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The Stabilization of Zirconium Dioxide in the Ternary System CaO–TiO_2–ZrO_2

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Abstract

The subsolidus diagram of the ternary system CaO–TiO_2–ZrO_2 has been determined, then used for the study of the stabilization of zirconium dioxide. It has been found that only three of the eight elementary ternary subsystems are suitable for stabilization: ZrO_2–CaO.ZrO_2–CaO.TiO_2, ZrO_2–CaO.TiO_2–CaO.ZrO_2.2TiO_2 and ZrO_2–ZrO_2.TiO_2–CaO.ZrO_2.2TiO_2. The phase composition at thermodynamic equilibrium has been determined for twelve compositions in these three subsystems. The phases have been determined by X-ray diffraction on samples fired at temperatures in the range 1350–1450°C. It has been found that, for full stabilization of zirconium dioxide, at temperatures under 1450°C, it is necessary to choose compositions in the elementary ternary subsystem ZrO_2–CaO.ZrO_2–CaO.TiO_2. The cubic variety of the resulting zirconium dioxide is characterized by a = *5·10 Å. © 1997 Elsevier Science Limited.*

Man hat das Diagramm subsolidus des ternärischen Systems CaO–TiO_2–ZrO_2 festgesetz und das ist weiterhin fuer das Studium des Prozesses der Stabilisierung des Zirconium Oxides benutzt worden. Man hat bemerkt daß nur drei von den acht ternärischen wesentlichen Subsysteme an die Stabilisierung des Zirconium Oxides empfehlenswert sind: ZrO_2–CaO.ZrO_2–CaO.TiO_2, ZrO_2–CaO.TiO_2–CaO.ZrO_2.2TiO_2 und ZrO_2–ZrO_2.TiO_2–CaO.ZrO_2.2TiO_2. Für die 12 synthetisierte Massen, ist die im thermodynamischen Gleichgewicht mineralogische Komposition festgesetz worden. Man hat das auf die gebrannten Proben um 1350–1450°C ausgefertigte Diagramm subsolidus gewandt. Die reale mineralogischen Komponenten sind durch Roentgen Diffraktion ermittelt worden. Man hat festgestellt daß, zwecks der ganzen Stabilisierung des Zirconium Oxides um Temperaturen unter 1450°C, der Wahl der Massen in dem ternärischen wesentlichen Subsystem ZrO_2–CaO.ZrO_2–CaO.TiO_2 notwendig ist. Die kubische Abart des erhaltenen c-ZrO_2 hat a = *5·10 Å.*

On a etabli le diagramme subsolidus du système ternaire CaO–TiO_2–ZrO_2 qui on a ultérieurement utilisé pour l'etude du procès de stabilisation du dioxyde de zirconium. On a observé que seulement trois parmi les huit subsystemes ternaires élémentaires sont indiqués pour la stabilisation de celui-ci: ZrO_2–CaO.ZrO_2–CaO.TiO_2, ZrO_2–CaO.TiO_2–CaO.ZrO_2.2TiO_2 et ZrO_2–ZrO_2.TiO_2–CaO.ZrO_2.2TiO_2. Pour les 12 masses synthétisées, on a etabli la composition minéralogique a l'équilibre thermodynamique, en utilisant le diagramme subsolidus élaboré. Les components minéralogiques réels ont été déterminé par la diffraction Roentgen sur les échantillons frites aux températures dans le domaine 1350–1450°C. On a constaté que, pour la stabilisation totale du dioxyde de zirconium a la température sous 1450°C, il est nécessaires de choisir les masses du subsystem ternaire élémentaire ZrO_2–CaO.ZrO_2–CaO.TiO_2. Le paramètre du reseau pour c-ZrO_2 obtenu a été a = *5,10 Å.*

1 Introduction

Zirconium dioxide in the pure state cannot be used for the ceramic products, due to reversible polymorphous transformations with hysteresis loop, which it undergoes. These transformations are accompanied by volume variations, which led to cracking during firing. In order to avoid this phenomenon, different oxides are introduced into the lattice of the zirconium dioxide, leading to the stabilization of tetragonal or cubic lattices. One of the oxides most used for this purpose, is CaO[1-4] which in appropriate quantities controls the partial or full stabilization of the zirconium dioxide at temperatures over 1300°C.

