Comparative X-ray diffraction study of crystalline microstructure of tetragonal and monoclinic vanadium - zirconium dioxide solid solutions produced from gel precursors - *supplementary material*

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1. Supplementary material to the article

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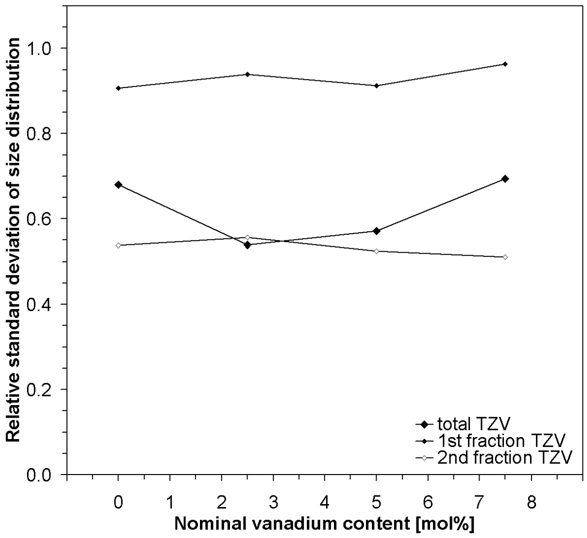
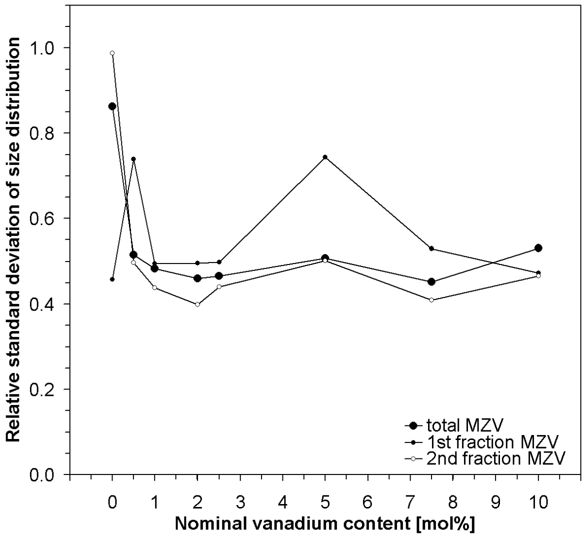
Note: This material is not intended to be published as a part of the article

1.1. Supplementary figures

These figures illustrate the contents of tables.



(a)



(b)

Fig. s1.
Evolution of the relative standard deviation of size distribution in tetragonal (a) and monoclinic (b) zirconias with nominal vanadium content [the ratio of standard deviation to mean value is given for each lognormal component (and corresponding fraction of crystallites) and for the total sample (*cf.* Table 4)]. On average, in tetragonal zirconias the ratio is about 0.93 for the first fraction of crystallites and about 0.53 for the second fraction, while in monoclinic zirconias the ratio is about 0.49 for the first fraction of crystallites (except samples MZV005 and MZV050, for which is about 0.74) and about 0.45 for the second fraction (except sample MZV000, for which is about 0.99) [*cf.* Table 3, Table 4, Fig. 5, Fig. 6, Fig. 7 and Fig. 8].

