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PRODUCTION OF REFRACTORY MATERIAL OF BADDELEYITE AND CORUNDUM

A. M. ABDEL REHIM

ABSTRACT

This work represents a study of the production of refractory material of baddeleyite and corundum from Rosetta zircon. This method is based on sintering of zircon with aluminum fluoride in presence of graphite. The desilication of zircon with the formation of baddeleyite and corundum was found to take place optimally at 850 °C at 1 hour using zircon, aluminium fluoride and graphite mixes of ratio 1:0.8:0.1. Also, the behaviour of zircon was studied under different sintering conditions.

INTRODUCTION

For production of high quality refractory material of baddeleyite and corundum mixture (zirconium and aluminium oxides), zircon is converted into the oxide and then mixed with corundum. The chemical processing of zircon for production of zirconium oxide achieved by different methods (2, 3, 5, 8, 9, 17). These include sintering of zircon with alkali or soda and hydrometallurgical digestion with alkali solutions. Sintering of zircon with aluminum fluoride is a good variant for direct production of refractory material of zirconium and aluminum oxides.

The fluorinating action of fluorine, fluorides and hydrogen fluoride are well known and the solid fluorinating agents are very important, since they have many advantages (6, 7, 10—12). The desilication of Rosetta zircon with aluminum fluoride in presence of graphite was previously investigated by thermal analysis (1). The DTA curves show a sharp exothermic peak at 580 °C, representing the burning of graphite with little formation of aluminum silicon fluoride. The endothermic peak at 820 °C represents the intensive desilication of zircon with aluminum fluoride and the volatilization of silicon tetrafluoride. The desilication results in the formation of baddeleyite and corundum which are suitable as high quality refractory material (1, 7—9, 12, 15, 17).

This work represents a study of the behaviour of Rosetta zircon during sintering under different conditions and the influence of different factors acting upon sintering. The optimum conditions of production of this refractory material of baddeleyite and corundum were determined.

EXPERIMENTAL WORK

This research was carried out with zircon concentrate separated from the Egyptian black sands. Its chemical and mineralogical composition are given in tables (1) and (2) respectively. It is seen that the concentrate contains some mineral impurities with which zircon is genetically connected as rutile, monazite, garnet and

others. They are present as fine grains and in small quantities. Non of these mineral impurities was detected by X-ray analysis. Hence, no individual mineral may be present as a major constituent and which is consistent with the mineralogical analysis data.

TABLE 1

Chemical composition of zircon concentrate

Chemical component	Content (%)
ZrO_2	62.73
SiO_2	32.65
Fe_2O_3	1.64
TiO_2	1.23
ThO_2	0.05
RE_2O_3	0.31
Al_2O_3	1.12
P_2O_5	0.22

TABLE 2

Mineralogical composition of zircon concentrate

Mineral	Content (%)
Economic Minerals:	
Zircon	94.81
Rutile	1.12
Ilmenite	0.47
Monazite	0.81
Magnetite	0.40
Gangue Minerals:	
Epidote	0.96
Glauconite	0.25
Garnet	1.10
Feldspars	0.15
Amphiboles	0.10

Mixes of zircon concentrate, aluminum fluoride and graphite in particular amounts were ground in an automated agate mortar and sieving till all the powder pass through 0.07 mm sieve and pestle for one hour to achieve homogenity. Sintering experiments were carried out in platinum crucibles heated in an electrical tube furnace under removal of volatilized silicon tetrafluoride. The temperature is regulated automatically with accuracy ± 10 °C. The duration of every run was considered from the moment of reaching the particular temperature.

X-Ray Procedure

The end products of zircon sintering at the optimum conditions were examined by X-ray powder diffraction analysis using a Siemens Crystalloflex diffractometer. The finely ground sintering product was mixed with sodium chloride as a standard. Its peaks occuring at $2\Theta = 31.38°$ and 45.44° were used for corrections. Nickel filtered copper radiation was used. Exposure was one hour. Scanning speed was 1° 2Θ per

minute at one cm per min. chart speed. Intensities were collected to maximum $2\Theta = 65°$. The sensitivity of the experiment was 4×10^4 impl./min and the statistical error is 1.5%.

