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# Aluminium titanate formation by the gas-phase hydropyrolysis method

W. F. KLADNIG
*Maschinenfabrik Andritz AG, Ruthner Division, Forschungszentrum, A-1120 Wien, Eibesbrunnergasse 20, Austria*
H. MAYER
*Institut f. Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, A-1060 Wien, Getreidemarkt 9, Austria*

A novel process of aluminium titanate formation by thermal decomposition of an aqueous nitric-hydrofluoric solution containing stoichiometric amounts of aluminium and titanium is described. The solution is decomposed by spraying it into a heated reactor with subsequent oxide formation and recycling of the corresponding nitric and hydrofluoric acids by means of an absorption system. The oxides formed were mostly amorphous, in a fine dispersed, homogeneously distributed form of highly reactive state. X-ray (RDA) analysis showed crystalline forms of $TiO_2$ (anatase), complex titanium oxides, such as $Ti_3O_5$, $Al_2TiO_5$ (tialite) and AlO(OH) (boehmite). Complete formation of tialite from this oxide mixture was studied by thermogravimetry, differential thermogravimetry and differential thermal analysis. RDA of compounds formed after the successive and stepwise heating of this powder in a muffle helped in the understanding of tialite formation. The reaction was found to be time dependent and to be completed at 1400° C. Decomposition of the tialite formed into $Al_2O_3$ (corundum) and $TiO_2$ (rutile) was observed in the temperature range 900 to 1070° C.

## 1. Introduction

Aluminium titanate (tialite), formed by the reaction of $Al_2O_3$ and $TiO_2$, has gained considerable attention as a fine ceramics material, mostly in automotive engineering. Its excellent thermoshock resistance, in particular, makes it a very valuable material for application in refractories and in metallurgy. Several reviews on aluminium titanate formation have been published [1-4].

The usual means of production is by solid-state reaction from $Al_2O_3$ (corundum) and $TiO_2$ (anatase or rutile) powders according to the equation

$$Al_2O_3 + TiO_2 \rightarrow Al_2TiO_5 \text{ (tialite)}$$

Its formation is, in fact, a very complex process, strongly dependent on time and temperature.

Publications presenting these reaction pathways give very diverse information on the reaction conditions [1, 4]. The reaction by which a dense material is formed through a solid solution seems to be completed at temperatures from as high as 1500 to 1600° C, after a prolonged reaction time of up to 10 h. $Al_2TiO_5$, aluminium titanate, is a polycrystalline substance that exists in two forms, $\alpha$ and $\beta$ (tialite), the first only being stable at temperatures higher than 1820° C. The crystal structure of tialite is orthorhombic Cmcm [4, 5].

The process described here is a novel method of making tialite powder for ceramic processing. It basically consists in forming an aqueous solution of appropriate salts which is thermally decomposed by spraying it into a heated reactor system. This process, also called hydropyrolysis or spray-roasting, has been applied successfully in a number of cases for production of pure and mixed oxides [6]. This method of producing aluminium titanate is a novel application in industrial ceramics and is published here for the first time [7].

## 2. Experimental details

### 2.1. Materials

The materials used were $Al(NO_3)_3 \cdot 9H_2O$, p.a. grade, and titanium scrap, purest grade (min. 99.7%). The titanium metal was dissolved in 300 g $HNO_3\,l^{-1}$ (26%) and 50 g $HF\,l^{-1}$ (5%). In place of an aluminium salt, aluminium metal (scrap) has also been used.

50 l of this solution containing stoichiometric (1 : 1) amounts aluminium and titanium, i.e. 23.14 g $Al\,l^{-1}$ (0.857 $mol\,l^{-1}$) and 20.53 g $Ti\,l^{-1}$ (0.4285 $mol\,l^{-1}$) was used for the experiments.

### 2.2. Reactor system

Figure 1 shows the apparatus in which aluminium titanate is made by thermal decomposition of the solution (spray-roasting). A solution tank (8), contains the aluminium salts or aluminium scrap and the titanium scrap , dissolved in $HF/HNO_3$. This solution is then sprayed into the thermally heated (gas burner, 11) reactor (1) via a spray nozzle (G. Schlick, Coburg) at a throughput of 51 $lh^{-1}$.