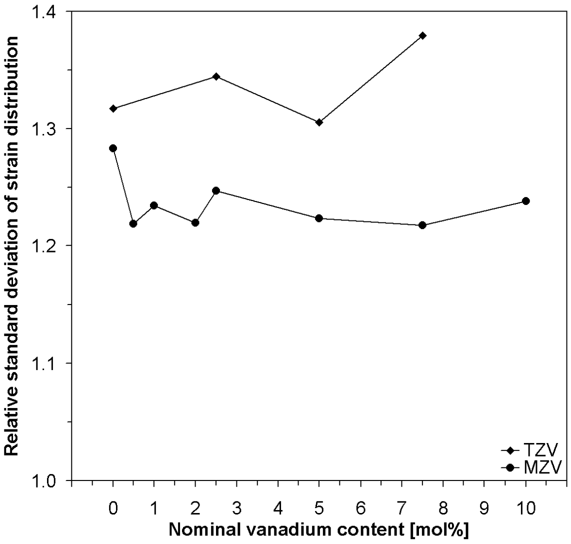
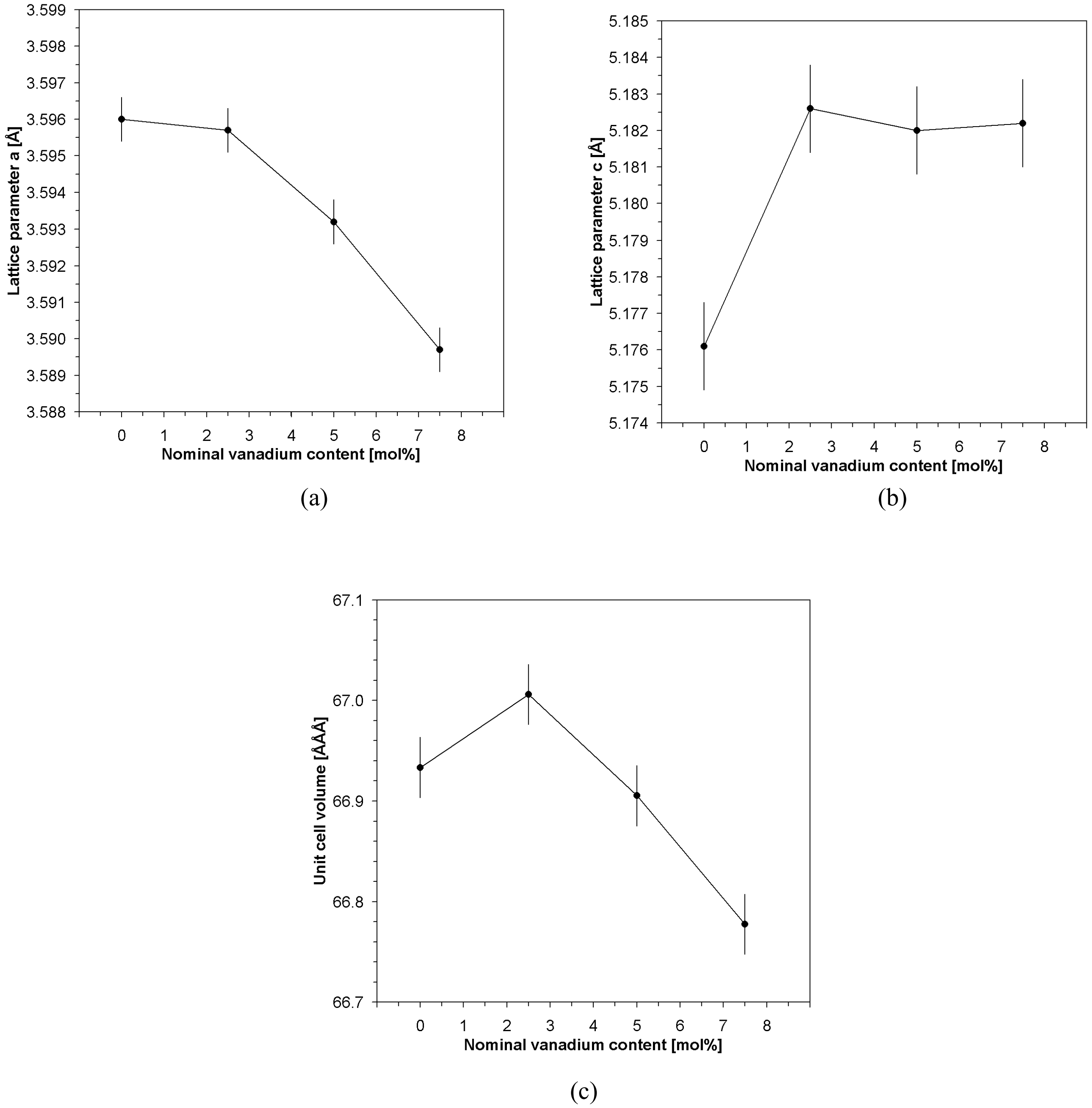


Fig. s2
Evolution of the second-order crystalline lattice strain distribution in tetragonal (TZV) and monoclinic (MZV) zirconias with nominal vanadium content [the ratios of standard deviation to mean-absolute value are given (cf. Table 3, Fig. 5, Fig. 6, Fig. 7 and Fig. 8)]. The ratios are about 1.34 for tetragonal zirconias and about 1.23 for monoclinic zirconias (except sample MZV000, for which is about 1.28).

