

Pushing the Limits of Metal Oxide Particle Production: The Pulsation Reactor

N. Zobel, M. Ommer, T. Khalil, T. Rensch

IBU-tec's Pulsation Reactor is a technology for producing fine powders. It can be characterised as a thermal shock treatment with a unique functional principle: a periodically unsteady flame reactor in which gas-borne substances can be thermally treated at retention times between 0,2–2 s. Due to the pulsation of the hot gas flow, the axial velocity field is even more similar to a plug-flow than a turbulent flow without pulsation. This leads to a very narrow residence time distribution, which ensures a very homogeneous treatment of the educt. Additionally, the pulsating hot gas flow causes an increased convective heat and mass transfer to and from the particles.

In order to investigate the impact of the process conditions in the Pulsation Reactor on the resulting material properties, three different materials have been synthesized: aluminium oxide, cerium dioxide and iron oxide. The results show that the Pulsation Reactor platform enables specific control of the size and surface properties of metal oxide particles. The properties of the materials generated in Pulsation Reactors are significantly different from materials generated in conventional kilns such as rotary kiln or muffle furnace. In Pulsation Reactors metastable phases can also be produced.

1 Introduction

IBU-tec's patented Pulsation Reactor is a technology for producing fine powders. It can be characterised as a thermal shock treatment with a unique functional principle. This principle results in process parameters that differ from conventional processes and that ultimately lead to special properties in the generated powder materials. The Pulsation Reactor has proven to be particularly useful for the production of ceramic and nanoscale powders, as well as for

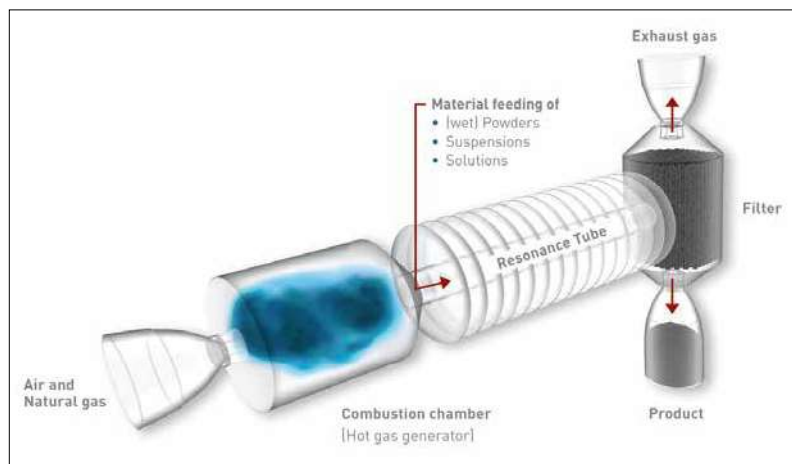


Fig. 1 Illustration of a Pulsation Reactor

the production of highly active catalysts. For instance, simple oxides such as zinc oxide or zirconium oxide can be produced with doping elements or mixed oxides such as spinel. In the following, the working principle of the Pulsation Reactor is presented, followed by three examples that demonstrate what material properties can be obtained.

2 Experimental

Fig. 1 shows the schematic of a Pulsation Reactor (PR). In principle, a Pulsation React-

or is a periodically unsteady flame reactor in which gas-borne substances can be thermally treated with retention times between 0,2–2 s.