Bannister and Barnes[5] have studied the solubility of titanium dioxide in zirconium dioxide and have shown that it is possible that it can be integrated in the lattice as mol 20 mol% by formation of monoclinic and tetragonal solid solutions. These latter are unstable and are eutectoidally split, changing into a monoclinic solid solution and titanium zirconate, so that the presence of the monoclinic solid solution can only be seen by X-ray diffraction at room temperature.

Agrawal *et al.*[6] have studied the ternary system $CaO–TiO_2–ZrO_2$ at a content of 8 mol% CaO and 4–10 mol% TiO_2. By means of diffraction analysis, three types of phase have been found in the samples sintered at 1800°C: c-ZrO_2 which contains 7–10 mol% CaO and 3–7 mol% TiO_2, m-ZrO_2 which dissolved *c*1 mol% CaO and 2–3 mol% TiO_2 and an unknown cubic phase coming from the crystallization of the liquid phase, issued in the sintering process and which contains 20–23 mol% CaO and 19–34 mol% TiO_2. The presence of titanium dioxide in the zirconium composition contributes not only to the achievement on an adequate mineralogic composition, but also exerts a favourable influence upon the tendency to sintering of these masses. Taking into consideration the special importance of the ceramic bodies from zirconium dioxide, the present paper studies its stabilization in the ternary system $CaO–TiO_2–ZrO_2$ in connection with the diagram of thermal equilibrium.

2 The Subsolidus Diagram of the Ternary System $CaO–TiO_2–ZrO_2$

With a view to the development of the subsolidus diagram of this system the known data for binary systems and ternary systems, respectively, were used. Thus, the first diagram of the phase thermal equilibrium of the binary system $CaO–ZrO_2$ was developed by Ruff *et al.*[7] where the presence of a single binary compound $CaO.ZrO_2$ with congruent melting at temperatures over 2300°C is to be observed. A large range of solid solutions of calcium oxide in zirconium dioxide up to 30 mol% is also noticeable. Later on Duwez *et al.*[7] studied the range rich in zirconium dioxide of the same system bringing in very important explanations concerning the formation of the solid solutions, showing that they can be monoclinic, tetragonal or cubic. Noguchi *et al.*,[7] studying the binary system $CaO–ZrO_2$, in the range of high temperatures, confirmed earlier data, but note also the possibility of the coming out of some solid solutions of zirconium dioxide in calcium oxide. In 1968, Garvie[8] studied the diagram of phase equilibrium of this binary system for a content of under 25 mol% CaO, highlighting, besides the calcium zirconate, a new phase, namely $CaO.4ZrO_2$. The possibility of the existence of two polymorphous varieties of this compound is also shown. This diagram has been later on examined by Stubican;[9] on this occasion, the existence of a third compound $6CaO.19ZrO_2$ has been noticed beside the components already mentioned. $CaO.4ZrO_2$ as well as $6CaO.19ZrO_2$ are stable in a very narrow range of temperatures; out of this range they split, changing into the zirconium dioxide and calcium zirconate, which is why they have been neglected in the development of the ternary subsolidus diagram.

Concerning the binary system $CaO–TiO_2$ there are several versions of the diagram of the phase thermal equilibrium. Thus Berejnoi[7] calls attention to the existence of three binary components, namely $CaO.TiO_2$, $2CaO.TiO_2$ and $3CaO.TiO_2$, all of them with congruent melting. Apart from Berejnoi, Coughanour *et al.*[7] and DeVries *et al.*[7] foresee the existence of two binary compounds $CaO.TiO_2$ and $3CaO.2TiO_2$; among them, the first one melts congruently and the second incongruently. In 1958 Roth[7] developed a diagram of thermal equilibrium where he highlights three binary compounds $CaO.TiO_2$, $4CaO.3TiO_2$ and $3CaO.2TiO_2$; amongst these the last two are incongruent in the presence of the liquid phase. In 1970 Jongejan and Wilkins,[7] using a high-temperature microscope, developed a new diagram, confirming the existence of the same compounds mentioned by Roth; for this reason, the diagram has also been used in this paper.

