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SINTERING OF ROSETTA ZIRCON WITH CALCITE

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ABSTRACT

Sintering of zircon with calcium carbonate or oxide was reported to take place completely at temperature range 1400—1500 °C.

This work represents a thermal investigation of sintering of Rosetta zircon with calcite in presence of graphite by using derivatograph. The products of sintering were identified by using a Siemens crystalloflex diffractometer. The process of sintering results in the formation of calcium zirconate $CaZrO_3$ and calcium silicate of composition $3\ CaO \cdot SiO_2$.

INTRODUCTION

Among the minerals of the black sand of Egypt is zircon which is found in an economic amount (7.29%). These sands are found along the Mediterranean coast of Nile Delta. These sands are enriched by gravity concentration methods followed by magnetic and electrostatic separation [ABDEL REHIM, 1974 and ANWAR *et al.*, 1970].

There are different methods of chemical processing of zircon to obtain zirconium oxide [ANWAR *et al.*, 1970; MIRSON *et al.*, 1965 and ZELIKMAN *et al.*, 1964]. These include sintering of zircon with soda, alkali or calcium oxide and hydrometallurgical leaching with alkali solutions. Sintering of zircon with calcium oxide takes place only at 1400—1500 °C. Addition of some components such as $CaCl_2$ and CaF_2 leads to the decrease of temperature of the process [GALKIN *et al.*, 1971; MIRSON *et al.*, 1965 and ZELIKMAN *et al.*, 1964].

Non metamict zircon did not give any thermal reaction. Several data from literatures can be found on the thermal investigations of zircon, calcite and other calcium silicates [EYSEL *et al.*, 1974; FRONDEL, 1953; GALKIN *et al.*, 1971; GARRELS *et al.*, 1960; IVANOVA, 1961; KONDRASHOVA *et al.*, 1952; MACKENZIE, 1964 & 1962.] The thermogram of calcite shows a strong endothermic peak at 880 °C which represents its dissociation to calcium oxide and the liberation of carbon dioxide.

Little is known about the thermal character of reaction of sintering of zircon with calcium carbonate. This work represents a thermal investigation of sintering of Rosetta zircon with calcite in presence of graphite at considerably lower temperature than the temperature range reported earlier by using a derivatograph. Also, it includes a study of the products of sintering by *X*-ray powder diffraction analysis.

EXPERIMENTAL WORK

This work was carried out with zircon, separated from Egyptian black sand. Its chemical, mineralogical and *X*-ray analysis are given in Tables 1, 2 and 3, respectively. The *X*-ray powder data of calcite used in the mix are given in Table 4.

TABLE 1

Chemical composition of zircon concentrate

Chemical components	Content, %
SiO_2	32.40
ZrO_2	64.21
TiO_2	0.73
Fe_2O_3	1.57
Al_2O_3	0.68

TABLE 2

Mineralogical analysis of zircon concentrate

Mineral	Content, %
Zircon	96.70
Rutile	0.45
Ilmenite	0.68
Monazite	0.20
Epidote	0.53
Garnet	0.76
Amphiboles	0.10

TABLE 3

X-ray powder diffraction data of zircon

d(Å) ASTM	*d*(Å) Observed	*I* ASTM	*I* Observed	*hkl*
4.434	4.438	45	65	101
3.302	3.304	100	100	200
2.650	2.653	7	12	211
2.518	2.520	45	65	112
2.336	2.338	10	25	220
2.217	2.223	8	12	202
2.066	2.068	20	45	301
1.908	1.911	14	12	103
1.751	1.752	11	20	321
1.712	1.712	40	60	312
1.651	1.652	14	40	400
1.547	1.548	4	4	411
1.495	1.498	3	2	004
1.477	1.478	8	20	420

As shown from Table 2, contaminants include some ilmenite, rutile, monazite, garnet, amphibole and others in fine grains and in small amounts. Non of the contaminants was detected by *X*-ray analysis, therefore, no individual mineral may be present as a major constituent which is in consistence with the mineralogical data. The total ZrO_2 content in pure zircon should be 67.22%.

