Laboratory and Computing Methods

ON THE DETERMINATION OF YTTRIUM, CALCIUM, AND MAGNESIUM IN THE ZIRCONIUM COMPOUNDS

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The conditions have been presented for the chelatometric determination of yttrium, magnesium and calcium in the spray-coating materials based on the oxide zirconium compounds after their decomposition by fusion with alkali fluorides and removal of the latter with sulphuric acid evaporated to fumes. Yttrium and calcium are determined chelatometrically after separating them as oxalates at pH = 2.2 ± 0.2 and pH = 4–10, respectively. Both oxalates are decomposed to oxides by fusion with sodium or potassium carbonates in a Pt crucible. The determination of magnesium necessitates masking the traces of zirconium by an α-hydroxyacid and hydrogen peroxide in a NH_4OH-NH_4Cl buffer solution, with eriochrome black T as indicator. The procedures have relative errors of 3.2, 1.4, and 1.2% for yttrium, clacium, and magnesium, respectively, provided that the oxide contents of about 10% are involved.

INTRODUCTION

Zirconium dioxide known in the nature as monoclinic mineral baddeleyite has found wide application in the recents years as the oxide ceramics or in a doped form as material preventing corrosion by the application of the plasma spray technique.

Its physico-chemical properties are dependent on admixtures, particularly on yttrium, magnesium, and calcium, which form mixed crystals with zirconium dioxide.

The varying portion of the covalent bond of the zirconium dioxide polymorphic structures, due to the impurities, affects the lattice dimensions and leads to varying chemical and physical properties, particularly to chemical and thermal resistivity.

This polymorphy is a reason for controversial literature data on the way of transferring zirconium dioxide into the solution to make the chemical analysis possible. Minerals baddeleyite (ZrO_2), zircon ($ZnSiO_4$), and also fused or highly heated mixtures of both cannot be decomposed in a mixture of hydrofluoric acid and conc. sulphuric acid under a normal pressure [1, 2]. American authors [3] were successful in decomposing zircon by heating with conc. sulphuric acid and ammonium sulphate. The acidic decomposition of zirconium dioxide by a mixture of conc. hydrofluoric acid and conc. sulphuric or hydrochloric acids under an enhanced pressure in an autoclave or in sealed glass ampoules [4, 5] is not reliable either.

An effective way of decomposing material based on zirconium dioxide is the fusion. Green [6] points out that not even small amount of zircon can be decomposed by fusion with sodium carbonate, whereas other authors [7, 8] state zircon to be slowly dissolved in a flux of sodium or potassium carbonates to form alkali zirconate. A repeated fusion at 950–1200°C is necessary for the decomposition.

Zircon is effectively fused in a mixture of sodium carbonate or sodium-potassium carbonate with sodium tetraborate in a ratio of 4:1 to 1:3 [9]. The taking up of the flux in water is very slow [10], the alkali zirconate is hydrolyzed [1], and by our experience, a portion of the sample still remains undecomposed. Hoffman [12] and other authors [13] recommend sintration of the zircon sample with sodium peroxide. When fusing materials with alkali disulphate Koleman et al. [4] found zircon and also silica to remain unchanged in the rest. Both elements can be analyzed in a separate way. Smith and James [14] state the only suitable fusing agent for the dissolution of zircon to be potassium hydrofluoride which, being in a four-fold excess, changes into a normal salt by careful heating to the red glow, and which is kept at this temperature for 30 minutes. A longer heating results in a loss of zirconium as zirconium tetrafluoride. The authors [14] dissolve the flux in dilute sulphuric acid and heat in a platinum dish to the fumes of sulphur trioxide to remove the fluorides. A mixture of alkali fluoride with disulphate was suggested in the year as early as 1919 by Powell and Scholler [15] to decompose zircon, monazite, and corundum. Other authors

