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Continuous Synthesis

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The development of non-oxide ceramic materials continues to be an area of intense investigation and development within the ceramic materials community. Historic compounds such as SiC, B_4C and Si_3N_4 have more recently been joined by a wide range of carbide, nitride, and boride compounds, as well as mixed compounds such as the MAX phases (e.g., Ti_3SiC_2) in these investigations. Product opportunities ranging from high-temperature electronics, improved personnel and vehicle armor, improved wear-resistant materials, and extreme environment tolerant materials all drive these efforts.

In order to capitalize on the often excellent properties provided by these materials, it is particularly important to manufacture the starting materials in a manner that ensures high phase and chemical purity, as well as non-agglomerated, finely controlled particle sized powders. Historical processes often involved batch reaction of low-cost, coarse reactants at high temperature for long times, followed by extensive crushing and milling steps. More advanced processes involve much higher quality raw materials, improvements in precursor mixing and handling methods, and more controlled calcining cycles to result in improved product powders.

As may be expected, the thermal processing portion of these new processes can be critical in ensuring a high-quality product. The related synthesis process often requires high temperatures in addition to oxygen-free environments. This sets the bounds for the associated thermal processing equipment necessary for this process step.

In development efforts, the equipment able to provide these necessary conditions typically includes relatively small-scale periodic furnaces that process material in one or more static containers. Materials considerations for the furnace and the containers, while limited, are still reasonably broad so that standard designs and relatively common materials (i.e., silicon carbide, aluminum oxide, graphite) are routinely available in suitable sizes, purities, and lead times.

Commercially Relevant Processes

In development, the requirements for process requirements such as material uniformity, significant gas phase exchanges, and rapid heating/cooling of the material can often be facilitated by the relatively small size of the furnace, low loading of products and containers, and control of the depth of the reactant powder bed. Typically, the first round of scale-up of such a process is to increase the size of the furnace and introduce multiple containers of material.

The success of this strategy is quickly limited by the distribution of the containers relative to the heating elements; larger production rates can lead to reduced product uniformity. Options for mitigating this problem, such as further reductions in bed depth, extending process time, etc., typically lead to increases in processing cost. At some point in development, the synthesis process must evolve into a continuous process in order to maintain product quality, increase throughput and reduce processing costs.

The most obvious and easiest method for scaling these types of reactions is to transport powder through an established thermal profile by some form of conveyance. For more traditional ceramics, the temperature and environmental conditions required for processing allow for a number of different designs that provide this conveyance. For higher temperature processes, particularly non-oxide processes, equipment options quickly converge to pusher-style furnaces.

By using large area containers and uniform, moderately thick reactant beds, and a furnace design with heating elements above and below the boats, bed heating can be relatively fast and very uniform. Pusher furnaces are used throughout the industry for these types of applications, and they are quite effective in supporting the commercial production of a variety of materials.

In many cases, pusher furnaces provide a suitable means of producing a product at the fully commercialized state. However, in some cases, limitations related to throughput, product uniformity and power efficiency may require an alternate solution to satisfy the needs for further scale-up. Thermal processes that agitate the product bed while transporting it through the heating profile often provide the necessary additional performance.

Process Improvements

The most obvious form of such a device is a rotary furnace. In such a furnace, reactants are introduced into one end of a rotating tube, and are conveyed at a set rate through a thermal profile by means of tube rotation and an incline applied to the tube. As the reactant bed moves through the tube, it is constantly stirred by the tube rotation.

The stirring action enhances thermal transfer to the bed, improves removal of product gases and increases solid/gas exchange in cases where the furnace gas is also a reactant. Because of these enhancements, the product material often exhibits an improved uniformity compared to static bed-processed materials. In addition, because only the reactant powder is heated and cooled, the thermal efficiency is significantly improved compared to pusher-style furnaces.

In practice, rotary furnaces provide the anticipated values of throughput and efficiency over a wide range of materials, as long as the materials behave properly during the process. In some cases, the nature of the reactant material can cause problems with the flow of material through the tube. Material adhesion to the tube can change bed mixing behavior, flow through the furnace and, in extreme cases, cause wide swings in material residence time. In other cases, material entrainment in the exhaust gas can affect throughput and material flow.