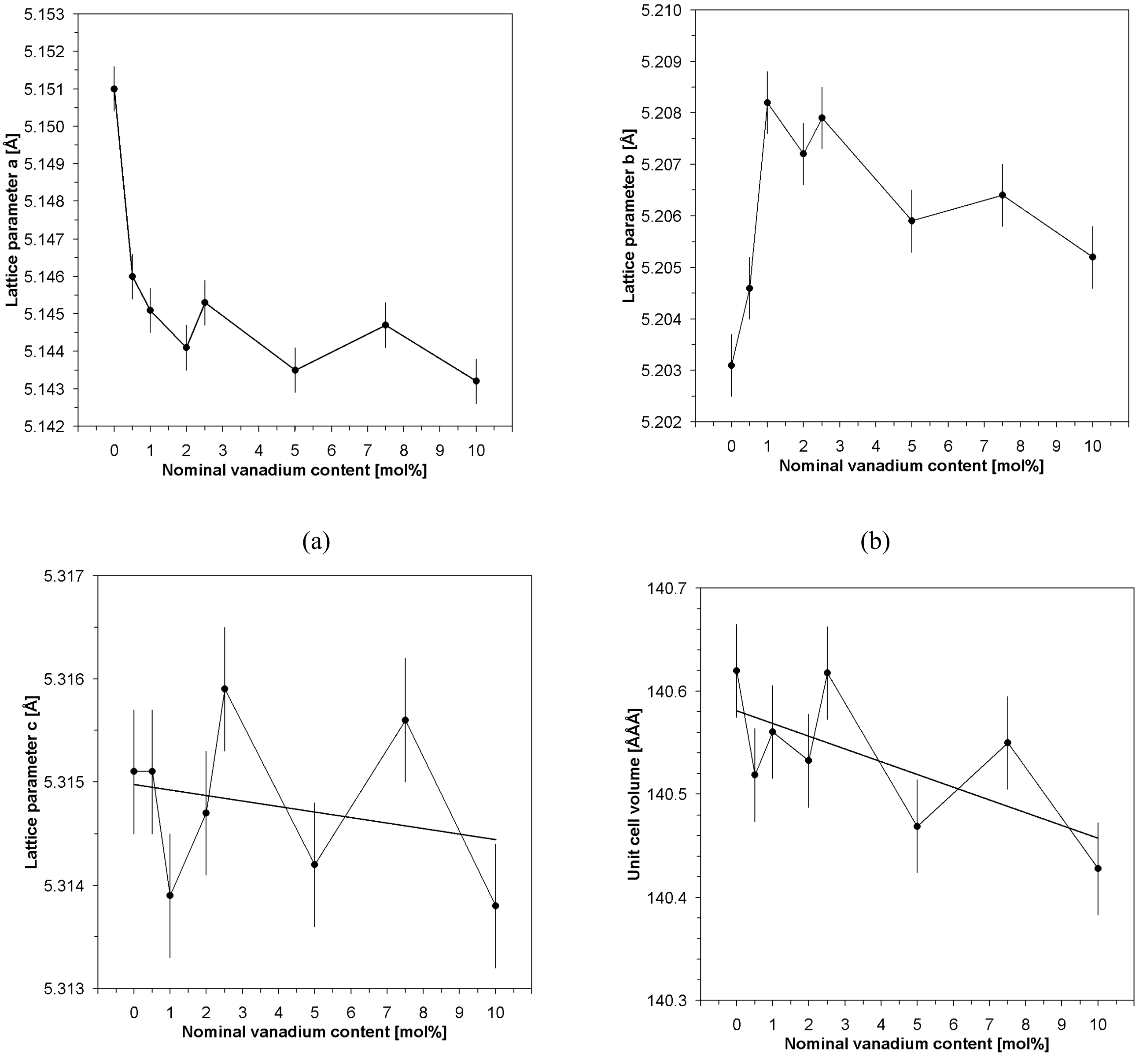


(a)