The generation of the pulsating hot gas flow (250–1250 °C) takes place within a hot gas generator via the combustion of natural gas with ambient air. The hot gas flows through a resonance tube and carries the thermally treated material. The educt – either a dry or a wet powder, a suspension or a liquid solution – can be fed into the combustion

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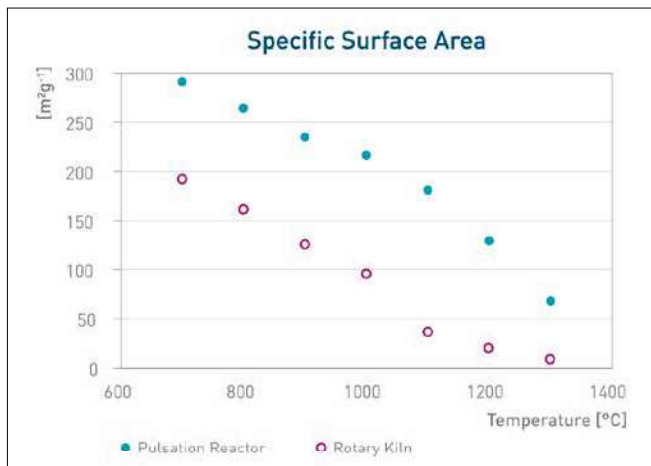


Fig. 2 SSA of Al₂O₃ determined for the samples synthesized using a Pulsation Reactor and a rotary kiln at different temperatures

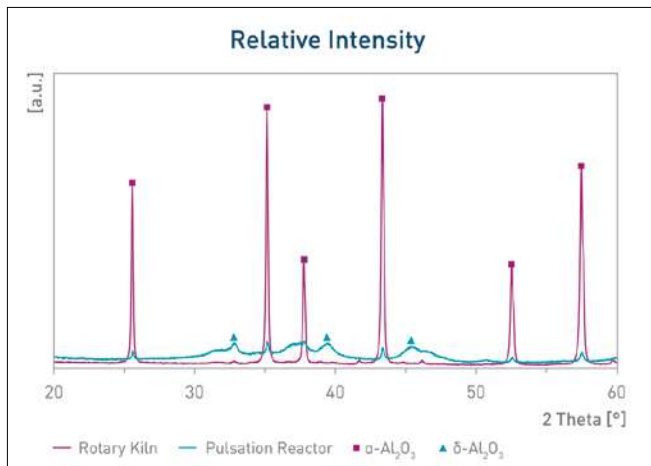


Fig. 3 X-ray diffraction patterns of a synthesized product using a Pulsation Reactor and a rotary kiln (1300 °C)

chamber or the resonance tube. The thermal treatment is carried out by the hot gas flow within the resonance tube and is terminated by suitable cooling with ambient air. The finished product can be separated in a particle filter and/or a cyclone. Due to the pulsation of the hot gas flow, the axial velocity field is more similar to a plug-flow than a turbulent flow without pulsation. This leads to a very narrow residence time distribution, which ensures a very homogeneous treatment of the educt. Additionally, the pulsating hot gas flow produces increased convective heat and mass transfer to and from the particles.

In order to investigate the impact of the process conditions in the PR on the resulting material properties, three different materials have been synthesized. Their properties are compared to materials that have been treated in conventional furnaces.

3 Results and discussion

3.1 Example aluminium oxide

Aluminium oxide (Al₂O₃) can exist in a number of different phases. The most important being cubic γ -Al₂O₃ and trigonal α -Al₂O₃



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(corundum). In economic terms, the primary use of aluminium oxide is as a precursor for metallic aluminium; 90 % of global aluminium oxide production is used for this purpose. Alumina however, has many more applications: in the chemical industry, it comes into play as an adsorbent, a carrier material for catalysts and a catalyst in its own right. Its high hardness makes it an ideal abrasive and polishing agent.

Sintered Al_2O_3 (corundum) is used as a refractory material in high temperature environments such as furnaces. Aluminium oxide-based ceramic materials are a vital component of modern electronics; their low dielectric loss factor makes them ideal dielectric materials. Here, the utilisation of PR and Rotary Kiln (RK) technology in modifying the characteristics of Al_2O_3 particles is described. During the trials, the correlation between the Specific Surface Area [SSA (BET)], as an example of the properties and application of both technologies were investigated. In both cases, $\text{Al}(\text{OH})_3$ (gibbsite) powder was used as raw material.

