SYNTHESIS AND PROPERTIES OF NANOFUNCTIONALIZED PARTICULATE MATERIALS

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Abstract -- A wide range of advanced technology for existing and emerging products based on high temperature metal-ceramic composites used in aircrafts, cutting tools, lithium-ion based rechargeable batteries, superconductors, field emission based flat-panel displays, etc. employ micron to submicron sized (0.1 - 10 microns) particulate precursors in their manufacturing process. Although there has been a significant emphasis given to control of the particle characteristics (shape, size, surface chemistry, adsorption, etc.), relatively little or no attention has been paid to concomitant designing desirable surface and bulk properties at the particulate level, which can ultimately lead to enhanced properties of the product. By attaching atomic to nano-sized inorganic, multi-elemental clusters either in discrete or continuous form onto the surface of the core particles, i.e. nano-functionalization of the particulate surface, materials and products with significantly enhanced properties can be obtained. In this paper, we demonstrate the synthesis of artificially structured, nano-functionalized particulate materials with unique optical, cathodoluminescent, superconducting and electrical properties. In this paper, we show the feasibility of the pulsed laser ablation technique to make very thin, uniformly distributed and discrete coatings in particulate systems so that the properties of the core particles can be suitably modified. Experiments were conducted for laser deposition on Al2O3, SiO2, core particles by pulsed excimer laser (wavelength = 248 nm and pulse duration = 25 nanosecond) by irradiation of a Ag and Y2O3:Eu3+ targets. ©1999 Acta Metallurgica Inc.

INTRODUCTION

Sub-micron to micron sized metallic and ceramic particles (100 nm to 10 microns) act at principal precursor materials for a wide range of existing and emerging products involving advanced ceramics, metals, composites which spans several industries such as aerospace, automobile, machining, vacuum electronics, batteries, data storage, catalysis, etc [1-2]. Particulate materials, as core technologies impact over 1 trillion dollar yearly on a worldwide basis [3]. To achieve desirable properties in the final product, typically the properties of the particles such as shape, size, composition, surface charge, flowability, etc., have been controlled. These characteristics play an important role in determining the final microstructure, and thus the product's properties. However with the rapid advancements in non-particulate technologies such as computers, telecommunications and electronics, there is a strong need to develop novel particulate systems which can result in value-added products [4].

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Increasing interest in the recent years has been focused on a wide variety of nanostructured materials, which possess grain or phase structures modulated on a length scale of less than 100 nm, because it is anticipated that their properties will be different from and often superior to conventional materials that have phase or grain boundaries over a coarser size scale [5-6]. Using artificial engineered nanostructured materials, it may also be possible to engineer the properties by controlling the size of the constituent domains and the manner in which they are assembled. Some of the recent efforts have been focused on synthesizing atomic clusters, zero dimensionality quantum well structures, one dimensional modulated multilayered materials, and three dimensional modulated nanophase materials and nanocomposite materials [3-7]. Although the synthesis of nanofunctionalized particulates is highly desirable from both fundamental and technological viewpoint, significant progress has not been made in this field due to several complicating factors [11-13]. Some of the cluster materials are in the form of multicomponent stoichiometric materials such as phosphorescent materials (e.g., Eu doped yttrium oxide, sulphide). This complicates the uniformly deposition of these species onto the core particle [9-10]. In addition, the functionalized surface should typically have nanometric dimensionality control for optimum interaction between bulk and surface properties. Techniques presently used in the literature such as fluidized bed coating, powder blending, mechanofusion processing, chemical precipitation and chemical vapor phase condensation are not capable of overcoming the above mentioned barriers [11-13].

EXPERIMENTAL

In this paper, we show the feasibility of the pulsed laser ablation technique to form discrete Ag nano particle coatings on core particles of Al₂O₃ and SiO₂. A schematic diagram of two types of nano-functionalized particulate materials is shown in Fig. 1. This schematic shows both discrete and continuous nano-functionalized layers onto core particles.