Efficiency of desilication and sintering of zircon

The efficiency of sintering and desilication of zircon was determined by the amount of silica removed with respect to that in the initial zircon concentrate. The end product of sintering was chemically analysed for its silica content by Riley method and by activation analysis.

Determination of thermodynamic constants

Before studying the conditions of desilication of zircon with aluminum fluoride, an attempt was carried out for calculation of its thermodynamic constants. The thermodynamic data given in Table 3 were used in calculation.

TABLE 3

Thermodynamic data used

Thermodynamic function	Value, Kcal/mol	Reference
$\Delta F°$ Corundum (c)	−378.2	(16, 18)
$\Delta F°$ ZrO_2 (c)	—244.4	(13, 16)
$\Delta F°$ AlF_3 (c)	—294.0	(14)
$\Delta F°$ SiO_2 (c)	—192.4	(13, 14)
$\Delta F°$ SiF_4 (g)	—360.0	(13)

The free energy of zircon can be calculated from the following reaction:

$$ZrSiO_4 \rightarrow ZrO_2 + SiO_2$$

At equilibrium conditions,

$$\Delta F°_{reaction} = \Delta F°_{ZrO_2} + \Delta F°_{SiO_2} - \Delta F°_{ZrSiO_4} = 0$$

$$= -244.4 - 192.4 - \Delta F°_{ZrSiO_4} = 0$$

$$\Delta F°_{ZrSiO_4} = -436.8 \text{ Kcal/mol.}$$

The reaction of sintering of zircon with aluminum fluoride may be represented as:

$$3\,ZrSiO_4 + 4\,AlF_3 \rightarrow 3\,ZrO_2 + 2\,Al_2O_3 + 3\,SiF_4$$

The standard free energy of the reaction:

$$\Delta F°_{reaction} = 3\Delta F°_{ZrO_2} + 2\Delta F°_{Al_2O_3} - 3\Delta F°_{SiF_4} + 3\Delta F°_{ZrSiO_4} - 4\Delta F°_{AlF_3}$$

$$= -733.2 - 756.4 - 1080 + 1310.4 + 1176$$

$$= -2569.6 + 2486.4 = -83.2 \text{ Kcal/mol.}$$

The equilibrium constant of the reaction of desilication of zircon may be calculated from equation at 25 °C:

$$\log K = \frac{-\Delta F^\circ}{4.575 \times 298} = -0.000733 \Delta F^\circ$$

$$= 0.000733 \times 832000 = 60.986$$

$$K = 9.68 \times 10^{60}$$

The equilibrium constant is very large and the reaction of desilication of zircon with aluminum fluoride may be practically considered as irreversible.

RESULTS AND DISCUSSION

The essential factors, which have a considerable influence on sintering of Rosetta zircon with aluminum fluoride in presence of graphite can be grouped as:
1 — Influence of graphite and its amount.
2 — Influence of the amount of aluminum fluoride.
3 — Influence of temperature and time.

1 — Influence of graphite and its amount

For studying the influence of graphite and its amount on desilication of zircon, a series of experiments were carried out using zircon mixes with aluminum fluoride, containing different amounts of graphite at ratio of zircon: graphite = 1:0.05, 0.1, 0.15 and 0.2, at 850 °C during 1 hour.

From the obtained results *(Fig. 1)*, it is shown that the desilication efficiency of zircon sharply increases with the amount of graphite, corresponding to ratio zircon: graphite = 1:0.1. Above this value, the efficiency decreases. Also, the desilication efficiency of zircon increases with the amount of aluminum fluoride corresponding to ratio of zircon: aluminium fluoride = 1:0.8 to 1:0.9.

It is observed that the addition of graphite in a suitable amount (at ratio of zircon: graphite = 1:0.1) in zircon mixes accelerates its desilication.