(b)

(c)

Fig. s3
Dependence on nominal vanadium content of lattice parameters a (a), c (b), and unit cell volume (c) of tetragonal zirconias. The error bars are approximately equal to the triple empirical standard deviation calculated from the results of Rietveld analysis of X-ray diffraction patterns (cf. Table 1).



(a) (b)

(c) (d)

Fig. s4
Dependence on nominal vanadium content of lattice parameters *a* (a), *b* (b), *c* (c, with the trend line) and unit cell volume (d, with the trend line) of monoclinic zirconias. The error bars are approximately equal to the triple empirical standard deviation calculated from the results of Rietveld analysis of X-ray diffraction patterns (*cf.* Table 1).

1.2. Discussion of phase transformations and formation of vanadium-doped zirconias (continuing paragraph 3.5)

The following speculations, although based on the results of the microstructure analysis and leading to interesting conclusions, need to be confirmed by in-situ study of processes of zirconia formation from gel precursors with corresponding transformations between tetragonal and monoclinic phases. On the basis of the above results a correlation between the microstructural characteristics of zirconia phases experimentally obtained and one of the crystallographic model of tetragonal to monoclinic phase transformation is observed.

1.2.1. Tetragonal zirconia

The formation of tetragonal zirconia from gel precursor heated to with a rate of 10K min^{-1} and annealed at temperature 723K during 24 to 48 hours is realised in two parallel processes of nucleation and growth of tetragonal and monoclinic crystallites. This temperature is minimal for initiating the crystallisation [Alarcón, 2001]. Since at such low temperature the long-time annealing is necessary for complete crystallisation of specimens, it is rather the nucleation that dominates, what causes the formation of small crystallites in resulting materials [*cf.* Table 3 and Fig. 5]. The crystallisation of tetragonal phase is more rapid and is realised rather during the end stage of the heating and at the initial stage of the annealing at 723K while that of a monoclinic phase is slower and is realised during the end part of the annealing. It has been reported that prolonged heating of zirconia gels at 773K gives rise to the formation of monoclinic form [Ward *et al.*, 1993]. Likewise, nanosize monoclinic zirconia has been produced by forced-hydrolysis even without any heat treatment [Hu et al., 1999] or after heating at very low temperature [Guo et al., 2005]. On the other hand, the transformation of major part of the monoclinic zirconia into the tetragonal one during cooling ends the process. The contents of both crystalline phases in a specimen at early stages of the crystallisation depend on the chemical composition of the gel precursor and on the thermal treatment. Each resulting specimen contains two fractions of smaller and bigger tetragonal crystallites with corresponding lognormal volume-weighted size distributions (and a rest of about 5 wt% of monoclinic phase). The bigger crystallites that grew immediately as tetragonal have sizes relatively less dispersed around the mean size than the smaller ones. A tetragonal prism with edges parallel to the principal crystal axis is a good model of the prevalent crystallite shape. The addition of vanadium favours the nucleation and anisotropic growth (faster in directions perpendicular to $[001]_t$ axis) of tetragonal crystallites. It results in the increase of second fraction content and in a change of the mean crystallite habit. The shape coefficient Q_t is smallest when the nominal vanadium content in gel precursor is 5 mol%. The crystallites of the biggest standardised size are in the zirconia doped with about 2.5 mol% of vanadium (like in the monoclinic zirconia with 2 mol% of vanadium, the only specimen with 2 mol% of vanadium analysed) and those of the biggest size in directions perpendicular to $[001]_t$ axis are in the zirconia doped with 5 mol% of vanadium; the growth of more equiaxial crystallite results in larger mean crystallite volume. On further increase of vanadium content to 7.5 mol%, less anisotropy of crystallite shape, less second fraction content, larger mean second-order strain, smaller mean crystallite size and smaller unit cell-volume result. It may be interpreted by considering a limit, about 6 mol%, of solubility of vanadium in zirconia; the excess of vanadium in a homogeneous gel precursor probably results in its precipitation in faces of growing crystallites, particularly mostly those perpendicular to the direction of rapid growth, and causes the mentioned effects. The precipitates form rather amorphous glassy phase since no secondary crystalline phase of vanadia was detected.

