Combustion Synthesis of Titanium Nitride under Fluidization

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Several investigators have studied the self propagating high temperature synthesis (SHS) of titanium nitride during the past decade and found that one of the most important scientific issues is increasing the conversion yield of the nitride. In general, conversion yield has been limited by the melting of titanium particles during the combustion synthesis because the melting point of titanium is lower than the combustion temperature. The titanium liquid tends to penetrate into interstitial spaces between the unreacted or unmelted particles especially in earth gravity leading to reduced reactant porosity. The reduction in porosity leads to less contact of nitrogen with the remaining titanium particles and low nitride conversion results. Recently, a technique was developed to increase the conversion yield of titanium nitride by using a fixed powder bed and supercritical nitrogen. The high initial nitrogen density at the supercritical condition provides the reactant particles with enough initial nitrogen that the conversion yield achieved was 74%, without significant formation of liquid barriers. The yield achieved was a significant improvement over those obtained by other techniques.

In order to increase the yield further, the fixed powder bed has been transformed into a fluidized bed with homogenous uniform dispersion. The dispersion is produced in a quartz tube 13 mm in diameter. The dispersion is comparable to the static dispersion to be achieved eventually in microgravity. The fluidized dispersion obtained in the laboratory and which is being studied in preparation for microgravity experiments is created by purging particles through a dual particle injection system into a co-flowing nitrogen stream that has passed through a sintered stainless steel base plate. The titanium particle dispersion appears to be both homogenous and uniform. As a result of fluidization, the interparticle distances are increased and controllable so that nitrogen accessibility to the titanium surface is increased. Testing of the yield dependence of the combustion synthesis on nitrogen accessibility is achieved by using a tungsten igniter coil affixed medially in the quartz tube.

For the tungsten igniter to be able to initiate the combustion synthesis process, the fluidized bed must provide a homogenous dispersion of titanium dense enough to reach the ignition limits in nitrogen. Particle loading and corresponding densities have been found for successful ignition of the fluidized titanium particles. Successful ignition leads to propagation of a flame counter to the direction of the flow of fluidizing nitrogen. The dispersion density necessary for flame propagation is maintained by the addition of purging particles throughout the experiment including an observed afterburn period. During this afterburn period, after the propagation of the flame, conversion to nitride continues apparently without significant melting of the remaining titanium.

The final titanium nitride product recovered from the successful fluidized bed experiments is a sintered matrix with some unreacted titanium particulates as indicated by scattered silver colored titanium particles in a mostly yellow-brown titanium nitride matrix. The titanium nitride from these investigations shows a spherical morphology with diameters ranging from sixty to one hundred microns. These spherical products are produced from rod-like titanium precursors. The titanium nitride product also is more porous than that reported in published investigations and is probably due to the fluidization process. During fluidization, the percolating titanium-nitrogen mixture aids in dissipating heat as well as forming the dispersion. This additional heat dissipation decreases the molten titanium that has lowered the yield in reported investigations. The product from these experiments do not show regions of molten titanium plated by titanium nitride, rather a sintered matrix of titanium nitride with some titanium sparsely intermixed.

Currently, the morphology of the titanium nitride product is examined using scanning electron microscopy (SEM). Photographs of the initial pure titanium as well as the titanium nitride are taken using SEM for comparison and are the basis for the discussion above. In future experiments, X-ray diffraction analysis also will be performed to determine the microstructure of the resultant titanium nitride. Similarly, in future experiments the flame propagation speed will be measured using two type-C thermocouples (W-5%Re by W-26%Re) as a function of temperature fluctuations at the flame fronts.

Preparations are currently underway to continue these investigations in the KC-135 parabolic flight plane, where microgravity effects will be attained. Better results in microgravity are expected since a true homogenous, non-stratified dispersion can be created without gravitational field effects and without the mixing effects due to the turbulent flow required to maintain fluidization on earth. Without turbulence, microgravity is expected to further increase the conversion yield and produce a dispersed particulate product instead of the sintered product presently found. The KC-135 will be used for these investigations due to the long observation time in the SHS of titanium nitride, which surpasses the five seconds allotted by the drop tower. Before progressing to microgravity conditions, further investigations in the fluidized bed in normal gravity are expected to lead to a more uniform product and increased product yield.