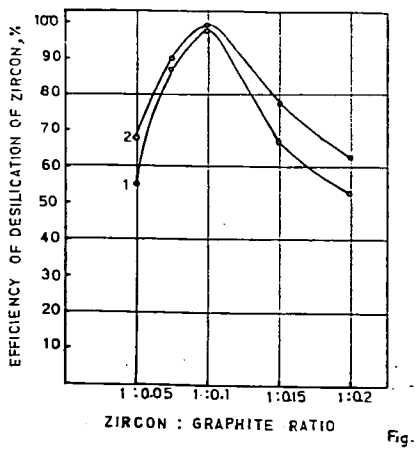

Fig. 1

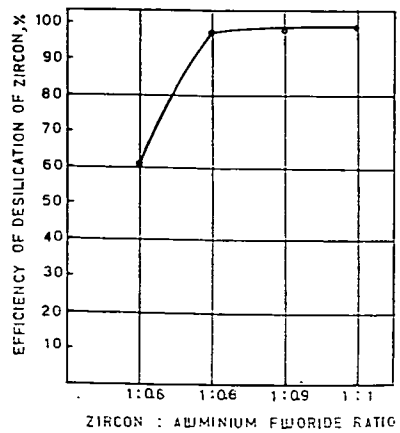

Fig. 2

2 — Influence of the amount of aluminum fluoride

For determination of the optimum amount of aluminum fluoride, at which complete desilication of zircon takes place, sintering was carried out using different amounts of aluminum fluoride corresponding to ratios of zircon : aluminum fluoride = 1:0.6, 0.8, 0.9 and 1:1, at 850 °C during 1 hour.

As shown in *Fig. 2*, the desilication of zircon sharply increases with the amount of aluminum fluoride at ratio of zircon : aluminum fluoride = 1:0.6 to 1:0.8. Beyond this value, any increase in the amount of aluminum fluoride has little effect on desilication of zircon.

From the results obtained, the optimum amount of aluminum fluoride can be considered as amount corresponding to ratio of zircon : aluminum fluoride = 1:0.8.

3 — Influence of temperature and time

To study the influence of both temperature and time on desilication of zircon, sintering experiments were carried out at fixed amount of aluminum fluoride and graphite, (corresponding to ratio of zircon : aluminum fluoride : graphite = 1:0.8:0.1) at temperature 600°—1100 °C during 1 hour and at 850° and 900 °C for duration 20—90 min.

From the obtained results *(Fig. 3* and *4)*, the following conclusions may be drawn:

1. In general, as the temperature increases, the desilication efficiency of zircon increases with time.
2. The sharp increase of desilication efficiency of zircon is observed as the temperature increases up to 800 °C, after that the desilication of zircon gradually increases. Above 900 °C, the temperature has no effect on the efficiency of sintering.

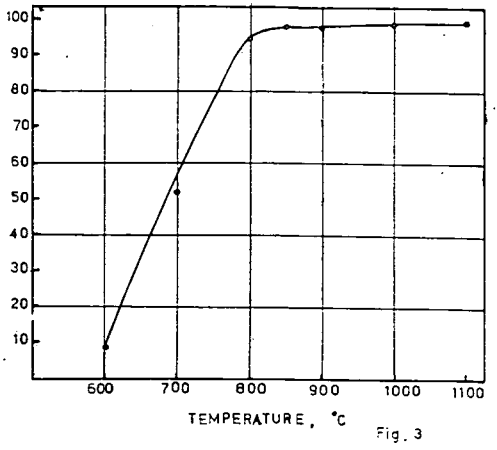

Fig. 3

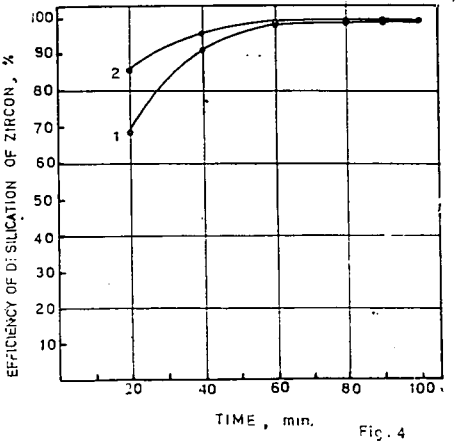

Fig. 4

3. At short time of sintering, the desilication of zircon is low. This is due to the fact that the reaction of sintering of zircon with aluminum fluoride takes place in solid state. This needs a long time for contact of solid reactants and also their preliminary complete mixing.

