Plasma Manufacturing of Near-Net-Shape Large Scale Nanocomposite Structures – A Potential Bulk Nanofabrication Tool

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ABSTRACT

We report a brief summary of the fabrication of cost effective, high throughput, near-net shape bulk nanocomponents using plasma spray forming – a potential 3-D engineering tool for large scale assembly of nanostructures. The development of a variety of nano/micro ceramic-ceramic, metal-ceramic, nanotube-ceramic components with retained nanostructure, enhanced oxidation resistance, and high fracture toughness, suitable for a wide range of industrial applications is presented herein. The chemistry and the microstructure of the developed components were studied using state of the art, advanced characterization techniques. Simulation studies were conducted in order to study the proper material selection in the development of advanced bulk nanocomposites through proper design of experiments (DOE).

Keywords: Plasma Spray, Near-Net Shape, Bulk, Large Scale, Nanocomposite

1. TECHNOLOGY NEED

The drive toward developing of materials with small particle size, light weight, and improved mechanical and chemical properties affects a large array of applications in the fields of structural engineering, homeland security, space exploration, and other social issues. In this regard, proper selection methods of consolidation of materials with retained nanostructures are important [1]. For example, Hot Isostatic Pressing (HIP), Laser Direct Consolidation, and Plasma Spray Forming are viewed as the most promising nanomaterial consolidation processes with a few limitations. The disadvantages of the HIP are the size limitation and the complexity of the sample geometry. The inconvenience of the laser process lies in the constraint of material selection. However, one can flow practically all types of materials which can melt in a plasma flame. In this research, we select Plasma Spray Forming (PSF) as one of the most versatile methods of designing large scale nanocomponents with the desired shape and size in minimal time. At present, plasma spraying has advanced from coating technology to materials processing technology with a growing importance in the field of bulk nanocomposite manufacturing [1].

2. PLASMA SPRAYING AND PROCESS CONTROL

Near-net-shape processing using PSF involves simultaneous control of powder melting and then particle acceleration for deposition on a rotating mandrel or substrate with a proper CTE (coefficient of thermal expansion) to release the parts after cooling. The plasma spray gun includes a water cooled copper anode and a tungsten cathode. Due to the applied high voltage an arc is created between them. As a result, the flowing gas (Ar and He) reaches excessive temperatures, dissociates and ionizes to form plasma. Powders are fed into the plasma where they can be melted in a control fashion, accelerated to supersonic speeds, and directed toward a rotating mandrel which is rapidly cooled to form a desired shape and size. Thus, the success of the process lies in the design of the mold mandrel material and the plasma spray parameters, which need to be standardized for each component.

Fig. 1. The Plasma spraying technique in the process of making nanocomposite parts.

3. RETENTION OF NANOSTRUCTURES

The powder particles can be injected internally or externally through the plasma flame to control the final microstructure. The particle size plays an important role. The smaller particles entering into the plasma flame have smaller momenta. Thus, for constant carrier gas rates, smaller size particles have less chance to flow through the hot zone of the plasma. For example, from the micrograph (Fig. 2 b) it is clear that the small nanoparticles reinforcements (Si_3N_4) are partially melted and reside along the grain boundaries of the matrix particles ($MoSi_2$). Therefore, it can be concluded that the nanosized particles contribute to the strengthening by preventing the grain growth. This results in increased fracture toughness of the composite, useful for many applications.

4. A FEW APPLICATIONS OF THE PLAMSA SPRAYED NANOCOMPONENTS AND COATINGS

4.1.1 Defense and Aerospace Applications

Fig 2 shows the successful development the unique near-net-shape nanocomponents with retained nanostructures.

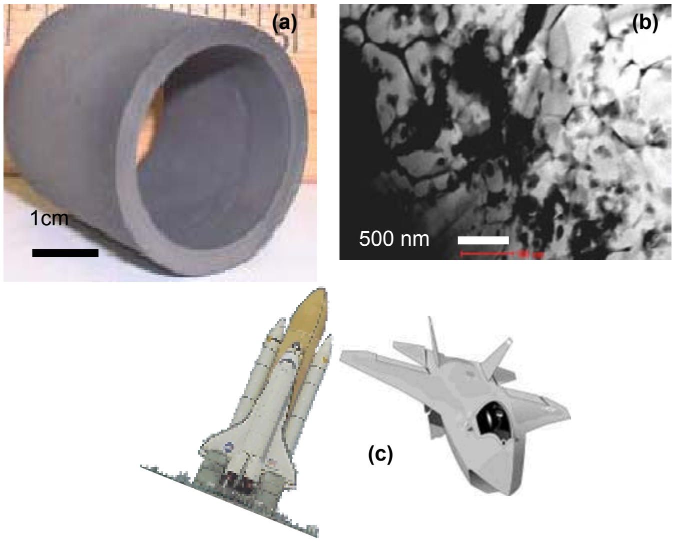

Fig. 2. Plasma sprayed thick nano-$MoSi_2$-Si_3N_4 (a) bulk part and, the correspondent TEM (b) micrograph showing the homogeneous microstructures of the components for applications at specific extreme environments, such as landing gear, high fracture toughness and high temperature resistant materials (c).