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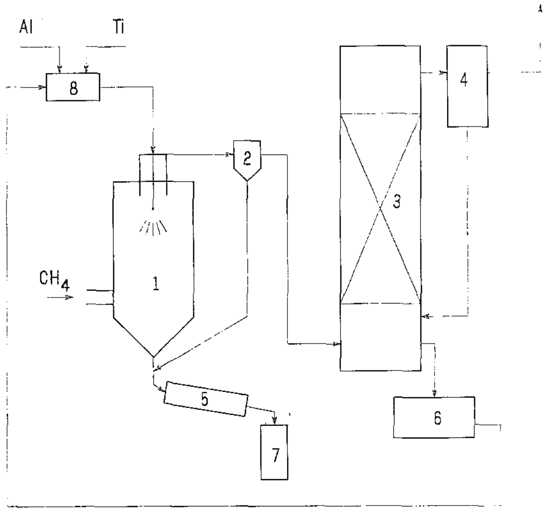

*Figure 1* Spray-roasting apparatus for thermal decomposition of solution.

The reaction was run at a temperature of 400° C, measured and controlled at the height of the burner zone. Contact times of the solution droplets within the reactor were calculated to be 1 to 2 sec. The powder oxide formed is collected at the bottom of the reactor. It may subsequently be transferred into an indirectly heated rotary kiln (5) for end-sintering into the proper crystallographic form. The spray-roasted powder is collected in a powder hopper (7). Fines of particles formed during the roasting are collected by a cyclone and returned to the reactor (2). Gases containing $H_2O$ vapour and $NO_x$ from nitrate decomposition, and gaseous HF are absorbed by an adiabatically working absorption column (3). The acid mixture thus being recycled is returned by a pump-line (6) into the dissolving tank (8). Exhaust gases are cleaned by a scrubber (4), before leaving through the chimney.

## 2.3. Analyses

Thermogravimetric (TG), differential thermogravimetric (DTG), and differential thermal analyses (DTA) were done using a Mettler, thermoanalyser, RDA measurement on a Philips PW1710 diffractometer. Scanning electron micrographs and microprobe analyses were performed using a Jeol-JSM-T 330 and a Link AN 10000 energy dispersive system. The samples were gold sputtered.

The crystal size distribution given within this report, was measured on a CILAS meter by the particle laser-beam scattering method. Sintering experiments of spray-roasted $Al_2O_3$. $TiO_2$ powders were performed in a thermally controlled muffle with molybdenum silicide heating elements at a constant heating rate of 10° C $min^{-1}$. Samples of tialite powder formed after the post-sintering process were compressed into cylindrical discs, 40 mm diameter, and thereafter sintered at 1500° C. Then they were cut by means using a diamond saw into bars of 35 mm × 4.5 mm × 3.5 mm size in order to determine the three-point bend strength of the ceramic material. Rupture tests were performed on a Zwick 147, West Germany, rupture machine using a cross-head speed of 0.1 mm $sec^{-1}$ (10 N $mm^2$ $min^{-1}$).

## 3. Results and discussion

The oxide powder formed after spray roasting at 400° C was of fine grain size and white in colour. The Bulk density as measured was low (0.34 g $cm^{-3}$) but compacting abilities were good. Average particle size distribution, measured by CILAS, resulted in $d_{50} = 20.5\,\mu m$, $d_{10} = 3.3\,\mu m$, $d_{90} = 45.0\,\mu m$ after 3 min ultrasonic treatment. The X-ray microanalysis revealed equal formation of titanium oxide and aluminium oxide ($TiO_2 \cdot Al_2O_3$) in a homogeneous distribution (Fig. 2).

The powders formed were of a hollow spherical droplet-like form as can be seen from the scanning electron micrograph in Fig. 2. RDA of the fresh spray-roasted powder revealed such phases as $TiO_2$ (anatase), mostly, and titanium suboxides such as $Ti_2O_3$ and $Ti_3O_5$, AlO(OH) (boehmite) and $Al_2TiO_5$ (tialite); these phases, however, were in small amounts (Table I).