The temperature, as a key parameter of both reactors, varied within the range of 700–1300 °C. The expected behaviour for the SSA of Al_2O_3 could be achieved with both technologies (Fig. 2). The obtained SSA decreases with increasing temperature, due to sintering of the material.

However, significantly higher surface areas can be obtained in PR as compared to RK, due to the significantly higher residence time in RK which leads to a higher degree of sintering resulting in a lower SSA. The evaluation of the X-ray diffraction pattern (Fig. 3) shows a varying behaviour for PR and RK samples which were treated at the same temperature (1300 °C). It can clearly be observed that under PR conditions the metastable $\delta\text{-Al}_2\text{O}_3$ is predominantly generated, while under RK conditions (higher residence times) the stable $\alpha\text{-Al}_2\text{O}_3$ is formed.

3.2 Example cerium oxide

Cerium dioxide (CeO_2) is used in gas mantles, as a polishing agent or as an oxidation catalyst. In this study, a liquid cerium nitrate solution (15 mass-%) was fed as a precursor into a PR. The CeO_2 produced in the PR was analysed and subsequently fed into a RK, where it was thermally treated for 1 h at the same temperature as previously in the PR. The resulting material was then analysed for a second time. The results are depicted in Fig. 4.

In both the Al_2O_3 and CeO_2 examples, the SSA of the material produced in the PR is significantly greater than the SSA of the material treated in the RK at the same temperature, which may be related to the significantly higher heating rates and shorter residence times in the PR as compared to the RK.

Furthermore, the SSA decreases with temperature due to sintering. For the same reasons, the crystallite sizes obtained in the PR are significantly smaller than after thermal treatment in the RK. While in the PR the crystallite sizes remained below 16 nm, they increased up to 94 nm upon thermal treatment in the RK.

3.3 Example iron oxide

Iron oxide is a widely used material with many different applications, such as pigment for paints and colours, coating on magnetic tapes or catalyst material. Iron oxide can exist in a

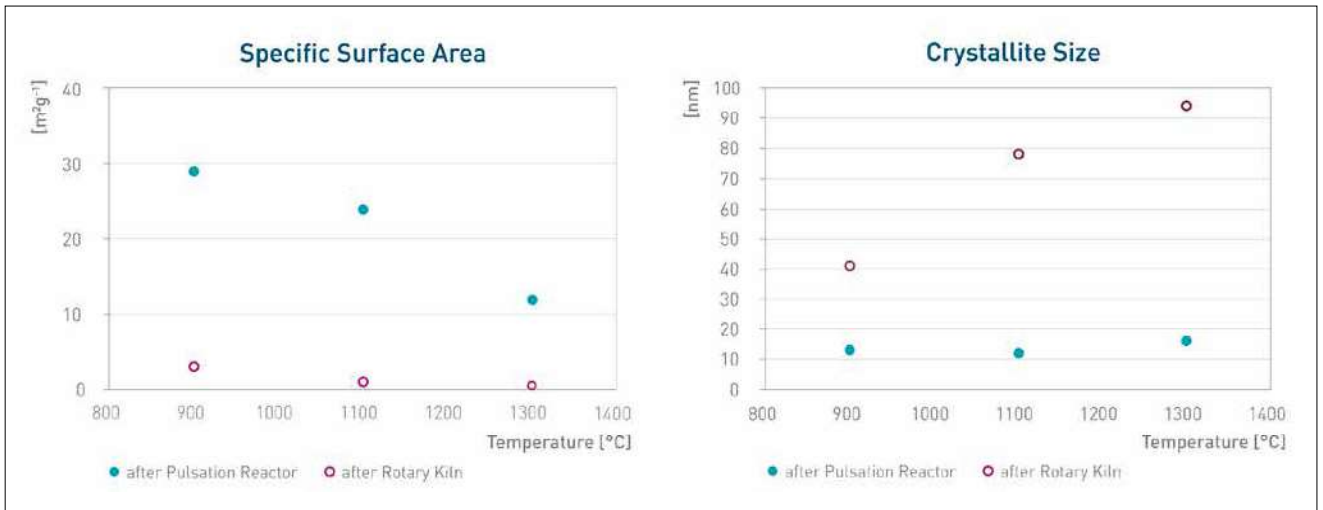


Fig. 4 SSA (l.), and crystallite sizes (r.) of CeO₂ determined for the samples synthesized using a Pulsation Reactor and a rotary kiln at different temperatures