4.1.2. Materials Selection Process

Ceramic/Ceramic

The material selection is based on both simulated and experimental results. For example, $MoSi_2$ is a brittle material at low temperature even though it has a high melting point, low density, and excellent high temperature oxidation resistance. Further, it exhibits a poor oxidation resistance of $MoSi_2$ at low temperatures. The problem is due to the "pesting" behavior of $MoSi_2$ [2-5]. The addition of Si_3N_4 is important for increasing the fracture toughness of the composite above 800°C, which is otherwise difficult in silicon-based matrix composites [5]. Therefore, it was assumed that the addition of nanoscale Si_3N_4 to $MoSi_2$ would possibly solve the "pesting" problem and increase the fracture toughness.

Metal/Ceramic

Similarly, Ni/Al_2O_3 (not shown here) is of interest due to the following reasons: alumina has high strength and stiffness, good corrosion resistance, low thermal and electrical conductivity, and low density. Yet, Ni offers several advantages such as high melting point, high thermal expansion coefficient, and relatively low cost. Alumina nanocomposite with Nickel addition is expected to exhibit improved fracture toughness and superior ferromagnetic properties. Therefore, this composite system can be a potential candidate for various applications in diverse environments such as military and aerospace applications.

In the case of $MoSi_2/Si_3N_4$ nanocomposite, the room temperature fracture toughness was calculated to be ~5-7 MPa $m^{1/2}$. It should be noted that this result is almost twice the value reported for a monolithic $MoSi_2$. Therefore, it can be assumed that the enhancement of room temperature fracture toughness of near-net-shape reinforced $MoSi_2$ composites can be attributed to the homogeneously dispersed Si_3N_4 nanoparticles.

It is important to note, that it is rather a difficult task to obtain a homogeneous dispersion of a second phase in the selected matrix, which would lead to enhanced mechanical properties of the composites. Pre-stock powder preparation is very important. To optimize and ensure a proper powder flow through the plasma gun, spray drying is used to make appropriate size agglomerates as part of the pre-stock powder feed preparation.

4.2. Energy Sector: Solution Plasma Spray

In addition to our current thermal plasma spraying possesses we utilize the advantages of SPS to fabricate homogeneous nanostructured porous coating layers or to seal the porosity of the bulk parts. In the plasma flame, the liquid droplets follow a series of chemical reactions including evaporation, droplet disintegration, pyrolysis, and melting. The droplets are deposited on a metallic substrate at high velocity and form a solid thermal resistant coating. The liquid precursors are chosen in such a manner that a direct phase transformation is completed in the flame to achieve the desired material chemistry as end applications. As a result, a unique microstructure is created which can lead to superior toughness and strain resistance to the high thermal shocks often experienced in gas turbine engines (Fig.3).

Fig. 3. A section of turbine blades can be coated using the solution plasma spray for enhanced properties

The as sprayed coatings or functional layers can be applied for insulation of the hot sections of metallic components such as vanes and blades, in combustors and engines, often subjected to extreme conditions and high temperatures.

4.3. In Human Health and Biomedical Applications

The effect of the nanosized materials can be utilized in the improvement of human concerns such as anti-aging and many other therapeutic applications. Most of the present day prostheses, sensor-based systems, and eye and ear implants can be made more efficient with current trends in the nanotechnology revolution. For example, Zirconia has been widely used for biomedical applications; however, in order for ZrO_2 to bond to the bones, the material needs to be stabilized for bio-compatibility with various oxide dopants. By manipulating the plasma parameters, a highly porous structure can be produced, which can be beneficial for the cells to spread, grow, and survive in bodily fluids.

