Spark Plasma Sintering for Multi-scale Surface Engineering of Materials

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Recently, significant progress has been made in understanding the effect of multi-scale microstructural features, including nano-, micro-, and macro-features, on the properties of materials. Controlling the length scale of microstructural features provides tremendous opportunities for enhancing the properties of materials, including extraordinary strength and hardness, unprecedented damage from tribological contacts, and improvements in a number of functional properties of the materials. Spark plasma sintering (SPS) process which combines the effects of uniaxial pressure and pulsed direct current is becoming increasingly important for the processing of bulk shapes of amorphous and nanostructured materials. These materials can also be good candidates for high-performance coatings. This article presents a review of our ongoing efforts to use SPS to produce engineered coatings of amorphous and nanostructured materials for various applications, including structural, tribological, and biomedical applications.

INTRODUCTION

Recent developments in the understanding of amorphous and nanostructured materials have established that the disordered atomic arrangement and microstructural features at the nanoscale can play an important role in enhancing the structural and functional properties of materials. One of the challenges facing the current industry is the preparation of such high performance amorphous and nanocrystalline materials for advanced technology. To obtain such high performance materials with the desired phase and/or controlled grain/feature size, one must have accurate control over the processing parameters used in preparing them. Significant efforts have recently been focused on synthesizing nanostructured materials in bulk useful shapes from starting amorphous- or nano-powders. Most of the thermal processing approaches such as solidification processing and powder metallurgical techniques (such as hot pressing) tend to induce crystallization in bulk amorphous materials or grain growth of the starting nano-grained material. On the other hand, these amorphous and nanostructured materials can also be good candidates for high performance coatings.

Various coating technologies, including laser processing, thermal spraying, electrodeposition, physical/chemical vapor deposition, and cold spraying, have traditionally been used for engineering microstructure and composition at the surfaces of various materials. Many of these technologies have successfully demonstrated improvements in structural and functional properties, including wear resistance, corrosion resistance, biocompatibility, electrical conductivity, etc. While each technology offers some advantages over the other, they are also associated with some distinct disadvantages. Depending on the combination of coating and substrate materials, major disadvantages of the various coating technologies include slow deposition rates, non-uniform coating, weak interfacial bonding (delamination), undesirable phase transformations, porosity, and cracking. In view of the recent developments in the area of amorphous and nanostructured materials, significant efforts have been made to explore the possibilities of using traditional coating processes for producing surfaces on these advanced materials. While traditional surface engineering techniques have been extensively used for tailoring surface microstructure and composition of conventional materials, the efficient fabrication of fully amor-
Phosphorous and nano-structured coatings has always been a challenge. For example, several efforts have been made in the past to fabricate amorphous coatings on crystalline substrates using various processes such as laser surface cladding\textsuperscript{14-17} and high velocity oxy-fuel coating/thermal spraying.\textsuperscript{18,19} Yue et al. reported laser cladding of Zr-based amorphous coating on magnesium alloy for structural applications.\textsuperscript{20} The laser cladding resulted in the formation of crystalline phases in the amorphous matrix of the coating. Wong et al. also observed the formation of crystalline phases in Ni-Cr-B-Si coating laser clad on Al-Si alloy.\textsuperscript{21} Basu et al. also attempted laser cladding of the Fe-based amorphous coatings on steel substrates and observed formation of intermetallic phases in the coating.\textsuperscript{22} While laser surface cladding provides very high cooling rates (up to $10^6$ K/s), most of these approaches have had limited success in retaining fully amorphous structure in the coatings. This can be primarily attributed to the dilution of the melt pool from the underlying substrate partially melted during laser processing. The rapid cooling rate associated with laser melting/cladding often results in refined dendritic microstructure. The formation of matrix grains with a size in the range of 100–200 nm is difficult with the achievable cooling rates in laser processing. However, laser processing can be used to fabricate the nanocomposite coatings by injecting nanoparticles into the laser melted pool.\textsuperscript{23} While cold spraying techniques have been successfully used to fabricate structural amorphous coatings, the process is likely to be limited for the coating of soft substrates due to efficient embedment of amorphous particles in these materials.\textsuperscript{24} Electrodeposition techniques also present significant potential for fabricating amorphous, nanocrystalline, and nanocomposite coatings.\textsuperscript{25} However, it is very difficult to fabricate thick coatings with uniform microstructure/texture/phase across the thickness. The process is also limited to only certain compositions of amorphous/nanocrystalline alloys (generally Ni-based alloys) depending on the substrate materials. Thus, there is a tremendous drive to develop flexible processes that allow rapid fabrication of amorphous/nanostructured coatings of controlled thickness on a variety of substrates.

**SPARK PLASMA SINTERING FOR SURFACE ENGINEERING**

Spark plasma sintering (SPS) is rapidly emerging as a robust process for fabricating bulk shapes of amorphous and nanostructured materials. Spark plasma sintering is a novel powder consolidation technique rendering significant advantages to the processing of amorphous and nanocrystalline materials into configurations which were previously unattainable (Figure 1). The process involves application of uniaxial pressure and pulsed direct current to sinter the materials at a relatively lower temperature and within relatively short time compared to conventional hot pressing. Due to shorter processing times, the SPS process offers enormous possibilities of sintering highly dense nanocrystalline materials.

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**Figure 1. Schematic of spark plasma sintering (SPS) process for fabricating amorphous and nanostructured materials.**

**Figure 2. Various approaches for processing coatings using spark plasma sintering:**
(a) sintering of coating by directly loading powder of coating material on substrate disc; (b) fabrication of coatings by sintering coating and substrate discs separately followed by subsequent SPS sintering together; (c) fabrication of coating by sintering layers of substrate and coating powder.