number of different variations, the most important being trigonal α -Fe₂O₃ (hematite), cubic γ -Fe₂O₃ (maghemite) as well as Fe₃O₄ (magnetite).

In this case, fine iron oxide particles have been synthesized in the PR from a liquid Fe(NO₃)₃ · 9H₂O solution at various temperatures. In a second step, the material was exposed to thermal post-treatment for 1 h in a Muffle Furnace (MF) at the same temperature as previously in the PR. The SSA of the generated materials is depicted in Fig. 5.

Basically, the same qualitative trends cited in the previous examples have been obtained: the SSA decreases with temperature and residence time. The interpretation of these results is supported by SEM (Scanning Electron Microscope) pictures shown in Fig. 6 and Fig. 7. A higher residence time at the reaction temperature in the MF leads to sintering/thermal annealing and to the generation of larger crystallites.

4 Summary and conclusion

The Pulsation Reactor platform of IBU-tec enables specific control of the size and surface properties of metal oxide particles.

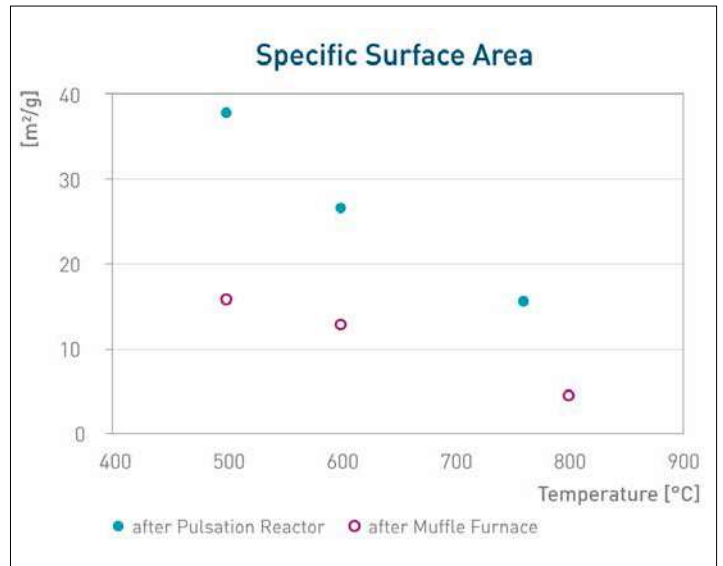


Fig. 5 SSA of Fe₂O₃ determined for the samples synthesized using a Pulsation Reactor and a muffle furnace at different temperatures