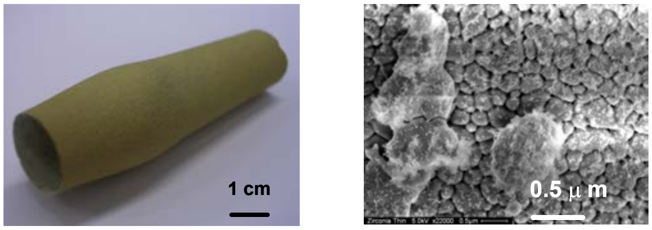

Fig.4. Hip replacements can have an extended life if produced from a biocompatible porous Ceria stabilized Zirconia material using the plasma spraying technique

4.4 Environmental Applications

Many automobile and gas burners technology can use the advantages of the nanomaterials (with high surface area to volume ratio) as components of the catalytic converters due to the presence of an extremely large amount of active sites for reaction. If specific type coatings are applied, harmful emissions such as carbon monoxide, nitrogen oxides, and unburned hydrocarbons could be converted into environmentally friendly by-products such as nitrogen, water and carbon dioxide. Catalytic converter substrates can be produced from the plasma sprayed ceramics. In addition, a washcoat from the Ceria/Zirconia can be applied. For example, due to its unique oxygen storage capacity CeO_2 is often incorporated in the three-way catalysts. CeO_2 acts as an oxygen buffer by storing excess oxygen under oxidizing conditions (oxidation) and releasing it in rich (reduction) conditions. With this process the transformation of (Ce^{3+}) to (Ce^{4+}) and vice versa is advantageous. As a result, CeO_2 oxidizes CO and HC.

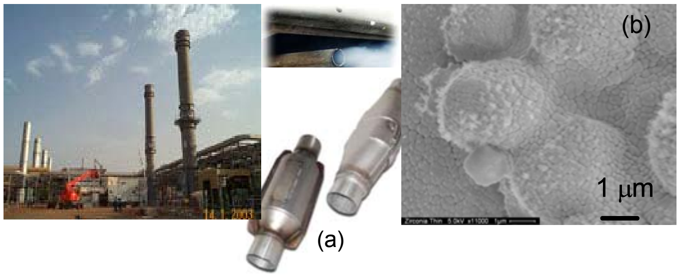

Fig. 5. Catalytic converters (a) are required for the pollution control. A washcoat from Plasma Sprayed Ceria/Zirconia (b) increase the effectiveness of the catalysts

The combination of $CeO_2$with ZrO_2 can be very effectively used as a washcoat for the catalytic converter. Zirconium oxide, when used in conjunction with Ceria, also leads to greater resistance at high temperatures. A problem that might be associated with the poisoning of the catalyst is related to the loss of catalytic activity due to the chemisorption of impurities on the active sites of the catalyst. For example, sulfur may affect the efficiency and oxygen storage capacity of the catalyst. As a solution to this problem, it has been found that Ceria, in combination with either Zirconia or Pd, has a major advantage toward the sulfur reduction reaction [11-13]. Plasma spraying can be effectively utilized for such functional coatings with improved properties.

5. THEORETICAL APPROACH IN MATERIAL DESIGN

Proper design of experiments needs an appropriate material selection methodology. Our group employs a simulation approach for Design of experiments (DOE). The role of the reinforcement in the improvement of the mechanical properties is theoretically studied using the *ab-initio* based Materials Studio software [8].

5.1 Benefit of nanostructures

The effects of nanoparticles size and structure and the stress distributions along the grain boundaries and the interfaces need to be considered. For example, in a nanostructured composite the reinforcement particles are usually dispersed at the grain boundaries or at the triple junctions and in small numbers within the matrix [9]. The nanoparticle reinforcement in the matrix leads to a homogeneous microstructure with enhanced material properties.

The accumulation of a second phase leads to the stabilization of the microstructure and minimizing the grain boundaries free energy. Hence, the increasing of the reinforcement content in the system can lead to the decreasing of the matrix particles and an increasing in the strength of the composite. In conclusion, it is seen that the presence of Si_3N_4 nanoparticles in $MoSi_2$ matrix amplifies the machinabiltiy and ductility of the $MoSi_2$ without sacrificing its properties. Also, the reinforcement nanoparticles serve as obstacles for crack initiation and propagation, and hence contribute to the increased fracture toughness; they can also locally bridge the crack or even porosity and lead to increased capability of energy absorption of the composite.

It should be noted that this paper is presented with only few examples. However, we report both fabrication and characterization of bulk nanopowders to nano/micro alumina, CNT-Vanasil alloy (Al-21%Si) and other plasma manufactured composites with retained nanostructures [1, 14-20].

6. REMARKS

In this report, we tried to convince the research community, that plasma processing is a promising engineering tool toward bulk nanostructured component manufacturing. The proper material selection and the utilization of plasma near-net-shape nanomanufacturing can be of potential interest to a large number of industrial and everyday life applications. Indeed, the theoretical and experimental results need to be combined to explain the mechanisms behind nanostructure retention and enhanced physicochemical properties.

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