[16] confirmed this fact for zirconium minerals and suggested to work with alkali fluoride and disulphate at a ratio of 1:10. Sill [17, 18] assumes the fusion with alkali fluoride and disulphate to be highly efficient and useful for a complete dissolution of a non silicate and silicate material, particularly for the elements liable to hydrolysis and capable to form resistent oxides as is the case with protactinium, niobium, and tantalum. On fusion with potassium fluoride the molten mass is treated with conc. sulphuric acid to form pyrosulphate. Silicon is thus simultaneously removed as volatile silicon tetrafluoride under one operation. Sill applies this procedure to the determination of protactinium and of α-rays emitting radium nuclides in soils, flying dust, and uranium ores [19]. The solubilities of trivalent iron salts [$Fe_2(SO_4)_3$] in concentrated sulphuric acid are simultanously studied [20]. The boron fluride compounds such as lithium, sodium, or potassium fluoroborates having the melting points within 400–500°C are efficient fusing agents for the refractories. For the determination of the amount of bivalent iron in the silicate ceramics, sodium metafluoroborate $Na_2B_2O_3F_2$ within 750–1050°C has also proved useful (a mixture of boric acid and sodium fluoride in a ratio of 1:1 [21–23]). For the decomposition of zircon, zircon sands, and baddeleyite concentrates, Borlera [24] recommends a reduction of the sample with carbon powder and subsequent chlorination at 350°C to free the sample from iron in the form of ferric chloride. After an increase of the temperature to 650°C zirconium tetrachloride is distilled off thus making possible the separation of zirconium from hafnium. Thermal decomposition of zirconium dioxide at the temperatures of 1400–1900°C has been examined in paper [25].

EXPERIMENTAL

Chemicals and apparatus

Fusing agents: potassium fluoride, potassium disulphate, potassium hydrogensulphate, lithium fluoroborate, boric acid, sodium fluoride, sodium tetraborate decahydrate, sodium carbonate, potassium carbonate, all of the A.G. purity

Oxalic acid, ammonium oxalate, 5% water solutions

Ammonia (0.91), water solution (1:1)

EDTA, volumetric solution 0.05 mol^{-1}, the factor was determined using the solution of a zinc salt with xylenol orange as indicator.

Lactic acid, 4% solution

Hydrogen peroxide, 5% solution

Tartaric acid, solid

Hexamethylenetetramine, solid

Indicators: xylenol orange, eriochrome black T, fluorexone – all mixtures with NaCl (1:100)

Standard 0.05 M water solutions of Ca^{2+}, Mg^{2+}, Y^{3+}, Zr^{4+} in the form of chlorides.

All the reagents used were of the A.G. purity.

A model solution of Zr^{4+} containing indiferent salts was prepared by fusion of 1 g of ZrO_2 with 4 g potassium fluoride and 8 g of potassium disulphate. Fluorides were removed by evaporation with 16 ml of conc. sulphuric acid to fumes, the cooled down flux was taken up in water and the solution put into a 100 ml volumetric flask. The zirconium content was established by chelatometry [26].

The determination by the AAS method was made using a Varian spectrometer AA-30 and the flame technique in the acetylene-air mode. The wavelenghts of 422.7 μm for Ca and 285.2 μm for Mg were employed.

WORKING PROCEDURES

The examined decompositions involving the fusion methods

1) The decomposition by fusion with potassium fluoride

Approximately 250 mg of the sample is in a Pt crucible fused with a four-fold excess of potassium fluoride at 950°C for a period of 20 minutes. On cooling down, 2g of potassium disulphate is added and the crucible content is shortly heated. Two aliquots of 4 ml of conc. sulphuric acid are gradually added to the cold flux which is then slowly heated till the appearance of the suphur trioxide fumes. The residue in the crusible is taken up in boiling water. The crucible is washed up and the solution is used to establish the contents of Y, Ca, Mg, and, if necessary, of other elements.

2) The decomposition with sodium fluorometaborate

A mixture of 100 mg of the sample, 0.7 g of NaF, and 1.03 g of H_3BO_3 (molar ratio 1:1) is in a platinum crucible heated at 850°C for 20 minutes. After taking up the flux in 75 ml of dilute sulphuric acid (1 $mol.l^{-1}$) in a plastic beaker the solution together with 5 ml of conc. HCl is put in a 100 ml volumetric flask and on adjusting to the mark the solution is used for the determination of the admixtures by the AAS method. If the fluoride ions are necessary to remove from the flux, i.e. in the case of the subsequent chelatometric determination, 4 ml of conc. sulphuric acid is added to the cold flux and the content of the crucible covered with a lid is carefully heated to fumes. The cooled flux in the crucible is taken up in 50 ml of water under a slight heating.