For the binary system $ZrO_2–TiO_2$ there are also several alternatives for the diagrams of phase thermal equilibrium. Thus, the diagram developed by Sowman and Andrews[7] does not contain any component, but foresees only existence of the solid solutions of titanium dioxide in zirconium dioxide and conversely. In the version developed by Brown and Duwez,[7] the existence of a binary compound $ZrO_2.TiO_2$, stable up to about 1800°C, is noted. The existence of a large range of solid solutions of titanium dioxide in zirconium dioxide with a monoclinic and tetragonal structure respectively is noted. Coughanour *et al.*[7] have also studied the diagram of thermal equilibrium of this system, confirming the existence of the beforementioned binary compound. Noguchi and Mizuno[7] have published in 1968 a diagram of the phase thermal equilibrium of this system, which confirms the existence of a single binary compound, zirconium titanate, and highlights the formation of the cubic solid solutions of zirconium dioxide at temperatures over 2300°C. McHale and Roth[10] have re-examined the diagram of the phase

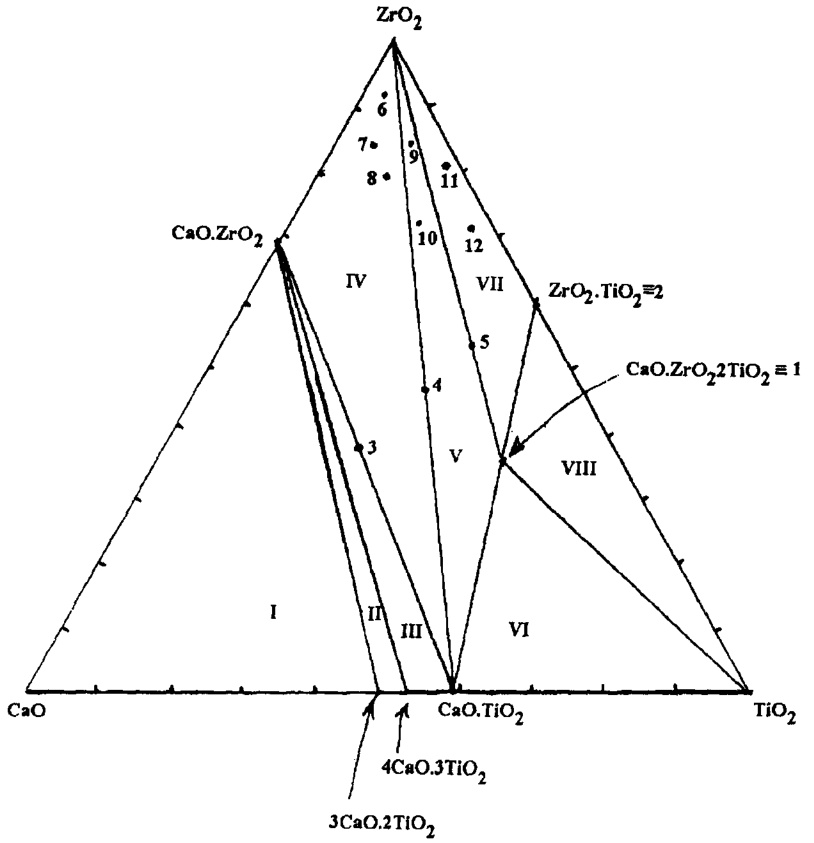

Fig. 1. The subsolidus diagram of the ternary system $CaO–TiO_2–ZrO_2$ and the positions of synthesized compositions in this diagram.

thermal equilibrium and have noted the existence of a second binary compound $ZrO_2.2TiO_2$, which has been highlighted on the occasion of research on some masses yielded by co-precipitation; it is stable only at temperatures under 1200°C and in a very narrow range of compositions, therefore it has not been taken into consideration in the present paper.

