-prepared and thermally treated samples was determined by field emission scanning electron microscopy at 5–10 kV (Models S-4100, Hitachi Ltd., Tokyo, Japan). To check the quality of the observation, some of the samples were etched with a diluted HF solution for 10 s, and subsequently washed with H_2O. All specimens were coated with gold/palladium in an ion beam coater.

The morphology of pure and vanadium-containing zirconia and zircon particles was also examined using transmission electron microscopy (Model H-800, Hitachi Ltd., Tokyo, Japan) at an accelerating voltage of 200 kV. Samples were crushed and dispersed in absolute ethyl alcohol and drops of the dispersion were transferred to a specimen copper grid carrying a perforated thin carbon film. Electron-diffraction patterns were also obtained on the same transmission electron microscope equipped with a rotating and tilting goniometric stage.

Energy-dispersive X-ray analysis was performed using a scanning electron microscope (Model JSM-6300, Jeol, Oxford, England) operated at 20 kV. This instrument is equipped with an energy dispersive X-ray spectrometer (Pentafet, Oxford Instruments, Knoxwille, TN). Specimens were mounted in a polymer resin and polished with progressively finer SiC papers. Before acquiring the X-ray spectra samples were carbon coated. The analysis entailed obtaining the overall analysis of the whole sample. This kind of analysis was obtained from a large area of the specimen and it was an average of the area of the image on the scanning electron microscope screen. It was therefore performed at low magnification (lower than x1K). Quantitative analyses of specimens were made using the SEMQuant program with ZAF correction procedures and the default standards.

3. Results and discussion

3.1. Composition and structure of dried gels

The specific starting composition of dried gels was determined by EDX/SEM at low magnification, i.e. lower than ×1000. Several analyses were obtained for each composition without larger dispersions. Table 1 displays the composition (in wt% of each oxide) for each one of the dried gel precursors. Also the SiO_2:ZrO_2:V_2O_5 molar ratio for each composition is included. From these molar ratios it can be inferred that in all samples a small excess of silica is present in samples.

As observed by infrared spectroscopy of dried gels discussed in a previous paper,[8] they contain bands at 1165, 1050, 800 and 460 cm^{-1} which are characteristics of an amorphous silica network. All gel precursors as prepared are amorphous to X-rays. These starting precursors, therefore, may be considered as triphasic gels in which both kind of particles, i.e. ZrO_2 and V_2O_5 colloidal sols, are homogeneously mixed in the amorphous silica matrix. This arrangement, however, permits predicting high reactivity at low temperatures and the possibility of attaining a suitable microstructure in the final product.

3.2. Thermal behaviour of the xerogels

The thermal evolution of the gels was followed by XRD in order to establish the effect of the amount of vanadium on the pathway to the final product. Several XRD patterns, obtained with increasing temperatures or holding times during heating in air of the specimen A (without vanadium), are shown in Fig. 1. The tetragonal ZrO_2 broad peaks at about 29.8, 34.0, 50.0 and 59.4 (2θ) appear first upon heating at 800°C for 3 h, and this poorly crystallized phase persists during heating to 1000°C for 3 h. After heating the sample at 1200°C for 3 h strong lines of tetragonal zirconia are observed. Further heating to 1400°C for 3 h causes some tetragonal to monoclinic transformation. Holding the sample at 1400°C for a short time results in the formation of zircon. Also a peak at 22.0 (2θ) associated with the crystobalite is present and it persits after annealing for 66 h at 1500°C.

Table 1
Composition of dried gels determined by EDX/SEM

Sample	SiO_2	ZrO_2	V_2O_5	SiO_2 /ZrO_2 / V_2O_5[a]
A	37.66 ± 0.23	62.34 ± 0.23		1.20/1.00
B	37.81 ± 0.24	62.04 ± 0.22	0.12 ± 0.07	1.25/1.00/0.0013
C	37.31 ± 0.26	62.40 ± 0.28	0.28 ± 0.05	1.22/1.00/0.003
D	36.90 ± 0.26	60.59 ± 0.22	2.51 ± 0.26	1.24/1.00/0.028
E	29.77 ± 0.22	56.36 ± 0.45	13.87 ± 0.39	1.08/1.00/0.165

[a] SiO_2–ZrO_2–V_2O_5 molar ratios.

The crystal phase data obtained during heating and then cooling in the furnace a sample of pure zirconia, i.e. the as-prepared zirconia, is strikingly different to the one observed for the specimen A. Thus, for colloidal zirconia crystallization occurs at about 500°C to produce essentially 100% tetragonal phase. The full transformation to the monoclinic phase takes place either holding at 500°C for 15 h or enhancing the thermal treatment temperature to 600°C for 3 h.

From the above results the first to be noted is that the temperature of crystallization of tetragonal zirconia is much higher than observed for pure zirconia. Also, the tetragonal to monoclinic phase transformation is delayed and takes place in a broad range of temperatures. Similar results have been obtained during the thermal treatment of gels with a zircon composition synthesized by different procedures.[5,17,19] It is noted that the common characteristic for these precursor gels is that they are in all cases truly "composites" in the sense that the powders are a homogeneous mixture of very fine particles of amorphous zirconia either coated by a layer or embedded in a matrix of amorphous silica. Some explanation has been advanced for these observations.[20,21] Firstly, the delay in the crystallization of tetragonal zirconia in the zircon system should be associated with the difficulty in releasing water molecules from the amorphous zirconia particles surrounded by a layer of amorphous silica. On the other hand, based on the stabilization of the tetragonal phase by a crystallite size effect and that the tetragonal to monoclinic transformation involves a positive change of volume, a certain type of blocking effect of silica would hinder particle growth, keeping the particle size of zirconia within its critical value in the tetragonal phase.