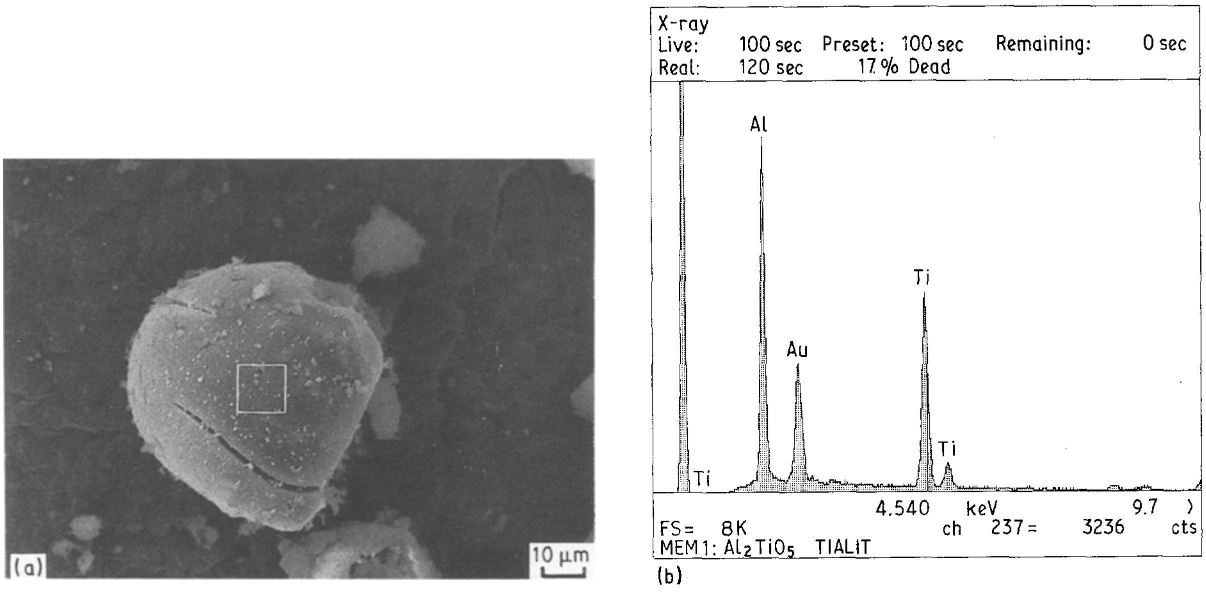

*Figure 2* (a) Scanning electron micrograph of thermally decomposed $Al_2O_3 \cdot TiO_2$ mixture and (b) microprobe analysis of thermally decomposed $Al_2O_3 \cdot TiO_2$.