4. At 850°—900 °C, complete desilication of zircon takes place during 1 hour. Longer time more than 1 hour has little effect on desilication of zircon, i has some influence on the growth of the crystalline products of sintering, namely baddeleyite and corundum.

From the results obtained, the optimum temperature, at which complete desilication of zircon occurs, can be considered as 850 °C at duration 1 hour.

Study of the products of desilication of zircon with aluminum fluoride

The reaction of sintering of zircon with aluminum fluoride in presence of graphit results in the formation of baddeleyite and corundum.

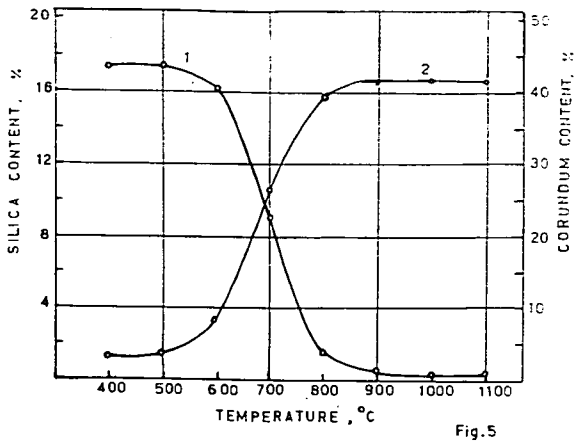

Fig.5

From *Fig. 5*, it is shown that the amount of combined silica in the chemical composition of zircon sharply decreases in the product of sintering as the temperature increases. It is observed that the desilication of zircon takes place intensively above 650 °C. Its complete desilication occurs at 850 °C, where the silicon content of the end product of sintering shows a minimum value.

Formation of corundum

The relation between the corundum content in the product of sintering and the temperature is shown in *Fig. 5*. It is observed that the amount of corundum sharply increases as the temperature increases from 600° to 800 °C. Above 850 °C, it reaches a constant value and the reaction of corundum formation takes place completely.

Formation of baddeleyite

Fig. 6 shows the relation between zircon content in the initial mix and baddeleyite content in the sintering product and temperature. The amount of zircon sharply decreases (opposite case, baddeleyite) at temperature range 600°—800 °C. At 850 °C, the amount of baddeleyite reaches a high value and there is no change of its content at higher temperature. At the same time, the zircon content reaches minimum. By

microscopic examination of thin sections of the end product of sintering at 850 °C, it is observed that only few relict zircon grains are detected. The whole mass of the section consists of baddeleyite and corundum.

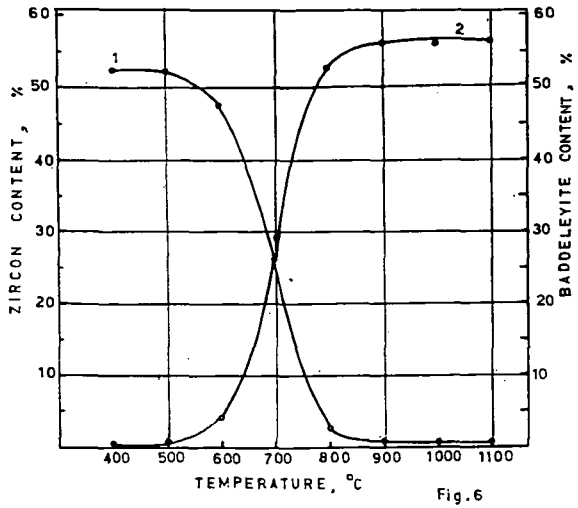

Fig.6

The product of zircon sintering with aluminum fluoride were studied microscopically. The product obtained at 650 °C consists mainly of zircon with few corundum and baddeleyite grains. At 700 °C, it is composed of zircon and baddeleyite-corundum