The crystallization of zircon, i.e. the last step on the whole process of final product formation, is first detected after heating to 1400°C for 3 h and when a further short annealing is completed. This temperature is lower than reported in the formation of zircon from gels. An interesting question regarding to which form of zirconia, i.e. tetragonal or monoclinic, reacts with the amorphous silica covering the zirconia particles can arise. Concerning this, it is noted that zircon starts to be formed after the tetragonal to monoclinic phase transformation takes place. This experimental evidence suggests that the monoclinic form is more favorable than the tetragonal one for the formation of zircon. However, this assumption should be checked by further experimental work.

The main steps leading to vanadium-zircon solid solutions in the thermal processing of gel precursors with increasing vanadia loading are shown in Figs. 2, 3, 4 and 5, corresponding to specimens B, C, D and E, respectively. On heating the first detected crystalline phase for the specimens, except in the case of specimen E, corresponds to a phase with tetragonal ZrO_2 structure. In fact, as previously reported, it was a V^{+4}-ZrO_2 solid

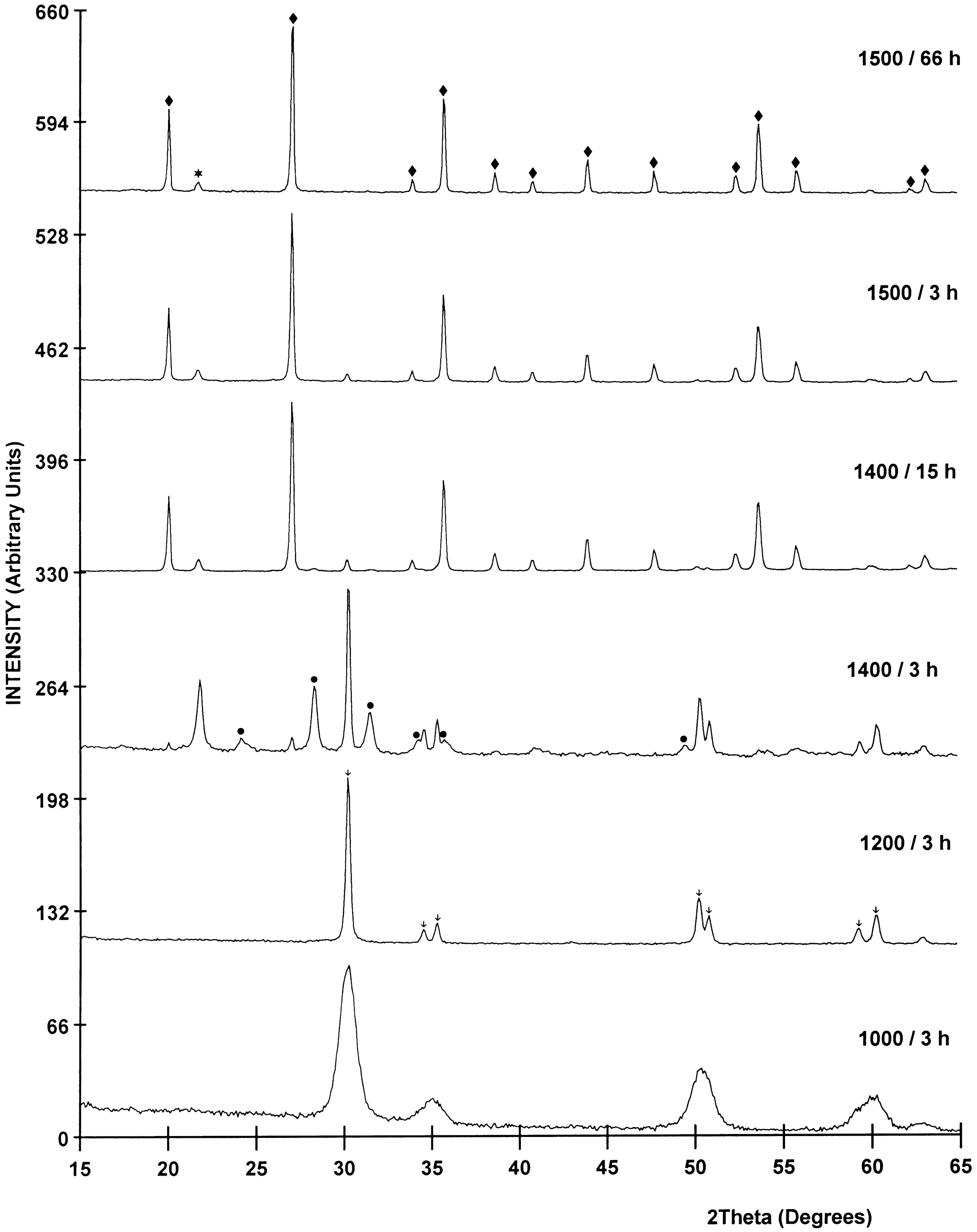


Fig. 1. X-ray diffraction pattern of sample A heated at several temperatures and/or for several times (↓ is tetragonal zirconia, ● is monoclinic zirconia, ⋆ is cristobalite and ◆ is zircon).