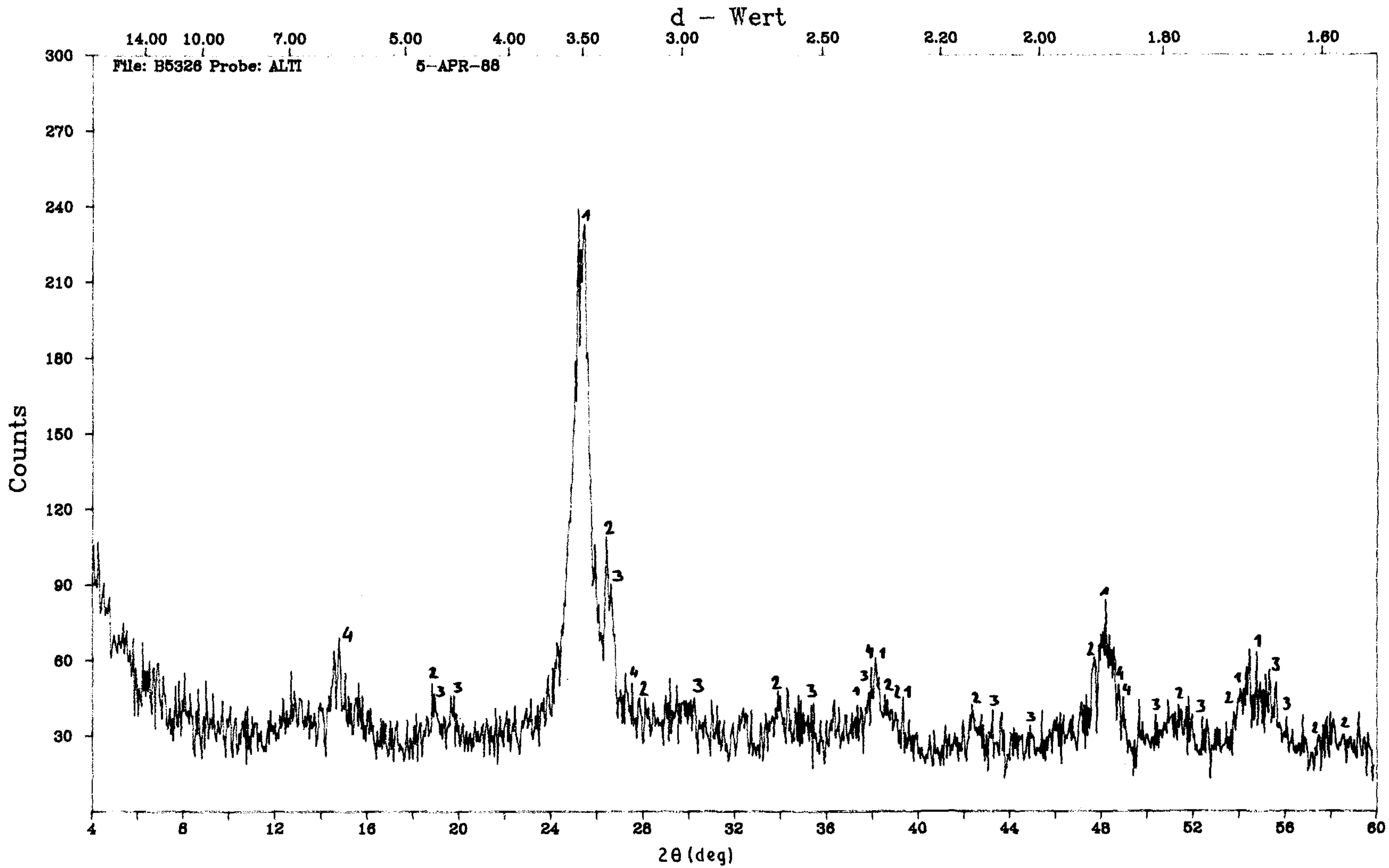

*Figure 3* Powder diffraction analysis of thermally decomposed $Al_2O_3 \cdot TiO_2$. 1, $TiO_2$; 2, $Al_2TiO_5$; 3, $Ti_3O_5$; 4, AlO(OH).

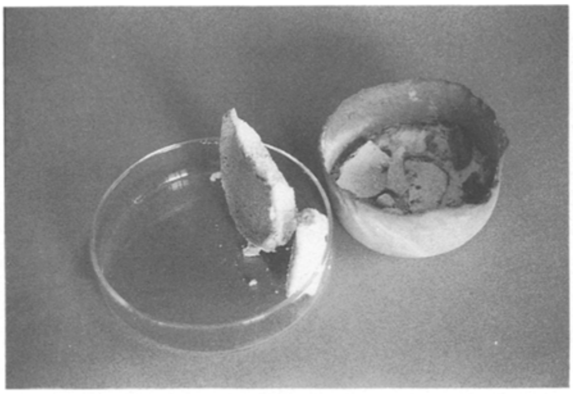

*Figure 4* Cake of $Al_2O_3 \cdot TiO_2$ powder removed from the muffle after sintering at 1070° C. Solid separation of tialite into $Al_2O_3$ and $TiO_2$.