As stated in the literature, the stabilisation of tetragonal zirconia after cooling zirconia gel precursors is mainly caused by the presence of oxygen vacancies, generated via dehydroxylation and deoxygenation (Chang & Doong 2005; Guo 2004). Also, it has been proved that the tetragonal to monoclinic transformation of ZrO_2 from gels takes place over the span of a few hundred degrees and the start temperature of the transformation depends on the maximum temperature at which gels were heated [Ward *et al.*, 1993]. Taking into account these facts, it is evident that the monoclinic to tetragonal transformation suggested in our model is rather unusual. However, it should be remarked that at these low temperatures very small crystallites of monoclinic zirconias could revert to the tetragonal form.

1.2.2. Monoclinic zirconia

The formation of monoclinic zirconia from gel precursor heated to with a rate of 10K min^{-1} and annealed at temperature 1573K (during 3 hours) is realised in two parallel processes of nucleation and growth of tetragonal and monoclinic crystallites. The crystallisation of tetragonal phase is realised over a temperature range starting above 723K during heating, while that of a monoclinic phase is realised during further heating and annealing at temperature 1573K [Alarcón, 2001; Hanink *et al.*, 2000]. The transformation of entire tetragonal zirconia into the monoclinic one is produced mainly during cooling. Each resulting specimen contains two fractions of smaller and bigger monoclinic crystallites with corresponding lognormal volume-weighted size distributions, with volume ratio about 1:2 (except pure zirconia). The bigger crystallites that had grown as tetragonal and afterwards transformed into monoclinic have sizes relatively less dispersed around the mean size than the smaller ones (except pure zirconia). In pure zirconia the second fraction of crystallites (0.89 of specimen total volume) dominates and the corresponding size distribution is dispersed more than in other monoclinic specimens; the addition of only 0.5 mol% of vanadium causes larger content of the first fraction and much bigger crystallites with less dispersed sizes in both fractions. A parallelepiped with edges parallel to the principal crystal axes is a good model of the prevalent crystallite shape. The addition of vanadium accelerates the nucleation and anisotropic growth of both tetragonal and monoclinic crystallites (faster in direction parallel to $[001]_m$ axis of resulted monoclinic crystallites). It results in a change of the mean crystallite habit. The shape coefficient Q_m is largest when the nominal vanadium content in gel precursor is 5 mol%, while $P_m \approx 1$ (except pure zirconia). The crystallites of the biggest standardised size are in the zirconia doped with 2 mol% of vanadium and those of the biggest size in direction parallel to $[001]_m$ axis (combined with larger size dispersion) are in the zirconia doped with 5 mol% of vanadium; the growth of more equiaxial crystallite results in larger mean crystallite volume. Like in the case of specimens processed at low temperature, when the vanadium content is

7.5 mol% or more, these specimens heated at 1573K (during 3 hours) also show less anisotropy of crystallite shape, larger mean second-order strain and smaller mean crystallite size. It may be interpreted by considering that the limit of solubility of vanadium in zirconia is a little larger than 5 mol%, about 6 mol%. It is to mention that the excess of vanadia at these high temperatures (higher than 973K) melts and most of free vanadia is lost by evaporation; on cooling the rest of excessive vanadia precipitates and solidifies in similar way as the referred above in specimens produced at low temperature and probably remains in cooled specimens as glassy phase.