3) The decomposition by means of a mixture of sodium tetraborate and sodium carbonate

A mixture of 100 mg of the sample, 0.8 g of sodium carbonate, and 0.4 g of sodium tetraborate (decahydrate dried at a temperature of 110°C for 2 hours) is fused for a period of 2 to 3 hours at a temperature of at least 850°C. The cooled flux is taken up in 50 ml of 0.5 M HCl.

Procedures for the determination of the admixtures

Determination of magnesium:

The element is determined directly in the extract where no fluoride ions are present. To the solution 2 ml of lactic acid, or 0.25 g of solid tartaric acid and 3 ml of hydrogen peroxide are stepwise added. On adjusting pH with a buffer solution (NH_3/NH_4Cl), magnesium is titrated with the EDTA solution and the eriochrome black T as indicator.

Determination of yttrium:

On extracting the flux, 50 ml of the oxalic acid solution or ammonium oxalate is under boiling added to the solution and the latter is shortly boiled. The pH value is adjusted to 2–3 with ammonia solution or sulphuric acid, and on rapid cooling down the solution is made to pH 2.5 ± 0.2 and let to stand for several hours (preferrably overnight). The precipitated yttrium oxalate is filtered by a filter of small porosity which is then dried, burnt down and again heated. The crucible content is fused with sodium carbonate. The flux is taken up in a 50 ml solution of H_2SO_4 (1:50) under a slight warming. The xylenol orange indicator is added to the still warm solution and the zirconium [4] ions coprecipitated in the form of oxalate are titrated with EDTA. After cooling down and adjusting pH with solid urotropine to 5.5 ± 0.2, the yttrium content is found using the EDTA solution. At the same time a treatment of a reference sample of a known yttrium content is necessary to accomplish.

Determination of calcium:

An excess of oxalic acid or ammonium oxalate is added to the extract solution containing calcium and the acidity is set with ammonia to pH = 5–7. Calcium oxalate thus formed is filtered off, the filter with the precipitate is heated in a Pt crucible and calcium is determined gravimetrically, or the crucible content is fused with potasium carbonate and on taking up the flux in a 50 ml solution of H_2SO_4 (1:50) calcium is determined by titration with EDTA in a potassium hydroxide medium, fluorexone being used as indicator.

RESULTS AND DISCUSSION

On the basis of preliminary results obtained on the zirconium oxide ceramic materials (natural badelleyite, zirconium oxide pure or synthetic doped with 5–40% of yttrium, magnesium, and calcium oxides) we employed the following decompositions:

a) decomposition by potassium fluoride followed by a fusion with alkali pyrosulphate or hydrogen sulphate,

b) fusion with sodium fluoroborate,

c) fusion with sodium carbonate and borax.

Table I

Dependence of the degree of the decomposition of zirconium dioxide, doped with 10% of calcium after a spray-deposition by the plasma burner, on the time of fusion

Fusing agent	Time (min)	Temperature (°C)	Degree of the decomposition (%)
mixture of $Na_2B_4O_7$ + Na_2CO_3	40	850	40
	100	850	95
	150	850	100

All the fusions used are outstanding for a quantitative decomposition of the materials in question. The fusing agents based on fluoride are suitable for the determination of impurities and admixtures where the determination of silicon or zirconium is not required. The separation of silicon proceeds quantitatively, the zirconium losses vary from 50 to 65% of the original content if procedure a) is employed. The interfering effect of the fluoride ions can be during futher treatment of the sample reduced by heating with sulphuric acid to fumes. The only effective decomposition for the determination of silicon is an alkaline fusion with sodium tetraborate. A quantitative decomposition of the zirconium material by fusion with a mixture of soda and borax requires 2 to 3 hours at a temperature of 850°C (Table I). The recommended fusion with alkali carbonates alone is appropriate for very fine powder materials which were not heated higher than 800°C. With samples heated at a higher temperature or with natural baddeleyite the decomposition by carbonates is little efficient or quite inefficient.