solution.[8] The temperature of crystallization of the gel precursors is dependent on the starting amount of vanadium. The higher the amount of vanadium the lower the crystallization temperature. Thus, for sample E, with the higher amount of vanadium, crystallization occurs at 600°C whereas sample A, without vanadium content, begins to crystallize at temperatures closer to 800°C. It is noted that sample E is amorphous after long thermal treatment at 500°C and after short annealing to 600°C a phase with the structure of the monoclinic form of zirconia as well as the binary phase zirconium vanadate, ZrV_2O_7 is detected. The former monoclinic phase of zirconia is actually a vanadium-containing solid solution of monoclinic zirconia.

The range of temperatures in which the tetragonal zirconia solid solution is metastable is also dependent on the amount of vanadium. The higher amount of vanadium the shorter the range of temperature. X-ray diffraction analysis of samples thermally treated at several temperatures and holding times, shown in the above Figs. 1–5, is evidence that the tetragonal crystalline form is metastabilized up to higher temperatures

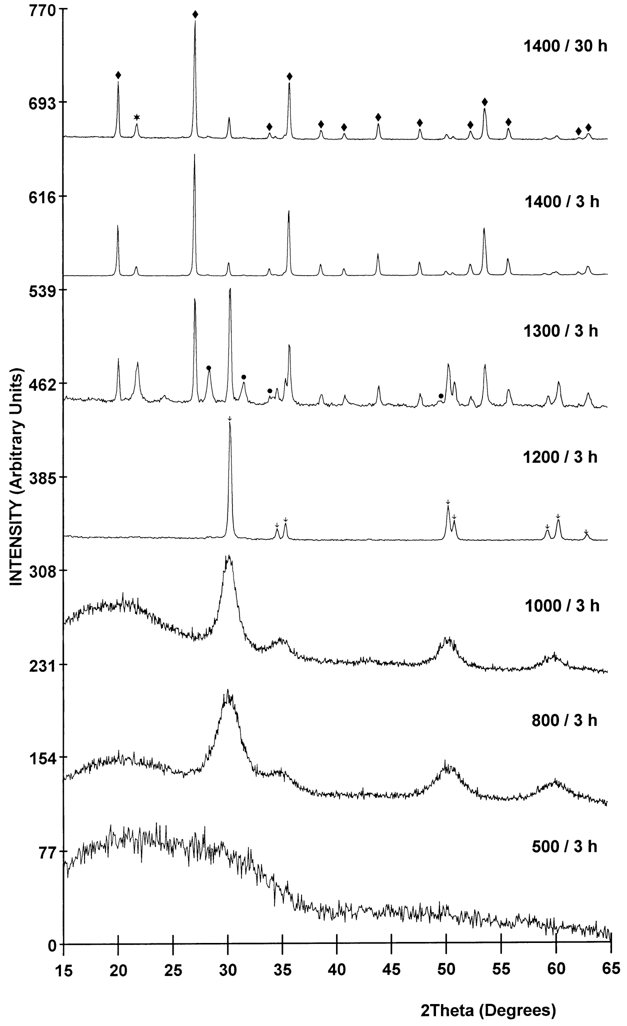


Fig. 2. X-ray diffraction pattern of sample B heated at several temperatures and/or for several times (↓ is tetragonal zirconia, ● is monoclinic zirconia, ⋆ is cristobalite and ◆ is zircon).

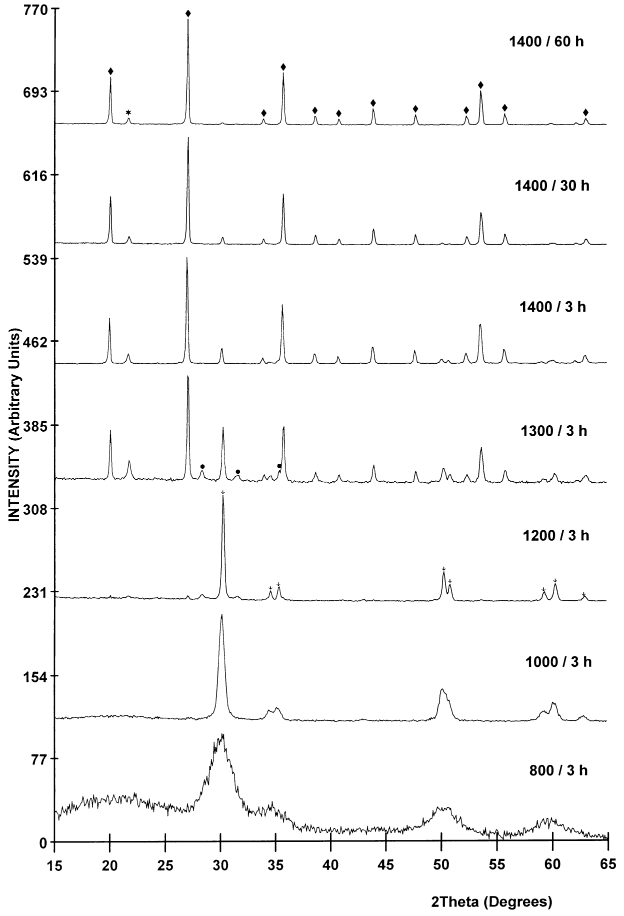


Fig. 3. X-ray diffraction pattern of sample C heated at several temperatures and/or for several times (↓ is tetragonal zirconia, ● is monoclinic zirconia, ⋆ is cristobalite and ◆ is zircon).