TABLE 4

X-ray powder diffraction data of calcite

d(Å) ASTM	*d*(Å) Observed	*I* ASTM	*I* Observed	*hkl*
3.86	3.850	12	12	102
3.035	3.035	100	100	104
2.845	2.840	3	3	006
2.495	2.498	14	16	110
2.285	2.284	18	22	113
2.095	2.095	18	18	202
1.927	1.926	5	6	204
1.913	1.913	17	17	108
1.875	1.875	17	22	116
1.626	1.626	4	4	211
1.604	1.604	8	10	212
1.587	1.586	2	2	1.0.10
1.525	1.524	5	6	214
1.518	1.521	4	4	208
1.510	1.509	3	2	119
1.473	1.472	2	2	215
1.440	1.438	5	6	300
1.422	1.434	3	3	0.0.12

TECHNIQUES OF WORK

Starting materials

Starting materials usually consisted of zircon mixes. Reagents used in mixes are calcite and graphite in particular amounts. Mixes were processed by repeated grinding in an automated agate mortar and sieving till all the powder pass through 200 mesh sieve and pestle for one hour to achieve homogeneity.

Sample container and apparatus

Sintering runs were carried out in ceramic crucibles, heated in an electrical furnace. The character of the reactions of sintering of zircon with calcite in presence of graphite was studied by thermal analysis using F. PAULIK, J. PAULIK and L. ERDEY derivatograph [PAULIK *et al.*, 1966].

This apparatus records simultaneously four thermal curves: (T).the change of temperature of the sample, (DTA) differential thermal analysis, (TG) thermogravimetric (quantitatively in mg) and (DTG) derivative thermogravimetric, on a single sample under controlled conditions. DTA and temperature measuring thermocouples are Pt/Pt-Rh wires. Ceramic crucible and a ceramic sample holder were used. Alumina, calcined at 1000 °C, was used as a reference material. The parameters during tests were as follows: Weight of sample 1 gm, T — 1200, DTA — 1/10, DTG — 1/10, TG — 500 mg and heating rate of 10 °C per minute. All determinations were carried out in air atmosphere under suction of carbon dioxide.

Phase identification and characterization

The end products of zircon sintering with calcite were studied both microscopically and by *X*-ray analysis.

X-ray Procedure

A Siemens Crystalloflex diffractometer was used with nickel filtered copper radiation. Exposure was one hour and scanning speed was 1° 2Θ per minute at 1 cm per minute chart speed. Intensities were collected to maximum $2\Theta = 65°$. The sensitivity of the experiment was 1×10^4 impl./min., and the statistical error was 1.5%.

Chemical analysis of the end product of sintering was carried out for the determination of the efficiency of sintering. Before studying the thermal character of the reaction of sintering of zircon with calcite, a calculation of its thermodynamic constants was estimated. The standard free energy (F°) and the equilibrium constant (K) of the reaction were -20.60 Kcal/mol and 1.29×10^{15}, respectively.

RESULTS AND DISCUSSION

The derivatogram of zircon mixture with calcite of amount 15% of theoretical value and graphite in the suitable amount 15% of zircon charge is shown in *Fig. 1.* The evaluation of the DTA curve of zircon mixture is based on its comparison with that of calcite and other components of the mix. The first small endothermic peak at