Individual ways of the decomposition, however, produce further drawbacks. Procedures a) and b) lead to a complication if, for example, ferric ions are involved, when the removal of fluorides by heating with conc. sulphuric acid to fumes provides a formation of insoluble acidic or neutral anion complexes of ferric salts [20]. In order to verify whether the decompositions are quantitative, we used the zirconium oxide samples with yttrium, magnesium, and calcium admixtures for the determination of the admixed elements both by chelatometry and by the atomic absorption spectrometry (Table II). The grain size of the zirconium samples used for the decomposition was within 40 to 80 μm.

The chelatometric determinations [26–27] were tested on the model samples. The determination of yttrium necessitates a separation of the latter from zirconium oxalate. As follows from Fig. 1 optimum

Table II

Results of the determination of Y_2O_3, CaO, and MgO in ZrO_2

	Admixtures found, weight % (Y, Si, Ca, Mg oxides)			
	chelatometry	gravimetry	AAS-OES	average value
1. ZrO_2 + Y_2O_3 Miletín	7.36, 7.39	–	–	7.38
1. a) vz. 1+1.53% Y_2O_3	8.87, 8.88	–	–	8.88
2. ZrO_2 + Y_2O_3 Miletín	7.00, 7.13	–	–	7.07
2. a) vz. 2+1.61% Y_2O_3	8.60, 8.66	–	–	8.63
3. ZrO_2 + Y_2O_3 Řež	4.47, 4.77 4.56, 4.60	–	–	4.60
3. a) vz. 3+1.57% Y_2O_3	6.18, 6.22	–	–	6.20
4. ZrO_2 + SiO_2		7.41, 7.44	–	7.43
5. ZrO_2 + SiO_2		4.43, 4.41		4.42
6. ZrO_2 + CaO	15.3, 15.40 15.43, 16.30	15.32, 15.60, 15.45, 15.60	15.26 15.40	15.41
7. ZrO_2 + CaO	7.26, 7.34 7.36	7.34, 7.30	7.32 7.29	7.32
8. ZrO_2 + MgO	8.53, 8.57		8.59, 8.57	8.57
9. ZrO_2 + MgO	5.30, 5.33		5.36, 5.38	5.36

conditions for the precipitation of yttrium oxalate lie within pH = 2–3 At pH = 2 the precipitation of yttrium oxalate is not complete, at a higher pH value the dissolution of the latter to an anion complex $[YOx_2]^-$ takes place. A detailed investigation of the dependence of the yttrium oxalate precipitate on the pH value shows that a 100% recovery of yttrium has never been reached, whether the yttrium ions were precipitated alone or along with calcium, as commonly recommended for the rare earths [28]. By comparing the dependence of the degree of the yttrium oxide precipitation from a pure solution and from a solution containing calcium on the pH value we can see that in the presence of calcium the pH range of the yttrium precipitation rises within 2.2–3.2 and the negative error is 2% abs. The precipitate was always contaminated by zirconium oxalate, this fact being not prejudicial to the chelatometric determination, but for accurate analyses the possibility to determine yttrium gravimetrically as oxide is excluded.

The precipitation of yttrium oxalate provides at the defined pH a very good reproducibility and it can therefore be utilized in the quantitative analysis. The result must be corrected by a correction factor comprising a non quantitative precipitation of yttrium oxalate. It is therefore necessary to analyze a reference sample, or at least to establish the chelaton factor for an approximate yttrium content, treated in the same way as the sample to be analyzed.