than 1200°C in samples A (without vanadium), B and C (with low amounts of vanadium). However, for samples D and E the temperature range, for which the tetragonal zirconia is metastable, is shorter. Thus, for sample E, thermal treatment even at as low a temperature as 600°C for 3 h in which crystallization is almost complete, is difficult to detect while the sample heat treated at 500°C, even after long annealing for 500 h, is fully amorphous.

The dependence of the temperature range in which the tetragonal ZrO_2 solid solution is metastable on the vanadium content in the specimen is striking. This fact can be associated with the chemical effects derived from the zirconia-vanadia solid solution formation. Monros et al.[22] claimed the effect of the chemical composition, and specifically the vanadium amount, on the stability of the tetragonal ZrO_2 included in the amorphous silica matrix in the SiO_2–ZrO_2–V_2O_5 ternary system. Also these authors state that the tetragonal to monoclinic martensitic phase transformation of ZrO_2 is dependent on the tetragonal ZrO_2 particle size being the critical size to which the transformation is carried out about 30 nm, very similar to the critical size proposed by Garvie,[23] for a system formed only by tetragonal ZrO_2 particles. However, the observed effect of lowering the transformation temperature on increasing the amount of vanadium can be understood by the instability of this V^{+4}-ZrO_2 tetragonal solid solution in the presence of an excess of vanadium. Thus, it can be suggested that the presence of melted V_2O_5 facilitates the nucleation and growth of the phase transformation.

As for the undoped zircon sample the phase transformation from the tetragonal to monoclinic form of V-zirconia solid solution and the formation of the final V-zircon solid solution are detected almost simultaneously. It means that obviously before formation of the zircon phase some instability in the tetragonal form of the zirconia phase may be produced. However, the monoclinic form is sometimes very difficult to detect, mainly because samples with high amounts of vanadium

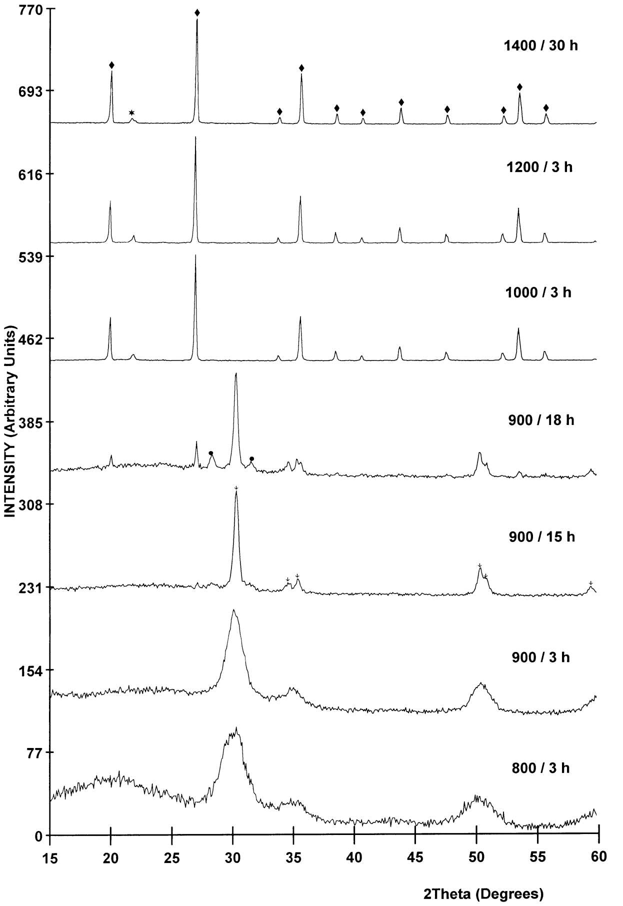


Fig. 4. X-ray diffraction pattern of sample D heated at several temperatures and/or for several times (↓ is tetragonal zirconia, ● is monoclinic zirconia, ⋆ is cristobalite and ◆ is zircon).