1.2.3. Tetragonal to monoclinic zirconia transformation

The thermal treatment temperature is the key factor influencing shapes and sizes of crystallites in resulting polycrystalline zirconia specimens. Tetragonal crystallites, after the nucleation at 723K, were annealed during between 24 and 48 hours at 723K in gel precursors for producing tetragonal zirconias. Monoclinic crystallites were obtained by increasing the temperature of gels with the rate of 10 K min^{-1} up-to 1573K for producing monoclinic zirconias. The final monoclinic crystallites may come from a fraction of tetragonal ones (referred to as second fraction), which transform on heating or cooling into monoclinic crystallites and from the crystallites nucleated as monoclinic ones on heating. Hence one can approximately assume that tetragonal crystallites which transform to monoclinic crystallites are similar to those of the second fraction of tetragonal zirconias. It will be demonstrated that there exists a correlation between the microstructural characteristics of vanadium-doped zirconia crystalline phases obtained in the present study and one of several crystallographic model of the $t \rightarrow m$ martensitic transformation. The tetragonal and monoclinic zirconias produced from gels with the nominal vanadium content x= 0.000, 0.025, 0.050 and 0.075 will be compared. The crystallite shape determined from experimental data will be considered as characteristic habits of small crystals in corresponding specimens. The $t \rightarrow m$ transformation is assume to be realised with the axes correspondence $[100]_t \rightarrow [001]_m$, $[001]_t \rightarrow [010]_m$, $[010]_t \rightarrow [100]_m$ and the parallel planes $(010)_t \parallel (100)_m$, as a shear deformation with rotation axis $[001]_t \parallel [010]_m$ (Hannink *et al.*, 2000; Garvie, 1970; Garvie *et al.*, 1975; Hugo & Muddle, 1989; Kelly & Wauchope, 1998; Kisi & Howard, 1998). Since both characteristic habits are defined by ratios $A_{2t}/C_{2t} > 1$ (while $B_{2t} = A_{2t}$) and $C_{2m}/B_{2m} > 1$ (while $B_{2m} \approx A_{2m}$), depending on vanadium content, it is to be assumed that the transformation commences on the entire crystallite face parallel to habit plane $(010)_t$ and is realised through subsequent sections of a tetragonal crystallite at the distance about C_{2t}, involving whole crystallite or resulting in its division into two or three smaller monoclinic crystallites (*cf. e.g.* Hannink *et al.*, 2000). After the transformation monoclinic crystallites grow changing shape to achieve their characteristic habits depending on vanadium content. The correlation of the shape coefficients A_{2t}/C_{2t} and C_{2m}/B_{2m} is demonstrated in Table 6 for the volume-weighted mean crystallite sizes of the second fractions of crystallites and it supports the choice of the considered variant of the martensitic transformation (although is based on a simple model of phenomenon). Some conclusions about different growth velocities in tetragonal and monoclinic phase can be drawn from this observations, but it requires further assumptions and speculations that can be omitted. In pure monoclinic zirconia whole tetragonal crystallites transform into single monoclinic crystallites due to their small sizes, and their shapes changes a little afterwards due to their further little growth.

Table 1 Analysis of prevalent shape of second fraction crystallites from selected tetragonal and monoclinic zirconias, in context of martensitic transformation *t→m* with the axes correspondence $[100]_t \rightarrow [001]_m$, $[001]_t \rightarrow [010]_m$, $[010]_t \rightarrow [100]_m$ and the parallel planes $(010)_t \parallel (100)_m$. The characteristic habit of tetragonal crystallites is defined by the ratio A_{2t}/C_{2t} (when $B_{2t} = A_{2t}$) and the characteristic habit of monoclinic crystallites is defined by the ratio C_{2m}/B_{2m} (when $B_{2m} \approx A_{2m}$), both depending on nominal vanadium content and correlated [*cf.* Table 3 and Table 4].