In the determination of calcium the precipitation of yttrium oxalate is quantitative within a wide range of pH(2.5–10) and the contamination by zirconium oxalate has not been observed. The separation fits the

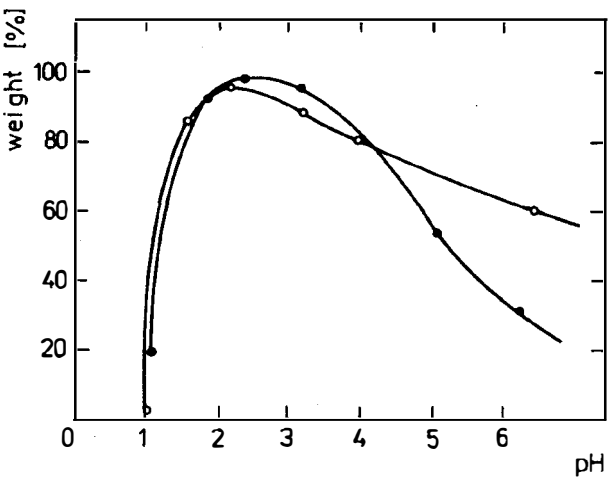

Fig. 1. Dependence of the percentage output of yttrium oxalate on pH. Given: 10 mg Y^{3+} (curve 1), 10 mg Y^{3+} + 10 mg Ca^{2+} (curve 2) precipitated by 50 ml of 5% oxalic acid. V = 150 ml, T = 80° C.

chelatometric as well as the gravimetric determinations. The error of the determinations is not higher than 2% rel.

A direct chelatometric determination of magnesium in the presence of zirconium and masking the latter with hydrogen peroxide is not possible to make because the indicator is blocked by free zirconium ions, and at the increased pH value a hydrolysis and hence a turbidity of the solution takes place. We attained the reliability of the determination of magnesium by masking zirconium by means of α-hydroxyacids (lactic acid, tartaric acid) put in the acidic solution and by subsequent adjustment of acidity with a buffer solution to pH = 10. On adding eriochrome black T as indicator and subsequent titration with a 0.05 M EDTA solution, the color change at the equivalence point is very distinct and unambiguous. The titration must be carried out immediately after adjustment of the acidity, otherwise a decomposition occurs. On the addition of a further portion of the indicator, however, it is possible to reliably put the determination to an end. The presence of only one component of the masking mixture, i.e. of merely hydrogen peroxide or of α-hydroxyacid only does not prevent the indicator from blocking. Using statistical evaluation the following errors of the determination have been found: 3.2, 1.4, 1.2% rel. for yttrium, calcium, and magnesium, respectively.

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PŘÍSPĚVEK KE STANOVENÍ YTRIA, VÁPNÍKU A HOŘČÍKU V OXIDICKÝCH SLOUČENINÁCH ZIRKONIA

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Jsou uvedeny podmínky pro chelatometrické stanovení ytria, vápníku a hořčíku v oxidických sloučeninách zirkonia používaných jako ochranné povlaky nanášené plasmovou technikou. Byly ověřovány tři metody rozkladu

přírodního i syntetického kysličníku zirkoničitého, a to rozklad s fluoridem draselným případně sodným, s fluoroboritanem sodným, a rozklad se směsí čtyřboritanu dvojsodného a uhličitanu sodného. Pro chelatometrické stanovení ytria, vápníku a hořčíku se ukázal jako nejlepší rozklad s fluoridem draselným spojený s odstraněním fluoridových iontů odkouřením s kyselinou sírovou do dýmů. Ytrium a vápník se stanoví chelatometricky po jejich vysrážení ve formě šťavelanů při pH = 2,2 ± 0,2 (ytrium) a pH = 4–10 (vápník) a po rozložení s uhličitanem sodným nebo draselným v Pt kelímku. Hořčík se v roztoku určí rovněž chelatometricky při pH = 10 na eriochromovou černň T jako indikátor. Stopy zirkoniových iontů v roztoku se maskují α-hydroxykyselinou (mléčnou, vinnou nebo citronovou) a peroxidem vodíku. Výsledky získané příslušnými postupy jsou zatíženy relativní chybou 3,2% (Y), 1,4% (Ca) a 1,2% (Mg) za předpokladu, že obsah jejich oxidů je okolo 10%.

Obr. 1. Závislost výtěžku šťavelanu ytritého v % na pH. Dáno: 10 mg Y^{3+} (křivka 1), 10 mg Y^{3+} + 10 mg Ca^{2+} (křivka 2) sráženo 50 ml 5% kyseliny šťavelové, V = 150 ml, T = 80° C.