Concerning the ternary system $CaO–TiO_2–ZrO_2$ the diagram developed by Coughanour *et al.*,[7] containing four binary compounds ($CaO.TiO_2$, $3CaO.2TiO_2$, $CaO.ZrO_2$ and $ZrO_2.TiO_2$) and a ternary compound ($CaO.ZrO_2.2TiO_2$) is known. The two compounds from the binary system CaO-TiO_2 included in the ternary diagram correspond to two of the compounds published by Roth and Jongejan.

The subsolidus diagram of the ternary system shown in Fig. 1 has been developed on the basis of the presented data and personal experimental research, using a computer program.[11] It consists of eight elementary ternary subsystems, whose percentage of the occupied area is also shown (Table 1). A large weight in this system is noticed for the first subsystem $CaO–CaO.ZrO_2–3CaO.2TiO_2$. In spite of all this, within the subsystem, technical compositions cannot be synthesized, due to the free CaO, which determines the inconstancy of the volume. In order to stabilize the zirconium dioxide, of great importance are the elementary ternary subsystems IV, V and VII, occupying approx. 35% of the surface of the ternary system.

3 Synthesis of the Compositions

As raw materials, calcium carbonate, titanium dioxide and zirconium dioxide of chemical purity have been used; 12 compositions, shown in Fig. 1 have been synthesized. The first five compositions have a special position: 1 and 2 have exact compositions corresponding to the compounds $CaO.ZrO_2.2TiO_2$ and $ZrO_2.TiO_2$; 3,4 and 5 are placed in the binary pseudosystems $CaO.TiO_2–CaO.ZrO_2$, $ZrO_2–CaO.TiO_2$ and $ZrO_2–CaO.ZrO_2.2TiO_2$ All the other synthesised compositions are contained by the three elementary ternary

Table 1. The elementary subsystems of the ternary system $CaO–TiO_2–ZrO_2$

Subsystem number	*Ternary elementary subsystem*	*Area occupied (%)*
I	$CaO–CaO.ZrO_2–3CaO.2TiO_2$	33·48
II	$CaO.ZrO_2–3CaO.2TiO_2–4CaO.3TiO_2$	2·02
III	$CaO.ZrO_2–4CaO.3TiO_2–CaO.TiO_2$	4·88
IV	$ZrO_2–CaO.ZrO_2–CaO.TiO_2$	18·38
V	$ZrO_2–CaO.TiO_2–CaO.ZrO_2.2TiO_2$	9·72
VI	$TiO_2–CaO.TiO_2–CaO.ZrO_2.2TiO_2$	14·98
VII	$ZrO_2–CaO.ZrO_2.2TiO_2–ZrO_2.TiO_2$	6·50
VIII	$TiO_2–CaO.ZrO_2.2TiO_2–ZrO_2.TiO_2$	10·04
	Total	100

subsystems ZrO_2–$CaO.ZrO_2$–$CaO.TiO_2$, ZrO_2–$CaO.TiO_2$–$CaO.ZrO_2.2TiO_2$ and ZrO_2–$ZrO_2.TiO_2$–$CaO.ZrO_2.2TiO_2$ mentioned as very important for the stabilization of the zirconium dioxide. The mixtures of raw materials in the ratio of 1 : 1 : 1 balls: material: water were homogenized in a mill for 6 h. The suspensions were dried at 120°C until constant mass. The powders obtained were uniaxially pressed under 300 MPa pressure at room temperature, with 1 min hold, to form pellets 20 mm diameter with 4–5 mm thicknesses. All these pellets were thermally treated at temperatures in the range 1350–1450°C, for 2 h at the maximum temperature. With a view to establishing the X-ray diffraction spectrum the samples were ground in a zirconia mill where the main acting force was the friction. The X-ray diffraction spectrum was obtained with Cu K_α radiation.

4 Results and Discussion

For all synthesized compositions, the phase composition has been determined by two procedures: in an analytic way on the basis of the developed subsolidus diagram and using a computer program, the results being shown in Table 2, and experimentally by X-ray diffraction, the results being shown in Table 3.