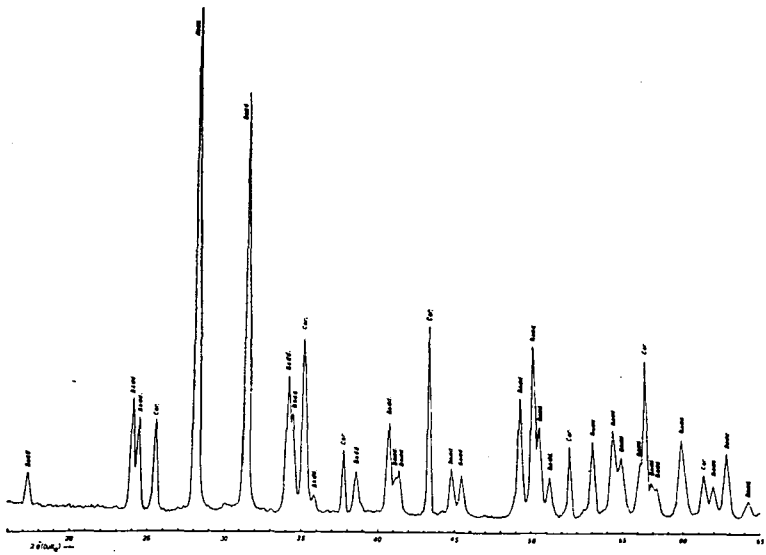
Fig. 7.

in approximately equal amounts. As the temperature increases, the amount of zircon decreases, till it reaches minimum. At 850°—900 °C, baddeleyite and corundum constitute the total composition of the end product of sintering with few fine relict zircon

grains. Baddeleyite and corundum show simultaneous crystallisation. They have different crystal forms, elongated, tabular, rounded and irregular form. Corundum appears colourless, with very high relief, non cleavage, moderate birefringence and optically uniaxial negative. Some grains show striations.

Baddeleyite appears pale yellow, with high relief, showing poor cleavage and optically biaxial negative.

The grain size of the obtained refractory material depends upon temperature and time of sintering. At 850 °C, and 1 hour, the grain size ranges 0.05—0.15 mm.

The X-ray diffraction patterns of the end product of sintering *(Fig. 7)* shows only the peaks of baddeleyite and corundum. They are intense and narrow, suggesting good crystallinity. Zircon peaks are completely disappeared, indicating its absence.

The unit cell dimensions and constants of the artificial baddeleyite and corundum are given in Table 4. Baddeleyite ctystallises in monoclinic system, while corundum crystallises in hexagonal system. It is observed that the calculated cell dimenisons, constants and optic axial angles of the synthetically formed baddeleyite and corundum are consistent with the corresponding data of the natural minerals.

TABLE 4

Unit cell dimensions and axial angles of baddeleyite and corundum

Mineral	No. of lines used	a	b	c	α	β	γ	V
		Å	Å	Å	deg. min.	deg. min.	deg. min.	Å^3
Baddeleyite (Monoclinic)								
Synthetic	23	5.2458 ±0.0611	5.2030 ±0.0769	5.2849 ±0.0722	90 0.00	80°48' ±1.051	90 0.00	142.26 ±0.01
Standard		5.26	5.21	5.37	90	80°36'	90	
Corundum (Trigonal)								
Synthetic	8	4.7424 ±0.0109	4.7424 ±0.0109	12.9807 ±0.0209	90 0.00	90 0.00	120 0.00	252.83 ±0.004
Standard		4.751	4.751	12.98	90	90	120	

The behaviour of zircon has been studied under different sintering conditions with aluminum fluoride in presence of graphite. It is found that the sintering process results in the production of monoclinic baddeleyite and hexagonal corundum.