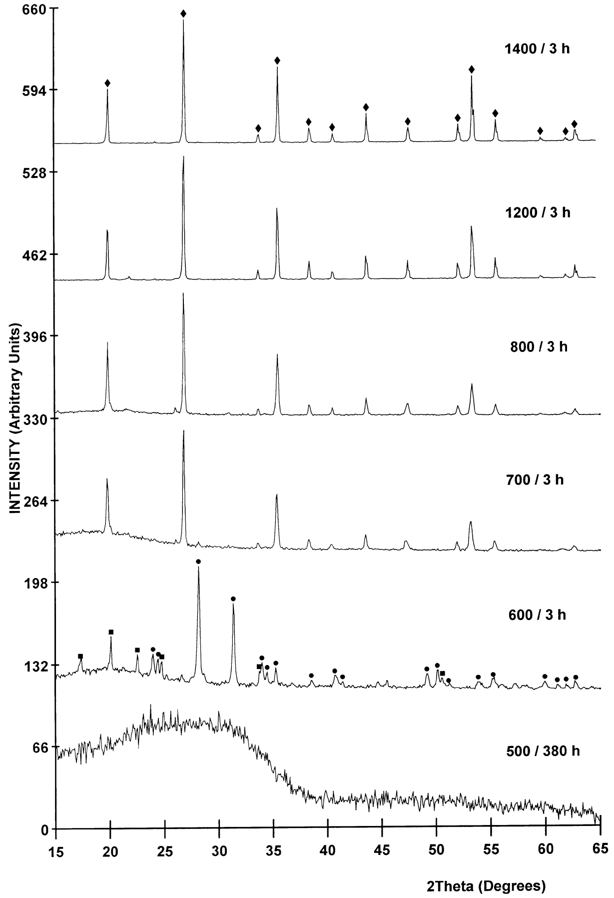


Fig. 5. X-ray diffraction pattern of sample E heated at several temperatures and/or for several times (● is monoclinic zirconia, ■ is ZrV_2O_7 and ◆ is zircon).

transform from amorphous to zircon in a rather narrow range of temperatures and/or time periods. These facts are shown for samples B, C, D and E in Figs. 2, 3, 4 and 5, respectively. As can be seen for sample D (Fig. 4), a solid solution with the zircon structure is formed at lower temperatures than for samples with low vanadium contents (B and C in Figs. 2 and 3, respectively). Thus, after holding for a short time, the sample D at 1000°C the formation of the zircon phase is complete whereas for sample B higher temperatures than 1400°C are required. In the case of sample E containing the highest amount of vanadium the zircon formation is already completed at 700°C.

The reactivity in this ternary system can be understood assuming the role played by the vanadium in both steps: the phase transformation and formation reaction of zircon phase. It can be accepted that the excess of V_2O_5, none entering in solid solution , which melts at a temperature close to 700°C, bring about a liquid phase that will facilitate the reactivity in both steps and mainly in the one which appears to be the controlling one in the zircon formation, i.e. the phase transformation to monoclinic ZrO_2.

3.3. SEM/EDX microanalysis of thermally treated samples at various temperatures

The average content in oxides (as wt%) of the dried gel precursors and specimens after thermal processing at either intermediate temperatures, i.e. 1000°C/3 h or 1200°C/3 h, and the final temperature, i.e. at 1400°C/30 h, are shown in Table 2. From these results an evaluation of vanadium losses by volatilization may be done. Thus, it is inferred that vanadium losses are practically negligible in specimens with lower nominal amounts of vanadium (samples B and C). However, for compositions with higher amounts of vanadium losses are greater. Thus, they can exceed the 80 wt% of the nominal vanadium for sample D and the 90 wt% for sample E.

It is to be remarked, as it was claimed before,[8] that for samples B to D all the vanadium in the calcined samples at 1400°C is inside the zircon phase, i. e. as a vanadium-containing zircon solid solution. It can also be assumed from the present results that for samples in which the starting vanadia loading is up to five times higher than its limit of solubility in the zircon phase, the excess of vanadium can be volatilized by heating at slightly higher temperatures than that required for the zircon formation.

3.4. *Microstructural evolution of samples*

On the basis of the transformations carried out in the specimens on heating at different temperatures, which are dependent on the initial vanadia loading, we will relate in this point these changes with the observed microstructure in order to get a more complete picture of the reactivity from the gel precursor to the zircon phase (either pure or vanadium-containing solid solution) in this system.

The TEM observations of the dried gels with the compositions B and E are shown in Figs. 6 and 7, respectively. After drying at 110°C the gels remain amorphous but display a two phase morphology characteristic of a matrix containing a second-phase inclusion. The mean diameter of the included particles is less than 10 nm. After heating at the temperatures at which the formation of a phase with the structure of tetragonal zirconia is detected the microstructure suffer changes as can be seen in Figs. 8, 9a and 10a. At this stage, by FESEM an arrangement is observed in which particles and/or small aggregates of particles of either undoped (for sample A) or vanadia doped tetragonal zirconia (for samples B to D) are forming agglomerates, in which the amorphous silica phase is located between the particles of zirconia giving rise to a system with high chemical homogeneity and consequently high reactivity. Fig. 8 displays the FESEM micrography of sample B heated at 1200°C/3 h. In fact, at this step the amorphous phase (silica) is situated as the outer coating (of the composite particles) thus keeping the crystalline zirconia particles separated

Table 2
Evolution of the chemical composition (wt% in oxides) after thermal treatments