Fig. 2 shows a schematic diagram of the experimental setup to fabricate the particulate coatings. An excimer laser irradiates the target material through the ultraviolet transparent quartz window. Typical energy densities employed in the experiments were approximately 2-3 J/cm². The laser plume is directed perpendicular to the target material to an agitated bed of core particles. The core particles are suspended in the system by a mechanical agitation method. The thickness and surface coverage of the coating is controlled primarily by the repetition rate of the laser and the residence time of the suspension. By controlling the energy as well as the background pressure in the system, the composition and size of the nano particles can be controlled. Earlier work has shown a correlation between the cluster size and the background gas pressure [14-15]. When the background gas pressure is increased, the cluster size changes from a few atoms to nanometer dimensions. The experiments have been conducted using Al₂O₃.
RESULTS AND DISCUSSION

Due to the fact that the size of the ablated nano particles is below the resolution of the SEM, the presence of the coating on the surface was determined by chemical analysis.

Figures 3 (a), (b), respectively show SEM and Ag chemical images of Ag/Al₂O₃ composite particles synthesized by the laser ablation process. The SEM micrograph shows approximately 18 µm faceted alumina particles, however it does not reveal the presence of a nano particle film on the surface. From the WDX Ag chemical map shown in figure 3(b), it appears that the Ag is distributed uniformly on the surface of the Al₂O₃ particles.

Fig. 3(c) shows a Z-contrast scanning transmission electron micrograph (STEM-Z) image of the Ag nanoparticles on the Al₂O₃ core particle substrate. The image shows a discrete coating of Ag nanoparticles, polycrystalline, ranging in size depending on process parameters from 4.5-33 nm [16].
Figure (4) (a) TEM image showing a continuous thin film of $Y_2O_3; Eu^{3+}$ deposited on the core particle, (b) PL spectra from coated core particles showing the standard Eu peak at 611 nm.

Nano-functional particulate materials can be designed to achieve properties which cannot be obtained with existing particulate materials. An example of this is shown for particulate requirements for field emission based flat panel display applications [8]. This emerging technology has several advantages in terms of low power consumption, high brightness, large viewing angle and is expected to replace liquid based crystal technology in specific applications [8]. In this application, the multiple field emission electron beam sources directly strike a phosphor particulate based screens possessing red blue or green activators to produce light which is emitted out of the surface.

The phosphor screens are typically made from powder materials which exhibit a multitude of shapes and sizes distributions, thus causing non-uniformity in the thick film microstructure. Additionally, upon continuous irradiation with intense electron beams, the brightness of the screens degrade thus limiting its usefulness and have become a major impediment for commercialization [8]. Figure 4(a) shows a TEM micrograph in cross section of a $Y_2O_3; Eu^{3+}$ luminescent (611 nm emission) nano coating on 1 μm spherical SiO₂ core particles revealing important microstructural characteristics of the 25 nm $Y_2O_3; Eu^{3+}$ layer. It can be readily observed that the deposited layer is continuous over the perimeter of the curved surface of the 1 μm core SiO₂ particles. More studies are presently being conducted to understand the nature of layer growth on curved interfaces. These nano-functionalized particulates were heat treated at 700°C for 1 hr. in oxygen to activate the phosphor layer. Fig. 4(b) shows the typical photoluminescence spectrum obtained from $Y_2O_3; Eu^{3+}/SiO_2$ nano-functionalized particles. The figure shows that the particles yield a dominant red light emission peak at 611 nm due to $^5D_0-^7F_2$ transition. Due to shielding effects of 4f electrons by 5s² and 5p⁶ electrons in outer shells of Eu ion, one expects a sharp emission within Eu ions. The photoluminescence brightness was significantly higher when the samples were annealed in oxygen at 700°C for 1 hour.

CONCLUSIONS

A novel technique using pulsed laser ablation to synthesize engineered particulate materials has been presented. TEM observations have shown that the backfill gas pressure and molecular weight have significant effects on Ag nano particle formation during ablation. Further
STEM characterization of the interfaces is presently underway.  

In short, it is felt that PLD method represents a viable method to surface modify particulate systems, which are required for a wide variety of current and future applications.

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