Thus, for composition 1, during the whole range of temperatures studied, the reflections of diffraction specific to $CaO.ZrO_2.2TiO_2$ are only to be seen. Concerning composition 2, for which the molar ratio ZrO_2:TiO_2 is equal to 1 : 1, a more complex behaviour is observed: at a temperature of 1350°C, it has the phase components: m-ZrO_2, $ZrO_2.TiO_2$ and traces of free titanium dioxide. As the temperature increases, the phase composition evolves to the equilibrium component, which is zirconium titanate. Composition 3, beginning from 1350°C, consists of two equilibrium compounds, namely $CaO.TiO_2$ and $CaO.ZrO_2$. The analysis of these masses showed that, in the given working conditions there is possible the formation of the four compounds belonging to the elementary ternary subsystems, which allow the stabilization of the zirconium dioxide. Number 4 and 5 are placed in the binary pseudosystems where the zirconium dioxide may stay free. For 4, which contains at equilibrium a large quantity of $CaO.TiO_2$, peaks corresponding to the cubic solid solution of zirconium dioxide have been noticed over the whole studied range of temperatures. Close by these peaks are the reflections of $CaO.TiO_2$ and the very faint peaks of the m-ZrO_2. This shows that $CaO.TiO_2$ is soluble in zirconium dioxide leading to the stabilization of the latter. For 5, only the diffraction peaks corresponding to m-ZrO_2 and $CaO.ZrO_2.2TiO_2$ have been highlighted over the whole range of temperatures, corresponding to the equilibrium components specific for this mass. It follows consequently that $CaO.TiO_2.2ZrO_2$ is not soluble in the zirconium dioxide and cannot lead to its stabilization.

Compositions 6–12 are placed in the elementary ternary subsystems. Thus, 6–8 are placed in the elementary ternary subsystem ZrO_2–$CaO.TiO_2$–$CaO.ZrO_2$. By X-ray diffraction it has been noticed that 6 has a different behaviour, depending on temperature. Thus at 1350°C it consists only of the monoclinic variety of zirconium dioxide. Over 1400°C, beside this, the cubic variety is noticed, because the two formed compounds $CaO.TiO_2$ and $CaO.ZrO_2$ are soluble in the lattice of the zirconium dioxide. However, quantitatively, these two components are not enough for the full stabilization of the zirconium dioxide. In the case of 7, the presence of only cubic solid solutions, characterized by a = 5·10 Å is noticed over the whole range of temperatures. This can be explained by the presence of an increased quantity of calcium zirconate in the phase composition of this material. For 8, placed in the same subsystem, a more complex behaviour has been observed.

Table 2. The mineralogic composition of the samples at thermodynamic equilibrium, analytically calculated, by framing in the subsolidus diagram of the ternary system CaO–TiO_2–ZrO_2, % weight

Sample	*ZrO_2*	*$ZrO_2.TiO_2$*	*$CaO.TiO_2$*	*$CaO.ZrO_2$*	*$CaO.ZrO_2.2TiO_2$*
1	—	—	—	—	100
2	—	100	—	—	—
3	—	—	43·32	56·68	—
4	47·38	—	52·62	—	—
5	26·71	—	—	—	73·29
6	86·72	—	8·51	4·77	—
7	70·74	—	8·51	20·75	—
8	73·45	—	17·02	9·53	—
9	80·56	—	7·23	—	12·21
10	73·84	—	22·97	—	3·19
11	65·46	16·40	—	—	18·14
12	41·23	34·58	—	—	24·19