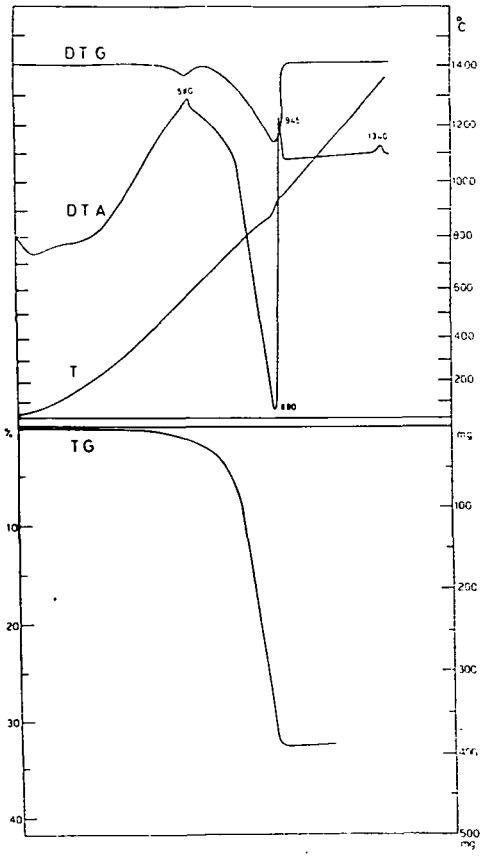

Fig. 1. Derivatogram of zircon sintering with calcite in presence of graphite. Weight of sample 1000 mg. Heating rate 10 °C/min.

70 °C represents the dehydration of the mix. The sharp exothermic peak at 580 °C may be due to the burning of graphite and the combustion of volatiles. This is accompanied by some decrease in weight (TG). The large endothermic peak at 880 °C, represents the intensive dissociation of calcite and the reaction between zircon and the resultant calcium oxide. This process is connected with a remarkable decrease in weight (TG) due to the liberation of carbon dioxide. According to the thermal curve of this mixture, the beginning of sintering and decomposition of calcite follows directly the end of the exothermic reaction.

The exothermic peak at 945 °C may be connected with the reaction between zircon and calcium oxide and probably transition of the resulted calcium silicate to another form. The transition temperature is previously recorded near to this value [EYSE *et al.*, 1974].

There is a small exothermic peak at 1340 °C which is under study and probably due to the congruent melting of resulted sphene, since the temperature of melting of sphene was recorded as 1382 °C.

The *X*-ray powder diffraction pattern shows the first appearance of calcium zirconate and silicate above 700 °C as shown in figures 2 and 3.

The sintering process results in the formation of calcium zirconate and calcium silicate of composition $3CaO \cdot SiO_2$ instead of $CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ as recorded previously [MIRSON *et al.*, 1965 and ZELIKMAN *et al*, 1964]. Their *X*-ray powder diffraction data are given in Tables 5 & 6. The obtained calcium zirconate will be directed for dissolution process using hydrochloric or sulphuric acid for extraction of zirconium.

For studying the effect of temperature on sintering of zircon, some runs were carried out using zircon mixes with calcite and graphite in amount 15% of zircon charge, at temperature ranging from 850 °C up to 1050 °C during 5 hours.

From the obtained results (Table 7), it is shown that the sintering efficiency of zircon sharply increases with temperature. It is observed that nearly complete sin-

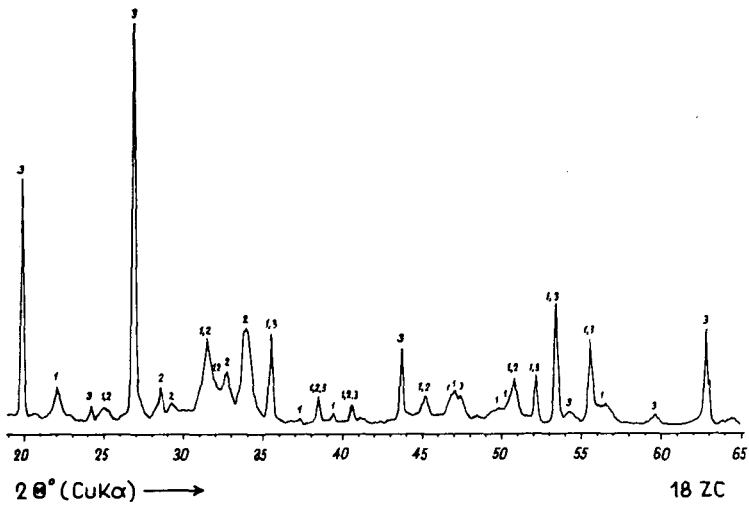

Fig. 2. *X*-ray powder diffraction pattern of the products of zircon sintering at 700 °C
1 — Calcium zirconate
2 — Calcium silicate
3 — Zircon