Sample	Thermal treatment	SiO_2	ZrO_2	V_2O_5
A	Dried gel	37.66 ± 0.23	62.34 ± 0.23	
	1000°/3 h	38.31 ± 0.15	61.69 ± 0.15	
	1400°/30 h	38.80 ± 0.08	61.20 ± 0.08	
B	Dried gel	37.81 ± 0.24	62.04 ± 0.22	0.12 ± 0.07
	1200°/3 h	38.70 ± 0.14	61.17 ± 0.22	0.13 ± 0.09
	1400°/30 h	38.68 ± 0.25	61.17 ± 0.26	0.15 ± 0.05
C	Dried gel	37.31 ± 0.26	62.40 ± 0.28	0.28 ± 0.05
	1200°/3 h	38.12 ± 0.13	61.66 ± 0.15	0.22 ± 0.11
	1400°/30 h	38.04 ± 0.12	61.70 ± 0.16	0.26 ± 0.06
D	Dried gel	36.90 ± 0.26	60.59 ± 0.22	2.51 ± 0.26
	1400°/30 h	38.77 ± 0.74	60.58 ± 0.74	0.49 ± 0.12
E	Dried gel	29.77 ± 0.22	56.36 ± 0.45	13.87 ± 0.39
	1400°/30 h	35.11 ± 0.60	63.34 ± 0.70	1.55 ± 0.20

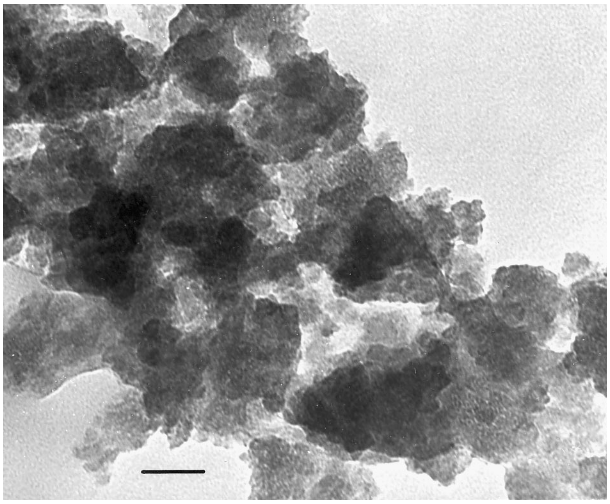


Fig. 6. TEM micrography of dried gel of sample B (bar = 50 nm).

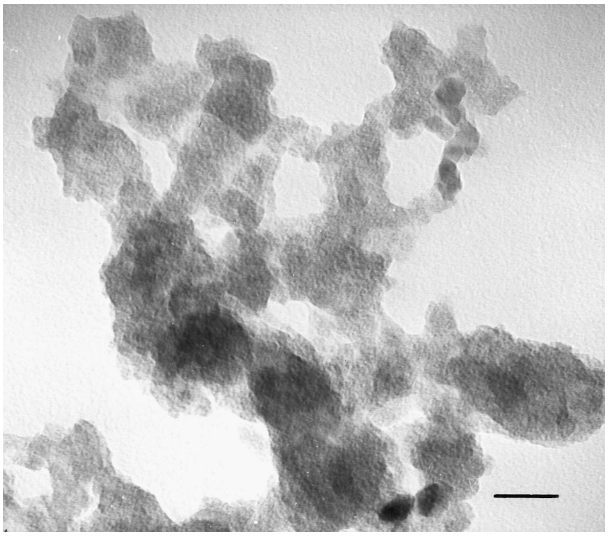


Fig. 7. TEM micrography of dried gel of sample E (bar = 35 nm).

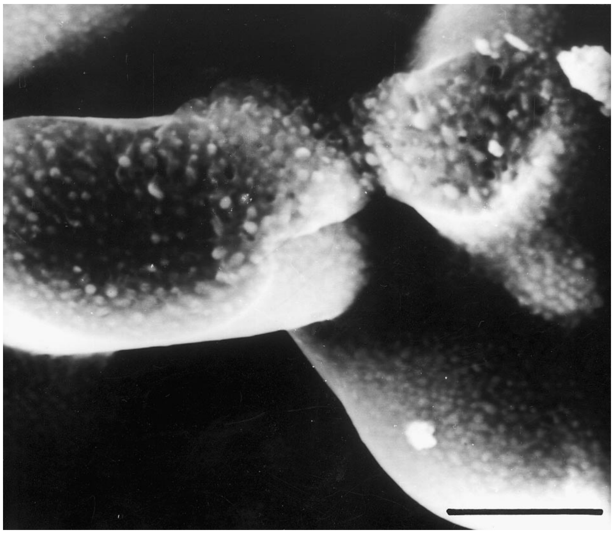
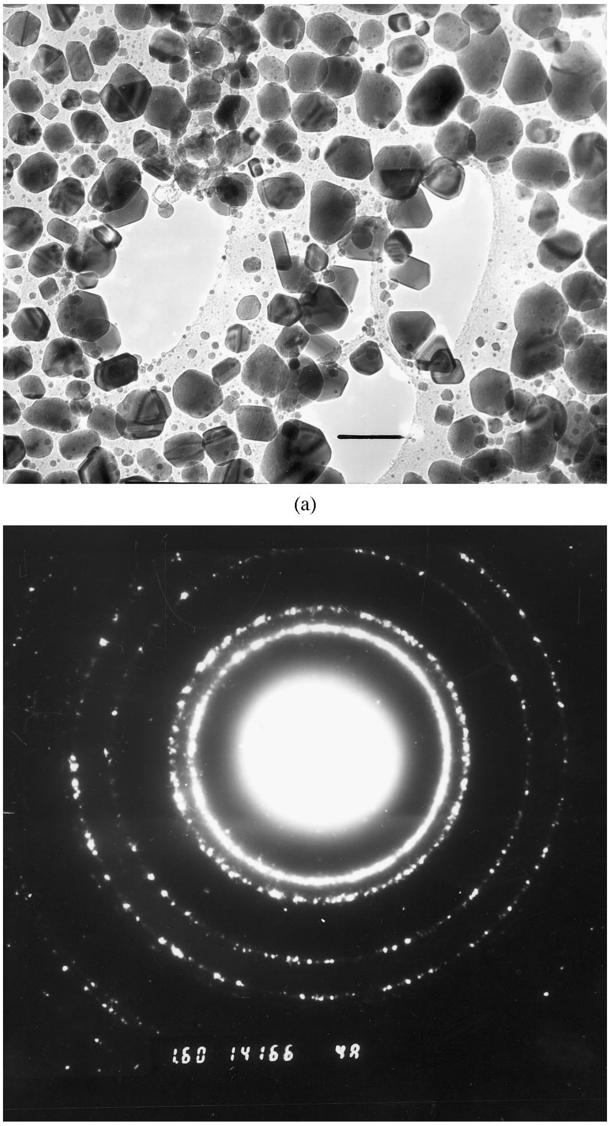