Table 3. The composition of samples determined by X-ray diffraction

Sample	*Temperature (°C)*	*m-Z*	*c-Z*	*CT*	*CZ*	*CZT_2*	*ZT*	*T*
1	1350	—	—	—	—	+++	—	—
	1400	—	—	—	—	+++	—	—
	1450	—	—	—	—	+++	—	—
2	1350	++	—	—	—	—	+	t
	1400	+	—	—	—	—	++	t
	1450	—	—	—	—	—	+++	—
3	1350	—	—	++	+++	—	—	—
	1400	—	—	++	+++	—	—	—
	1450	—	—	++	+++	—	—	—
4	1350	t	+++	++	—	—	—	—
	1400	t	+++	++	—	—	—	—
	1450	t	+++	++	—	—	—	—
5	1350	+	—	—	—	+++	—	—
	1400	+	—	—	—	+++	—	—
	1450	+	—	—	—	+++	—	—
6	1350	+++	—	—	—	—	—	—
	1400	+++	+++	—	—	—	—	—
	1450	++	+++	—	—	—	—	—
7	1350	—	+++	—	—	—	—	—
	1400	—	+++	—	—	—	—	—
	1450	—	+++	—	—	—	—	—
8	1350	+	+++	t	—	—	—	—
	1400	+	+++	t	—	—	—	—
	1450	t	+++	—	—	—	—	—
9	1350	+++	—	—	—	+	—	—
	1400	+++	—	—	—	+	—	—
	1450	+++	—	—	—	+	—	—
10	1350	+	+++	—	—	—	—	—
	1400	t	+++	—	—	—	—	—
	1450	t	+++	—	—	—	—	—
11	1350	+++	—	—	—	+	+	—
	1400	+++	—	—	—	+	+	—
	1450	+++	—	—	—	+	+	—
12	1350	+++	—	—	—	+	+	—
	1400	+++	—	—	—	+	+	—
	1450	+++	—	—	—	+	+	—

+++:Most intense X-ray reflections.
++:X-ray reflections of medium intensity.
+:X-ray reflections of weak intensity.
t:Traces.

Thus at temperatures of 1350–1400°C, very intense X-ray peaks, specific for this cubic variety of zirconium dioxide, have been highlighted. Peaks corresponding to the monoclinic variety of this last mentioned and traces of calcium titanate have also been found. At a temperature of 1450°C the m-ZrO_2 is practically found as traces. Numbers 9 and 10 are placed in the elementary ternary subsystem ZrO_2–$CaO.TiO_2$–$CaO.ZrO_2.2TiO_2$. Experimentally, for 9, only the specific diffraction peaks for m-ZrO_2 and $CaO.ZrO_2.2TiO_2$ have been observed over the whole studied range of temperatures. In contrast, in the case of 10, the emergence of the cubic solid solution of the zirconium dioxide is noticed even from 1350°C. This can be explained by the growth in the amount of calcium metatitanate which, by solubility, leads to the stabilization of the zirconium dioxide. The last two compositions are placed in the elementary ternary subsystem ZrO_2–$ZrO_2.TiO_2$–$CaO.ZrO_2.2TiO_2$ and have entirely similar behaviour. Thus only the specific diffraction reflections for the three equilibrium components: m-ZrO_2, $ZrO_2.TiO_2$ and $CaO.ZrO_2.2TiO_2$ are observed over the whole range of temperatures. It follows that, using compositions from this subsystem, the stabilization of zirconium dioxide cannot be realized, because even zirconium titanate is soluble in zirconium dioxide by formation of solid solutions dissociating during the cooling process; the ternary compound $CaO.ZrO_2.2TiO_2$ mentioned earlier is not soluble in the zirconium dioxide and cannot contribute to its stabilization.

5 Conclusions

The following conclusions can be drawn from the results obtained:

(a) Although the subsolidus diagram of the ternary system contains eight elementary ternary subsystems, theoretically, only three of them are suitable to be used for stabilization of zirconium dioxide: ZrO_2–CaO.ZrO_2–CaO.TiO_2, ZrO_2–CaO.TiO_2–CaO.ZrO_2.2TiO_2 and ZrO_2–ZrO_2.TiO_2–CaO.ZrO_2.2TiO_2.

(b) X-ray diffraction studies on thermally treated samples in the temperature range 1350–1450°C have shown that, in practice, the stabilization is possible only for the first two subsystems mentioned .

(c) For full stabilization of the zirconium dioxide under 1450°C, it is necessary to choose compositions in the elementary ternary subsystem ZrO2–CaO.ZrO_2–CaO.TiO_2.

(d) The lattice parameter for the c-ZrO_2 obtained was $a = 5.10$ Å.

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