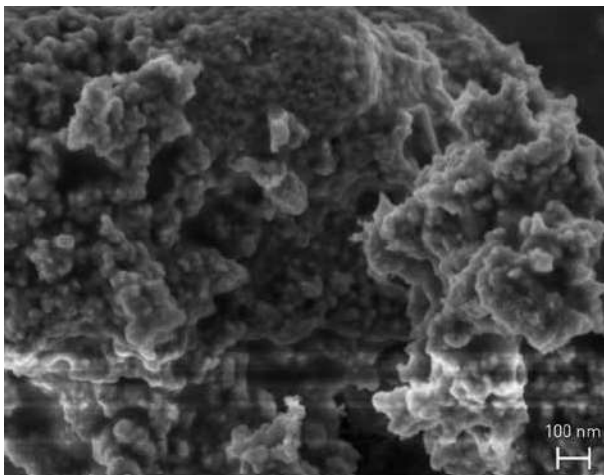


Fig. 6 SEM of Fe₂O₃ treated in the Pulsation Reactor at 500 °C

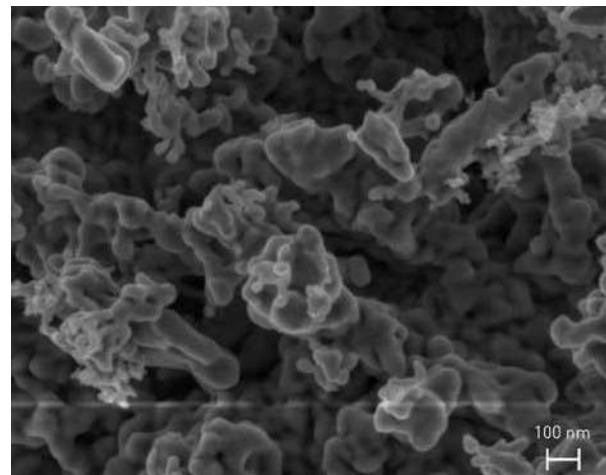


Fig. 7 SEM of Fe₂O₃ post-treated in the muffle furnace at 500 °C

Periodic Table of the Elements

1 H Hydrogen 1.008																	2 He Helium 4.0026														
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.806	6 C Carbon 12.0096	7 N Nitrogen 14.0064	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.1797														
11 Na Sodium 22.989	12 Mg Magnesium 24.304											13 Al Aluminum 26.9815	14 Si Silicon 28.0855	15 P Phosphorus 30.9738	16 S Sulfur 32.059	17 Cl Chlorine 35.446	18 Ar Argon 39.948														
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.9559	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798														
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.9058	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium [98]	44 Ru Ruthenium 101.07	45 Rh Rhodium 101.065	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.904	54 Xe Xenon 131.293														
55 Cs Caesium 132.905	56 Ba Barium 137.327	57 La Lanthanum 138.905	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.222	78 Pt Platinum 195.084	79 Au Gold 196.9665	80 Hg Mercury 200.592	81 Tl Thallium 204.382	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon [222]														
87 Fr Francium [223]	88 Ra Radium [226]	89 Ac Actinium [227]	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [263]	107 Bh Bohrium [264]	108 Hs Hassium [265]	109 Mt Meitnerium [266]	110 Ds Darmstadtium [267]	111 Rg Roentgenium [268]	112 Cn Copernicium [269]	113 Nh Nihonium [270]	114 Fl Flerovium [271]	115 Mc Moscovium [272]	116 Lv Livermorium [273]	117 Ts Tennessine [274]	118 Og Oganesson [276]														
																		58 Ce Cerium 140.12	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.967
																		** 90 Th Thorium 232.0377	** 91 Pa Protactinium 231.036	** 92 U Uranium 238.029	** 93 Np Neptunium [237]	** 94 Pu Plutonium [244]	** 95 Am Americium [243]	** 96 Cm Curium [247]	** 97 Bk Berkelium [247]	** 98 Cf Californium [251]	** 99 Es Einsteinium [252]	** 100 Fm Fermium [257]	** 101 Md Mendelevium [258]	** 102 No Nobelium [259]	** 103 Lr Lawrencium [260]

Fig. 8 Elements treated in IBU-tec's Pulsation Reactors

The properties of the materials generated are significantly different from materials generated in conventional kilns, such as the rotary type or muffle furnaces. In Pulsation Reactors, metastable phases can also be

produced. The experimental results of the material examples addressed in this work (Al_2O_3 , CeO_2 and Fe_2O_3) can be viewed as representative of a whole group of metal oxides which could be developed with de-

fined properties using Pulsation Reactor and rotary kiln thermal process engineering supplied by IBU-tec. The elements that have been thermally treated in IBU-tec's Pulsation Reactors thus far are summarised in Fig. 8.

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