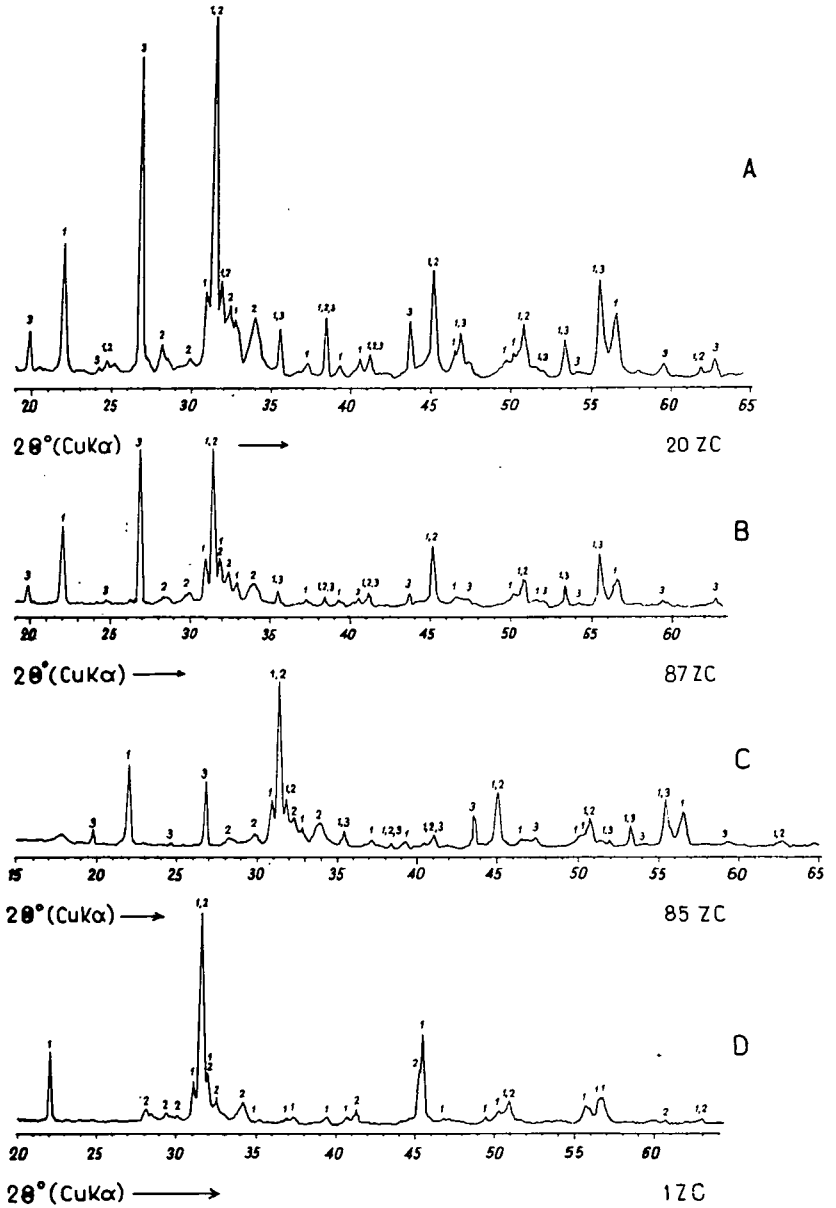

Fig. 3. *X*-ray powder diffraction pattern of the products of zircon sintering with calcite in presence of graphite (A), (B), (C) and (D) at 850, 900, 950 and 1050 °C.
1 — Calcium zirconate
2 — Calcium silicate
3 — Zircon