Rosetta zircon is optimally desilicated with the formation of baddeleyite at 850 °C and time 1 hour, using zircon mixes with aluminum fluoride and graphite at ratio 1:0.8:0.1, respectively. Under these conditions, the efficiency of desilication of zircon reaches 98.8%. The end product of sintering (with silica content 0.37%) is a refractory material of zirconium and aluminum oxides, which is useful for many industrial purposes.

REFERENCES

ABDEL REHIM A. M. [1974]: Desilication of zircon with aluminum fluoride in presence of graphite. Thermal Analysis, Vol. 1, Proceedings of the Fourth Internat. Conf. Therm. Analysis, Budapest, p. 523—539.

ANWAR Y. M., ABDEL REHIM A. M. [1972]: High pressure hydrometallurgy of alkaline leaching of Egyptian zircon. Bull. Fac. Sci. Alex. Univ., Vol. **10**, p. 173—193.

BENEDICT, M., PIGFORD, T. H. [1957]: Nuclear Chemical Engineering. McGraw Hill Book Co. Inc., New York, London.

EVANS, H. I., JR. D. E. APPLEMAN, HAND-WERKER, D. S. [1963]: The least squares refinement of crystal unit cell with powder diffraction data by an automatic computer indexing methods. Annu. Meet. Amer. Crystallogr. Soc., Cambridge, Mass Program. p. 42.

FARAH, M. Y., EL-YAMANI, S. I. [1963]: On alkaline sintering of Rosetta zircon. Thirty Fourth Internat. Cong. Indust. Chem., Beograd, 1963.

JOLLY, W. L. (Ed.) [1965]: Preparative Inorganic reactions. Inter. Science Publishers, New York, London, Sydney.

LAINER A. I., BORISOV, G. B., MIRKIN, L. V. [1968]: Izv. Vish. Utsh. Zav., Nonferrous Metallurgy, N. 5, p. 45—48.

LUSTMAN, B., KERZE, F. [1955]: Metallurgy of Zirconium. McGraw-Hill Book Co. Inc, New York.

MIRSON, G. A., ZELIKMAN, A. N. [1965]: Metallurgy of Rare Metals. Metallurgizdat.

OLSHANSKY, YA. I. [1958]: On the interaction between silica and metal fluorides. (Trans. Fifth Conf. Exp. Techn. Min. Petr.), Public. Acad. Sci. USSR, p. 114—118.

OPALOVSKY, A. A., FEDOROV, V. E., FEDOTOVA, I. D., [1973]: Reaction of alkali and ammonium bifluorides with aluminum and silicon. Jour. Therm. Analysis, Vol. 5, p. 475—482.

QUERESHI, M. H., BRETT, N. H. [1968]: Phase equilibria in ternary system containing zirconia and silica, II. The system Al_2O_3—ZrO_2—SiO_2 Trans. Brit. Ceram. Soc., N. 67, p. 569—578.

ROBERT C. WEAST *et al.* [1972]: Handbook of chemistry and physics. The Chemical Rubber Co., 51st Edition.

ROBIE, R. A., WALDBAUM, D. R. [1968]: Thermodynamic properties fo minerals and related substances at 298.15 °K (25 °C) and 1 atm. U. S. Geol. Surv. Bull., N. 1259, p. 255.

TAUBER, E., JAMES, R. J. [1971]: Zircon and its uses. Jour. Austral. Ceram. Soc., N. 7, p. 27—33.

WAGMAN, D. D., EVANS, W. H., PARKER, V. B., HALOW, I., BAILEY, S. M. and SCHUMM, R. H. [1968]: Selected Values of Chemical Thermodynamic Properties. U. S. Nat. Bur. Stand. Techn. Note 270—3, p. 264.

ZELIKMAN, A. M., SAMSONOV, G. V., KRAIN, O. E. [1964]: Metallurgy of Rare Metals. Izdatelstva Metallurgia, M.

ZEN E-AN [1973]: Gibbs free energy, enthalpy and entropy of ten rock forming minerals. Calculations, Descriptions, Implications. Amer. Min., v. 57, p. 524—553.

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A. M. ABDEL REHIM
Dept. of Geology, Alexandria
University, Alexandria
Egypt