Second fractions of tetragonal and monoclinic zirconias							
	x	A_{2t}	B_{2t}	C_{2t}	C_{2m}	A_{2m}	B_{2m}
TZV000/MZV000	0.000	405	405	259	548	420	533
TZV025/MZV025	0.025	481	481	274	1531	1343	1354
TZV050/MZV050	0.050	521	521	153	2347	942	973
TZV075/MZV075	0.075	473	473	199	1698	1179	1117

Second fractions of tetragonal and monoclinic zirconias					
	x	A_{2t}/C_{2t}	C_{2m}/B_{2m}	$(C_{2m}/B_{2m})/(A_{2t}/C_{2t})$	A_{2m}/B_{2m}
TZV000/MZV000	0.000	1.56	1.03	0.66	0.79
TZV025/MZV025	0.025	1.75	1.13	0.65	0.99
TZV050/MZV050	0.050	3.40	2.41	0.71	0.97
TZV075/MZV075	0.075	2.37	1.52	0.64	1.06

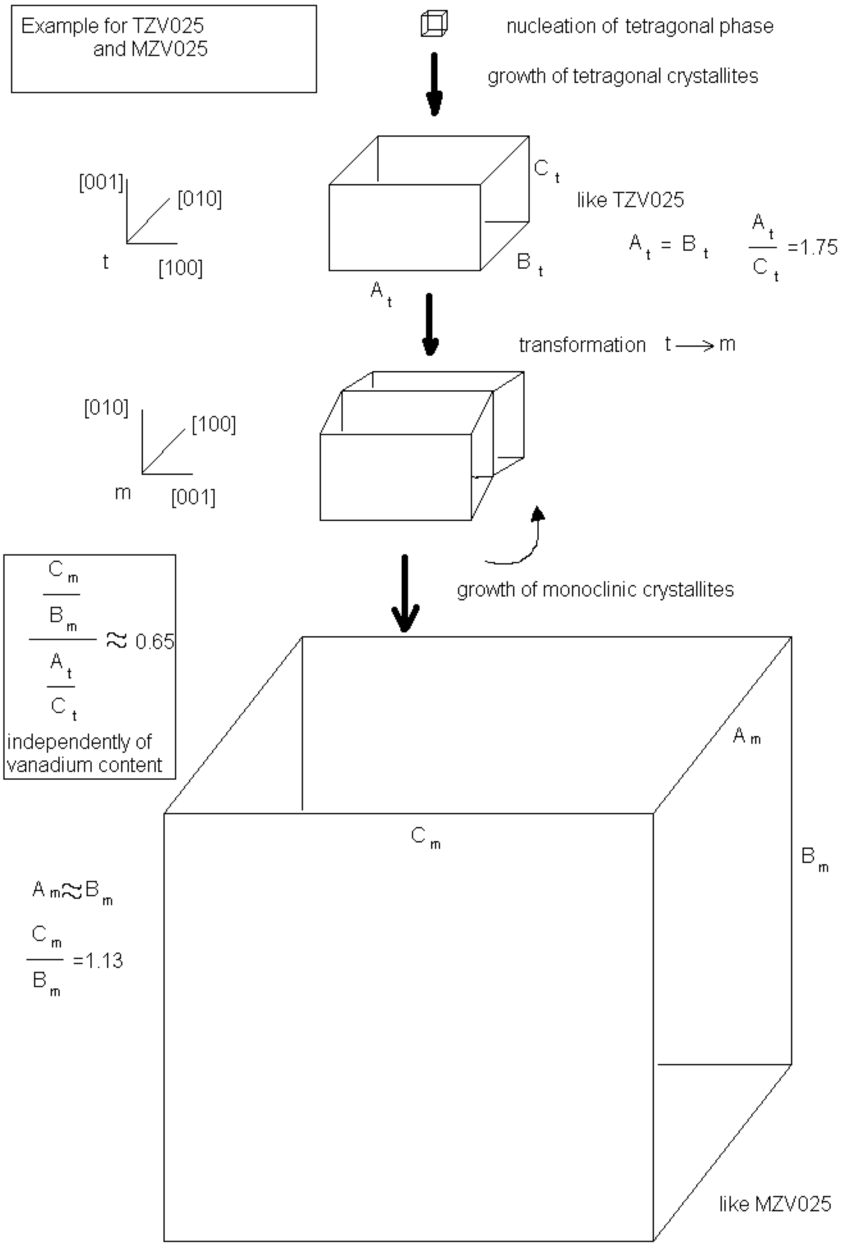


Fig. s5
Idea of possible course of tetragonal to monoclinic zirconia transition reconstructed from microstructure characteristics, particularly from mean volume-weighted sizes and shapes of second fraction crystallites resulted after thermal treatment in samples TZV025 and MZV025.