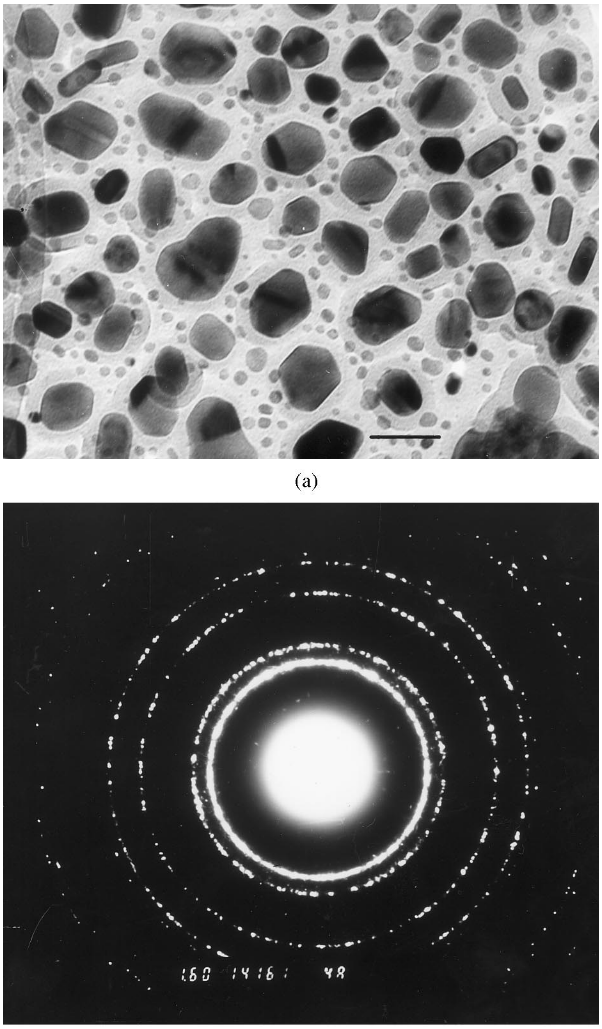
Fig. 8. FESEM micrography of sample B heated at 1200°C/3 h (bar = 1 μm).



(a)

(b)

Fig. 9. (a) TEM micrography of sample A heated at 1200°C/3 h (bar = 125 nm); (b) SAED of the same sample.



(a)

(b)

Fig. 10. (a) TEM micrography of sample C heated at 1200°C/3 h (bar = 100 nm); (b) SAED of the same sample.

from each other (i.e. the formation of a continuous network of the crystalline phase is prevented). The TEM micrographies of these specimens display individual particles. Figs. 9a and 10a, corresponding to samples A and C after heating to 1200°C and holding for 3 h, are shown as representatives. It can be noted that in addition to the existence of very fine particles of spherical form, particles of hexagonal, pyramidal, rectangular and square shapes are also evident. SAED patterns obtained from the above particles shown in Figs. 9b and 10b, respectively, display a typical diffraction pattern for the monoclinic form of zirconia.[24] This result can be understood because when irradiated with an intense electron beam (which results in heating) in HREM, tetragonal zirconia particles can become monoclinic.[19,24] It is noted that in this step of the reaction for the formation of the different zircon phases (undoped or doped with several amounts of vanadium) truly microcomposite particles with sizes up to 30 nm are formed in which the zirconia core particles are coated with an outer layer of amorphous silica. This arrangement in which the zirconia and silica which comprise the composite particles are mixed on a fine scale might facilitate the reaction to produce a zircon phase.