TABLE 5

X-ray powder diffraction data of calcium zirconate

d(Å) ASTM	*d*(Å) Observed	*I* ASTM	*I* Observed	*hkl*
4.01	4.006	80	90	200, 020
3.58	3.587	40	20	120, 210
2.87	2.872	80	60	$\bar{2}02$
2.83	2.836	100	100	220, 022
2.79	2.794	80	68	202
2.70	2.714	10	28	$\bar{2}12$
2.55	2.547	10	28	$\bar{1}03$, $\bar{3}01$
2.51	2.513	40	25	103, 301
2.43	2.430	40	25	$\bar{1}13$, $\bar{3}11$
2.41	2.409	40	25	131
2.39	2.400	40	25	113, 311
2.33	2.338	20	22	$\bar{2}22$
2.29	2.287	20	111	222
2.22	2.219	40	20	023, $\bar{3}21$
2.13	2.128	10	9	132, 231
2.00	2.002	100	90	400, 040
1.957	1.945	20	22	401, 104
1.939	1.932	40	36	014, 041
1.845	1.839	10	14	$\bar{1}33$, $\bar{3}31$
1.828	1.829	10	13	133, 331
1.811	1.812	40	20	$\bar{2}04$, $\bar{4}02$
1.789	1.792	60	50	024, 042
1,751	1.753	10	9	$\bar{1}42$, $\bar{2}41$
1.727	1.713	10	9	214, 412
1.651	1.651	80	78	$\bar{2}24$, $\bar{4}22$
1.642	1.643	6	6	$\bar{2}42$
1.625	1.628	60	40	242
1.617	1.624	80	50	224, 422
1.498	1.499	40	15	$\bar{2}34$, $\bar{4}32$

tering of zircon (96.6%) takes place at 1050 °C. The products of sintering of these runs were identified microscopically and by *X*-ray diffractometer. By microscopic examination of thin sections of the products of sintering at 850, 900, 950 °C, it is observed that considerable numbers of zircon grains were detected in the runs at 850 and 900 °C. At 950 °C the amount of zircon grains decreases in the sintered product. This gives good idea about incomplete sintering. The product obtained in the run at 1050 °C consists mainly of calcium zirconate and silicate with few fine grains of zircon.

The *X*-ray powder diffraction patterns of these products of sintering at 850, 900, 950 and 1050 °C are shown in *Fig. 3*. Zircon is present in large amounts in the runs A, B and C and its peaks are completely disappeared in the product of run D at 1050 °C. It is observed that the X-ray peaks of zircon are less intense as the temperatures rises. The X-ray peaks of calcium zirconate and silicate are narrow and intense, suggesting good crystallinity.

The microscopic study of the product phases of zircon sintering with calcite is in good agreement with the X-ray powder diffraction patterns.

TABLE 6

X-ray powder diffraction data of calcium silicate ($3CaO \cdot SiO_2$)

d(Å) ASTM	d(Å) Observed	I ASTM	I Observed	*hkl*
3.07	3.090	90	40	201
3.01	3.020	30	15	202
2.84	2.838	70	80	009
2.787	2.794	100	100	204
2.739	2.744	6	10	116
2.649	2.639	100	70	205
2.362	2.365	20	12	207
2.331	2.338	6	7	211
2.303	2.310	4	4	212
2.224	2.220	50	30	119
2.198	2.189	16	22	214
2.006	2.004	12	40	303
1.971	1.986	18	50	210, 010
1.858	1.861	8	14	301
1.830	1.829	2	4	1.1.12
1.789	1.792	55	60	220
1.669	1.678	4	10	309
1.659	1.662	16	30	314
1.575	1.576	10	10	2.1.12
1.537	1.539	4	7	402
1.513	1.516	25	16	229, 318
1.505	1.510	6	6	404
1.482	1.478	12	10	405

TABLE 7

Effect of temperature on sintering efficiency of zircon

Temperature, °C	Sintering efficiency, %
850	56,8
900	67.3
950	83.7
1050	96.6

CONCLUSIONS

From the thermal investigation of sintering of Rosetta zircon with calcite of amount 15% in presence of graphite has revealed that nearly its complete sintering can be reached at 1050 °C. This temperature is distinctly lower than the temperature range reported earlier.

The microscopic and *X*-ray diffraction study shows that the sintering of zircon results in the formation of calcium metazirconate and calcium silicate of composition $CaZrO_3$ and $3CaO \cdot SiO_2$ respectively.

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