Fig. s6
TEM micrograph of sample TZV025. Small nanoparticles are of sizes mostly between 200 Å and 400 Å, similarly as individual crystallites (cf. Table 3 and Table 4).

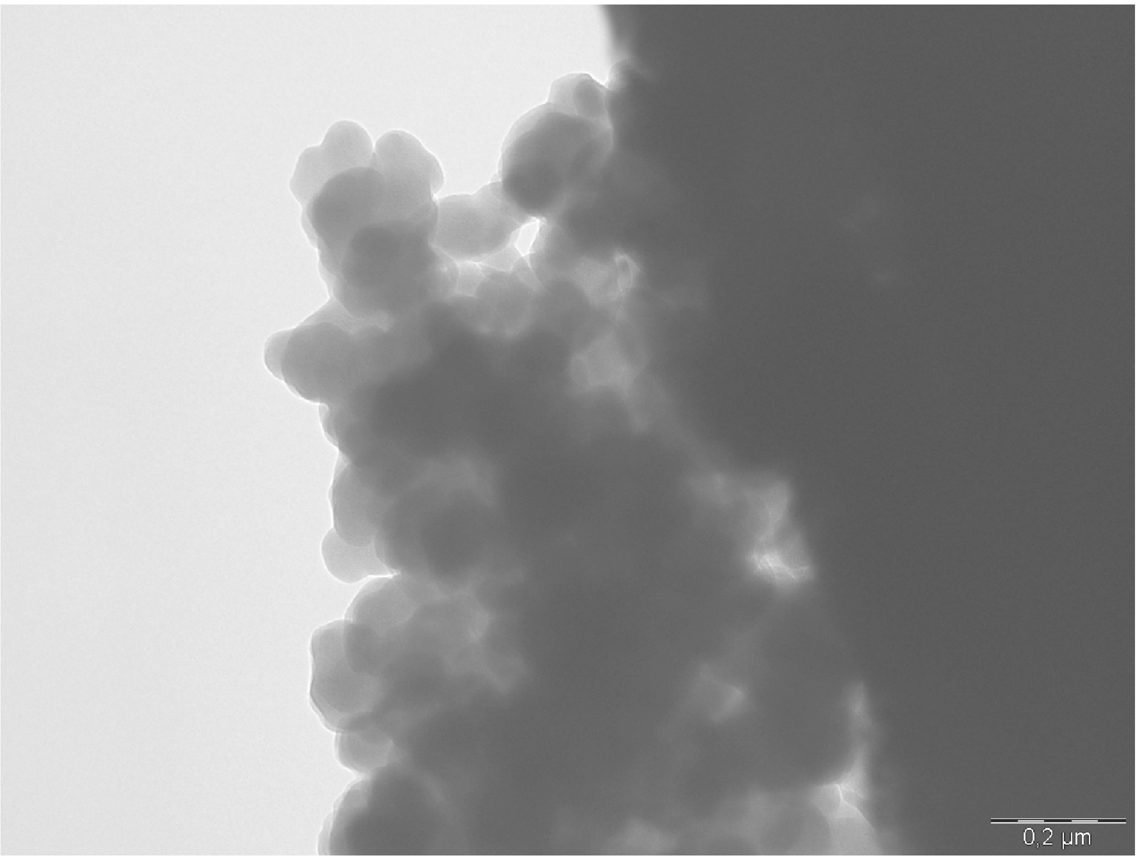


Fig. s7
TEM micrograph of sample MZV020. Small nanoparticles are of sizes mostly between 800 Å and 1600 Å, similarly as individual crystallites (cf. Table 3 and Table 4).

References (supplementary)

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