

The ceramic products resulting from this process are substantially pure alpha-alumina. If desired, the chemical composition of the structures can be modified by including in the coating composition finely divided particles of filler refractory oxide. The filler refractories may, if desired, be one or more of those which will react with the alumina as it is formed. If a reactive filler, such as magnesia and/or silica is used, the honeycomb structure will contain the corresponding reaction product such as spinel, cordierite, or mullite. The products of this process are characterized by outstanding strength and thermal shock resistance.

As disclosed in the Talsma patent, honeycomb structures may be fabricated by corrugating sheets of aluminum coated with fluxing agent and placing the coated sheets together node to node. Where sodium silicate solution is used as the fluxing agent, the body will have sufficient green strength to maintain its shape until it is fired. Alternatively, the honeycomb structure may first be fabricated from the aluminum foil using methods well known in the art and described in the patent literature. Reference is made to U.S. Pats. 2,610,934, 2,674,295, and 2,734,843 for teachings concerning the art of making honeycomb. Structures with nominal cell sizes ranging from  $\frac{1}{8}$ " to  $\frac{3}{4}$ " and foil thicknesses of 0.7 mil to 7 mils are readily available. Other sizes with cells ranging from say  $\frac{1}{32}$ " up to 2" or higher and with foil up to  $\frac{1}{4}$ " in thickness can be made and used in the process disclosed in the Talsma patent. The preferred structures are prepared using foil of about 2 mils thick.

An improvement in the process for making ceramic structures by the method of the Talsma patent is disclosed in co-pending U.S. application Ser. No. 367,856, filed May 15, 1964. In the process of this application the composition used to coat the aluminum template structure contains, in addition to the fluxing agent and filler refractory if any, small amounts of a vanadium compound. The products of the Talsma patent are characterized by having a double-walled structure. The double wall results from the fact that the aluminum foil, as it melts, flows outwardly through the oxide film formed on the outer surfaces of the foil and is oxidized at the outer surface of the oxide layer, thus leaving a large void in the final product corresponding approximately in thickness to the thickness of the original aluminum section. The inclusion of the vanadium compound in the coating composition causes the formation of bridges of refractory material between these double walls resulting in a product having even greater strength and thermal shock resistance than the products of the Talsma patent.

A further improvement in the process of the Talsma patent is disclosed in co-pending U.S. application Ser. No. 471,738, filed July 13, 1965 now U.S. Pat. 3,473,987. In the process of this application the composition used to coat the aluminum template structure contains aluminum powder in addition to the fluxing agent and filler refractory, if any. The aluminum powder, of course, is oxidized to alumina during firing along with the aluminum in the original metal template. This method provides structures which are similar to those of the Talsma patent in that they are double-walled, but the walls can be made much thicker than the central void. Thus the products are stronger than those of the Talsma patent.

A particularly preferred method for making catalyst support structures is disclosed in co-pending application Ser. No. 449,629, filed Apr. 20, 1965. The method is similar to that disclosed in Ser. No. 471,738, but silicon carbide is added to the composition used to coat the aluminum metal template. Upon firing, the silicon carbide reacts with the aluminum to provide mullite. Mullite structures are particularly preferred as catalyst carriers because of their high strength and low thermal expansion.

A further suitable method for making thin-walled ceramic structures is disclosed in co-pending application Ser.

No. 336,983, filed Jan. 10, 1964 now U.S. Pat. 3,338,995. In this method a "fugitive" material, e.g., paper, is coated with a composition including aluminum powder, a binder, a fluxing agent (of the type disclosed in the Talsma patent), and a liquid carrier. The "fugitive material" may be first coated then used to fabricate a honeycomb or similar structure or the honeycomb may be first fabricated from the fugitive material then coated. In either case, the coated structure is fired in an oxygen-containing atmosphere to burn out the fugitive material and oxidize the aluminum. Filler refractories can of course be included in the coating compositions to provide ceramics including compounds and/or solid solutions of alumina with other oxides.

Any high surface area, finely divided active alumina can be used in the process of the invention. These active alumina particles are characterized in that their surface area will range from 50 m.<sup>2</sup>/g. to 600 m.<sup>2</sup>/g. Preferred materials will range between 180 m.<sup>2</sup>/g. and 250 m.<sup>2</sup>/g. These particles will range in particle size from 8 to 60 microns and preferably on the order of 30 to 40 microns.

When referring to the surface area of the active alumina, this surface area can be measured by nitrogen absorption as described in "A New Method for Measuring the Surface Area of Finely Divided Materials and for Determining the Size of Particles" by P. H. Emmett in the publication "Symposium on New Methods for Particle Size Determination in the Sub-Sieve Range," published by the American Society for Testing Materials, Mar. 4, 1941, p. 95.

Activated alumina particles are commercially available. Thus, suitable for use in the process of the invention are such commercial activated alumina as:

Alcoa F-1 which is an alumina hydrate having 1 mole alumina per  $\frac{1}{2}$  mole of water and an average particle diameter between 30 and 40 microns.

Alcoa C-333 which is alumina trihydrate having an average particle size of about 8 microns and over 95% of the particles less than 44 microns.

To be useful in the process of the invention, some commercially available active aluminas should be washed free of salts. The presence of small amounts of salt can create problems in that settling occurs in the slurry, thus making a uniform coating difficult to obtain.

Further, in some embodiments of the invention, the activated alumina should be contacted with acid in order to acidify the alumina particles. This is necessary in that the particles should be in a pH range which is compatible with the colloidal boehmite used. Thus when the colloidal boehmite used consists of minute fibrils of boehmite, the activated alumina when mixed with this fibrous boehmite should have a pH such that the mixture pH is in the range of 3.0-4.5 with a preferred range of 3.5 to 4.0. It is found that when the pH of this mixture is outside of this range, settling or gelatin can occur.

The activated alumina particles are then mixed with colloidal alumina monohydrate, conventionally known in the art as colloidal boehmite. The colloidal boehmite acts as a bonding precursor in that during the subsequent drying and calcining of the coating, the activated alumina particles are bonded together and to the support by the action of heat upon the colloidal boehmite.

In general, once the coating has been applied, dried and calcined, the colloidal boehmite will compose 5% to 10% and generally around 6% of the content of the dry coating. The active alumina particles will comprise up to about 95% and generally around 90% of the dried coating.

The colloidal boehmites useful in the process of the invention are composed of discrete particles having one or more dimensions in the colloidal range, i.e., below 200 millimicrons. A particularly useful colloidal boehmite is a monohydrate alumina having 30% or more of its particles in the form of fibers. Exemplary of this material is