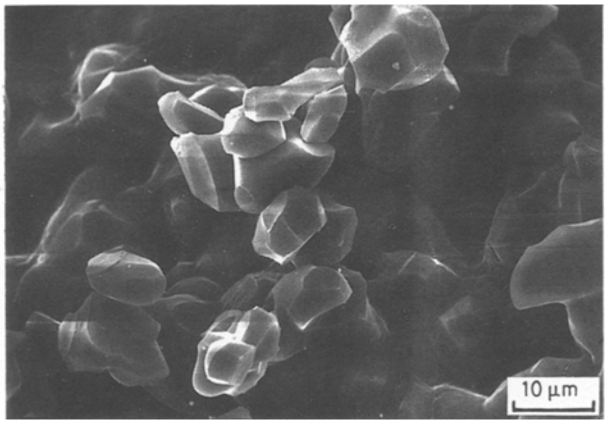

*Figure 5* Scanning electron micrograph of tialite after sintering the reactive powder mixture of $Al_2O_3 \cdot TiO_2$ at 1500° C.

Figure 3 shows the X-ray diffractogram of the original spray-roasted powder. A large amount of amorphous material and a high degree of microcrystallinity can be deduced from the high background and line broadening. Thermogravimetric analysis was run to follow the reaction pathways of tialite formation of powder sintering within the temperature range of 60 to 1570° C and gives the following results: total weight loss of the original spray-roasted powder was 23.1%, in amounts of 2.3% (60 to 170° C), 1.6% (170 to 380° C) and 1.4% (380 to 900° C). Between 900 and 1070° C, the weight loss had a maximum of 17.8%, i.e. the reaction seems to have maximum velocity. Also, the greatest amount of nitrous gases ($NO_x$) could be detected, obviously from residues of thermally stable nitrates of titanium. DTA reveals an exothermic reaction.

Thermodynamic data of tialite formation have been little reported but amount to 150 kcal $mol^{-1}$ [8] from X-ray powder diffractograms of samples taken from this sintering at 850, 1070, 1300 and 1070° C. At this stage the powder reacted violently, it seemed to boil and had a liquid-like consistency. The weight loss also showed a maximum, as reported above. Within this temperature range, the formation of tialite seems to be reversible and makes necessary a rapid quenching of the powder after sintering.

The powder cake of the decomposed material removed from the muffle is shown in Fig. 4. It consists of two visible layers; the inner one being $\alpha$-$Al_2O_3$ (corundum), the outer one the heavier $TiO_2$ (rutile) of sand-brown colour. The thermal decomposition reaction, as observed here, is in fact a very complex mechanism described in the literature by Hennicke *et al.* [8].

TABLE I Crystalline phases detected during sintering reaction of spray-roasted $Al_2O_3 \cdot TiO_2$

| Reaction temperature (° C) | Crystallographie phases detected |
|---|---|
| 850 | $TiO_2$ (anatase), $Al_2TiO_5$ (tialite),<br>Ti–O (suboxides), AlO(OH) (boehmite) |
| 1070 | $TiO_2$ (rutile), $\alpha$-$Al_2O_3$ (corundum),<br>$Al_2TiO_5$ (tialite) |
| 1300 | $Al_2TiO_5$ (tialite), $\alpha$-$Al_2O_3$ (corundum)<br>$TiO_2$ (rutile) |
| 1400 | $Al_2TiO_5$ (tialite), $\alpha$-$Al_2O_3$ (corundum)<br>$TiO_2$ (rutile) |
| 1500 | $Al_2TiO_5$ (tialite), $\alpha$-$Al_2O_3$ (corundum)<br>$TiO_2$ (rutile) |
| 1570 | $Al_2TiO_5$ (tialite) |

The sintering results indicate that after sintering at 1300° C most of the spray-roasted $Al_2O_3$ has reacted with $TiO_2$ to form tialite. The aluminium titanate finally formed did not show any crystal growth compared with the original powder mixture. CILAS analysis gave: $d_{50} = 21.7\,\mu m$, $d_{10} = 10.5\,\mu m$, $d_{90} = 35.7\,\mu m$ (after 3 min ultrasonic treatment).

Fig 5 shows a scanning electron micrograph of $\beta$-$Al_2TiO_5$ obtained from sintering at 1500° C a spray-roasted powder mixture $Al_2O_3/TiO_2$. In order to determine the ceramic properties of the tialite powder made by this process, the post-sintered material was compacted into cylindrical pellets, 13 mm diameter and 3 mm high, by means of a hand-press at 20 ton (2000 MPa) pressure. These samples underwent temperature shock tests by heating them for 2 h at 1500° C and subsequent rapid water quenching to 20° C.