These problems can sometimes be overcome by changing the physical form of the reactants. For instance, fine powders might be granulated into pellets or aggregates. Alternately, the use of internal features within the process tube can occasionally promote the desired bed behavior. At other times, the nature of the material does not allow for granulation, or the granules are not sufficiently strong to retain their shape throughout the process. In such cases, other means of high throughput and high efficiency processing are needed for more challenging feedstock.

Non-Traditional Design

In evaluating design alternatives to rotary furnaces, the following considerations should be made:

- Heating and cooling should be limited to only the process material. Containment should remain at temperature and the process material should move through it.
- The opportunity for product sticking or gas-phase entrainment during processing should be minimized.
- Product uniformity and reaction time should be maximized by minimizing or eliminating bulk bed effects.
- Heat and mass exchange should be provided between products and reactants for improved efficiency.
- Personnel efficiency and return on investment should be maximized.

One means of providing these advantages is under evaluation in the form of a vertical conveyor furnace (see Figure 1).1 In rotary furnaces, material is typically conveyed into the rotating tube using a screw feed device, and the rotation and angle of the container tube facilitates the movement of the material for the remainder of the process. In the vertical conveyor furnace, screw feeders provide all of the motive force to push the reactants into the hot zone. Material exits initially by force of gravity, and ultimately by a second screw feeder.

In the feeding portion, the reactant material is pushed up against gravity through a gradually tapering cone, part of which resides inside the hot zone of the furnace. The material is preheated during this conveyance through the walls of the conveyor and cone. At the top of the cone, the material at the very surface is exposed to direct radiation heating and the gas environment in the furnace chamber. Because of this direct exposure, it is anticipated that reactions occur uniformly and quickly over this surface layer of material, and that off-gassed material exits the process upward and away from the product.

Continued feeding of material from below causes this now-reacted layer to spill over the top of the cone and fall by force of gravity into the larger containment tube surrounding the cone. The initial movement of material from the top of the cone facilitates a very sharp drop in process temperature, which limits the potential for overheating problems such as melting/sublimation, sintering or excessive grain growth. The material continues to fall through the outer tube to a cooled portion of tube under the furnace hot zone. At the bottom of the exit tube is a second screw feeder, which removes the material from the apparatus and transports it to a product hopper.

By carefully controlling the rate of material removal from the outer tube, a bed of cooling material can be intentionally built up within the apparatus. By means of the design, this bed is in direct contact with the inner tube conveying the reactant material into the furnace. This contact allows for direct heat transfer from the product to the reactants, assisting in the preheating of the incoming material while at the same time cooling the exiting material. Thus, in addition to the container-less nature of the design, the thermal transfer between product and reactants significantly improves the power efficiency of the unit (see Figure 2).

Given the nature of this design, it is anticipated that a wide range of product feedstocks may prove suitable for processing in this equipment. The plug flow of material in the entry cone should minimize the sticking problems observed in rotary tubes, and should not necessarily require only materials that exhibit low angles of repose. Product mixing concerns during reaction are minimized, given that the peak process temperature is encountered at the immediate top of the reaction bed. This reaction zone is continuously removed and replenished in a fountain-like manner, ensuring that the entire bulk of material is exposed to radiative heating and solid-gas interchange in a nearly-uniform manner. Because the material is not continuously agitated, lower levels of fine powder entrainment are also expected.

A pilot-scale model of this design is currently being tested for high-temperature calcining applications for phase conversion. It is anticipated that it will provide significant advantages for the efficient processing of materials requiring high-temperature solid-solid and solid-gas reactions, such as carbides, nitrides, borides, and refractory metal powders.

For additional details, contact Harper International at 100 W. Drullard Ave., Lancaster, NY 14086; call (716) 684-7400; email info@harperintl.com; or visit www.harperintl.com.

Reference

1. Miller et al., "Vertical Conveyor Apparatus for High Temperature Continuous Processing of Materials," U.S. Patent Number 6,910,882, issued June 28, 2005.

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