After further thermal treating of samples the monoclinic form of ZrO_2 is present. The formation of the zircon phase takes place at higher temperatures and/or longer times. Nevertheless, as mentioned above for samples with the higher amounts of vanadium both processes of phase transformation and zircon formation occur almost simultaneously. Fig. 11 shows a SEM micrography of sample C that had been heated at 1300°C/3 h. XRD results indicate that zircon is the main crystalline phase as well as both monoclinic and tetragonal ZrO_2 as secondary phases. It is noted that the

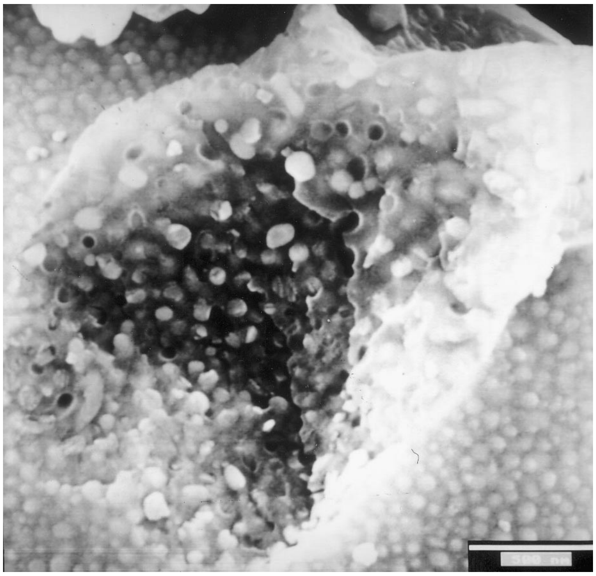


Fig. 11. FESEM micrography of sample C heated at 1300°C/3 h (bar = 500 nm).

particle sizes remain almost constant during the beginning of the zircon formation. The microstructure for samples after further thermal treatment, i.e. when the formation of zircon is almost completed, is quite different. Thus, the TEM observation of the different specimens after long annealing at as high temperatures as 1500°C, shown as representative in Fig. 12 for sample A after holding for 66 h at 1500°C, displays that all powders consisted of particles up to 50 nm in diameter in which zircon core particles are coated by a layer of amorphous silica. This result is in accordance with the excess of silica present as it was determined by EDX.

From the above microstructural evolution it can be suggested that zircon formation, at least at lower temperatures, occurs primarily by nucleación and growth within each microcomposite gel particle. The zircon formation is carried out after completion of the tetragonal to monoclinic phase transformation of either zirconia or vanadium-containing zirconia phases. If we assume that zircon formation in the microcomposite gel precursor follows a nucleation and growth process and since the zircon particle size is roughly the size of the tetragonal–zirconia composite it can be accepted that the growth rate of zircon should be higher than the nucleation rate in the zirconia-silica composite precursor. Since small aggregates of primary zirconia particles surrounded by a layer of amorphous silica are initially formed, the above reaction mechanism may lead to the entrapment of some zirconia particles within the growing zircon grains. Subsequent elimination of these particles (via reaction with residual silica) required chemical diffusion through the zircon grains, and as a consequence relatively high temperature are needed to complete the reaction. Of course, by increasing the amount of vanadium in the series of compositions, a strong increase in the speed of zircon formation occurs. This behaviour can be understood by taking into account the role played by the excess of vanadium, i.e. the amount of vanadium which is not solubilized in the zircon structure, that melts and facilitates the dissolution and diffusion of the zirconia particles.

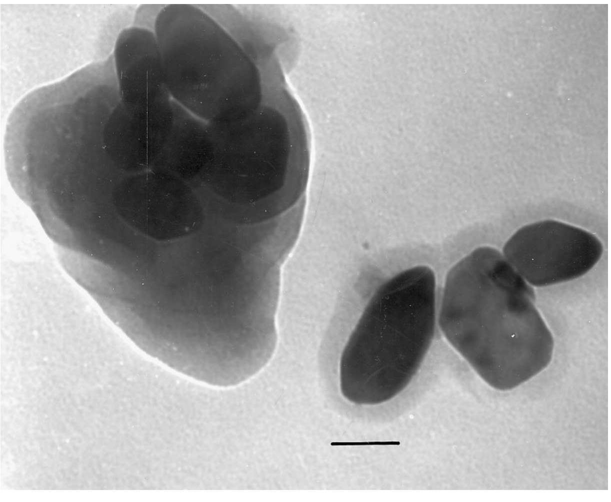


Fig. 12. TEM micrography of sample A heated at 1500°C/66 h (bar = 40 nm).

4. Conclusions

Vanadium-containing zircon gel precursors with increasing V_2O_5 contents (up to 14 wt% of V_2O_5) were prepared as microcomposite particles, consisting of an inner core of zirconia and an outer coating of amorphous silica. The crystallization behaviour and microstructural evolution over the temperature range up to the formation of either zircon or vanadium-containing zircon pigmenting systems from gel precursors were followed by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-rays microanalysis (EDX), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). The conclusions can be summarized as follows: (1) The method of preparation favoured the formation of a microcomposite precursor in which the nanoscale zirconia particles were coated by an amorphous silica layer. (2) The overall transformation of precursor gels to V-$ZrSiO_4$ powders proceeded rapidly for higher vanadia loadings. Vanadium acted in this system as mineralizer and dopant. (3) A large amount of vanadium was vaporized during calcination of precursors with high vanadia loading. Conversely, a considerable amount of vanadium oxide remained in solid solution into the zircon matrix for the lower amounts of vanadia. (4) High purity and non-agglomerated powders with controlled particle size of either undoped zircon or vanadium-containing zircon solid solution were observed to form by using the described synthetic procedure.

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