In another series of tests, tialite powder was compressed at 1 ton (100 MPa) into cylindrical discs, 40 mm diameter, in order to determine green densities (by a geometric method) and the sintered density after 2 h sintering in air at 1500° C. Small test bars (35 mm × 3.5 mm × 4.5 mm), were cut from these discs sintered at 1500° C to determine the three-point rupture strength of the aluminium titanate ceramic. The results obtained are given in Table III.

The physical parameters of tialite powder obtained by our process are given in Table II. The results obtained are in agreement with similar results given in the literature [10, 11].

TABLE II Tialite ($Al_2TiO_5$) powder characteristics

| | |
|---|---|
| Chemical analysis | $Al_2O_3$ min. 55%<br>$TiO_2$ 44%<br>Impurities: Fe, Cu, Nb |
| X-ray (RDA)<br>Spray-roasted powder | 100% $Al_2O_3$ (corundum)<br>100% $TiO_2$ (rutile) |
| X-ray (RDA)<br>post-sintered powder | 100% $\beta$-$Al_2TiO_5$ |
| CILAS | $d_{50}$ = 20–25 µm |
| Bulk density ($g\,cm^{-3}$) | 0.35 |
| BET ($m^2\,g^{-1}$) | 2–4 |

TABLE III Tialite ceramic–physical and mechanical parameters

| | |
|---|---|
| Green density (compressed discs at 100 MPa pressure) | 2.0–2.1 $\text{g cm}^{-1}$ |
| Sintered density (1500° C) | 2.9–3.1 $\text{g cm}^{-1}$ |
| Linear shrinkage | 10%–11% |
| Cyclic temperature shock resistance (1500° C/20° C | 3–5 times |
| Bend strength (three point) | $\sim 20\ \text{N mm}^{-2}$ |

In order to prove the superiority of the chemical reactivity of the powder spray-roasted according to our process, a test comparison was made by sintering a mechanically mixed, stoichiometric amount of chemically pure $\alpha$-$Al_2O_3$ (corundum) and $TiO_2$ (anatase). Sintering conditions were exactly the same as those described above. In contrast to spray-roasted $Al_2O_3/TiO_2$, no tialite formation could be observed after sintering at 1350° C.

## 4. Conclusions

The process of thermal decomposition of an aqueous Al–Ti solution was found to be advantageous in aluminium titanate (tialite) formation over the state-of-art-sintering of mechanically mixed powders of $Al_2O_3$ and $TiO_2$. The results obtained here are in good agreement with those described in the literature for tialite ceramics. Tialite production in a continuous process through pyrohydrolysis from aqueous solutions seems to compare favourably with other processes. Finally, it allows the use of pickle liquors from titanium metal production to be worked up into tialite for application in refractories along with the recycling of pickle acids, thus possibly making this process a viable and economic asset for pickle-acid recovery.

## References

1. CH. HAHN, *Sprechsaal* **118/12** (1985) 1157.
2. K. HAMANO, Y. OHYA and Z. NAKAGAWA, *Yogyo-Kyokai-Shi* **91** (1983) 50.
3. E. GUGEL and P. SCHUSTER, *Tonind. Z* **98** (1974) 315.
4. M. ISHITSUKA, T. SATO, T. ENDO and M. SHIMADA, *J. Amer. Ceram. Soc.* **70 (2)** (1987) 69.
5. V. P. TARASOVSKI and E. S. LUKIN, *Ogneupory* **(6)** (1985) 24.
6. H. K. KRIVANEC and W. K. KLADNIG, *Sprechsaal* **121** (1988) 1182.
7. W. KLADNIG, Maschinenfabrik Andritz, Ruthner Division, Austrian. Pat. No. 389693 (1989).
8. H. W. HENNICKE and W. LINGENBERG, *Cfi/Ber. Dt. Keram. Ges.* **9/10** (1985) 439.
9. *Idem, ibid.* **3** (1986) 100.
10. F. FREUDENBERG, A. MOCELLIN, *J. Amer. Ceram. Soc.* **71 (1)** (1988) 22.
11. "Ceramic Source" (American Ceramic Society Columbus, Ohio, 1989) p. T85.

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