Nanoscale Patterning and Welding by Solvent-free Dry Particle Spray and Focused Ion Beam

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Nano particle deposition system (NPDS) is one of dry particle spray methods such as cold spray and aerosol deposition. It can be used to build structures from metals, ceramics, and nanomaterials without any solvents at room temperature and under low vacuum conditions, reducing energy consumption. Recent advances in dry particle spray techniques, including NPDS, have demonstrated their use with advanced nanomaterials such as carbon nanotube. However, to date, this process has not been successfully scaled down to 100-nm scales. Here, we demonstrate the use of NPDS as dry particle spray method in the nanoscale regime with the help of a focused ion beam for nanoscale manufacturing. Nanoscale patterning and welding were achieved using a nano particle deposition system with miniaturized feature sizes that were smaller than 100 nm in scale.

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1. Introduction

Recently, environmental effects and energy consumption have become pressing issues for manufacturing industries, in addition to precision, accuracy, and speed, due to tough environmental regulations and the costs of high energy consumption.¹⁻⁴ Solvent-free manufacturing processes have become important to minimize environmental damage and hazardous material consumption, avoiding the use of solvents such as alcohol, acetone, toluene, or xylene. Several types of solvent-free manufacturing processes are in existence, such as physical vapor deposition and dry powder spraying. Spraying methods, such as cold spraying, aerosol deposition, and nanoparticle deposition system (NPDS), provide a low-temperature process with the advantages of low energy consumption and high deposition rates.⁵

Cold spraying can be used to deposit metals and metal-matrix composites through a nozzle at a high deposition rate to achieve materials with low porosity, low oxidization, and low residual stresses by accelerating the particles with a highly pressurized gas without melting them before impact with the substrate.⁶⁻⁸ Aerosol deposition uses aerosols by combining ultra-fine metal and metal oxide particles with a carrier gas at room temperature.⁹⁻¹¹ NPDS were developed to build different materials, such as metals and metal oxides, on various substrates using cold spraying and aerosol deposition.⁵ Compared with

other dry spray processes, NPDS have the advantages of low energy consumption and few system requirements, as they avoid high vacuums and high-pressure gases.¹²⁻¹⁴

Using these dry particle spray methods, single materials, multi-materials, and mixtures of metal/metal and metal/ceramic and nanomaterials such as graphene, nanotube, and so on can be formed as films on various substrates.^{10,15,16} However, nanomanufacturing capability has not yet been demonstrated for dry particle sprays, although various researchers have investigated particle-based deposition for a variety of purposes.

Here, the scaling-down of the manufacturing regime for solvent-free dry particle sprays is proposed by NPDS. Nanoscale substrate damage was investigated with both metal and ceramic particles, and methods for patterning and welding in the nanoscale regime are demonstrated.

2. Nanoscale Damage

Significant damage to the substrate can occur during conventional cold spraying or aerosol deposition.^{9,17,18} Thus, it is difficult or impossible to engineer a nanoscale surface using these manufacturing techniques. However, an NPDS has non-invasive deposition characteristics, as demonstrated by observing cross-sections with

Fig. 1 Interfaces between films and silicon substrates: (a) metal film-Sn on Si and (b) ceramic film-TiO₂ on Si

scanning electron microscopy,¹⁹ which shows no damage on the polymer surface.

For successful nanoscale deposition, the substrate damage from an NPDS must be almost zero or in the range of tens of nanometers. Here, a focused ion beam (FIB) was used to assist the NPDS, and transmission electron microscopy (TEM) techniques were implemented to observe the nanoscale damage between the film and substrate. To verify the damage caused by metal and ceramic particles, Sn and TiO₂ were deposited onto Si substrates. Each Sn and TiO₂ particle had diameters of 2-20 nm (Sigma-Aldrich) and 15 nm (Nanoarmor), respectively. The interfaces of the Sn and TiO₂ films on the Si substrates are shown in Fig. 1. The Sn and TiO₂ films formed by the NPDS caused no critical visible damage at sub-5-nm scales, and both the metal and ceramic particles adhered to the substrate well.

3. Nanoscale Application

3.1 Nanoscale Patterning

To create a nanoscale structure using a dry particle spray, a nanoscale template first was prepared on a silicon substrate using an FIB. This nanoscale template consisted of V-grooves with mouth widths of 700, 350, and 250 nm that were fabricated by FIB milling and material redeposition.²⁰ The dry particle spray was applied to the substrate using Sn and TiO₂ particles. The carrier gas was air, with a relative air pressure of 0.3 MPa, chamber pressure of -0.097 MPa, feed rate of 0.025 mm/s, and stand-off distance of 3 mm. A TSI 3400 A powder feeder was used to supply the particles to the deposition system.

An FIB cross-section technique was used to verify the cross-sections of the patterned Sn and TiO₂, as shown in the image of Fig. 2, which was obtained by scanning ion microscopy (SIM). The Sn and TiO₂ particles were evenly packed inside the smallest V-grooves, where the mouth width was 250 nm. These results indicate that both particles can be used to form <100-nm nanostructures at the apex of V-grooves. However, the particles were packed at different densities. For Sn, the nanostructure inside the V-groove observed by SIM ion channeling indicated that the ductile Sn particles experienced high strain rate

Fig. 2 Nanoscale patterning by dry particle spraying assisted by FIB: (a) metallic nanostructures of Sn and (b) ceramic nanostructures of TiO₂ on silicon substrates

Fig. 3 Nanoscale welding by dry particle spraying assisted by FIB: a Si-Sn-Si freestanding nanoscale cantilever

deformation and finally formed smaller grains, each with crystal orientations different from that of the original Sn particles.

It is noteworthy that the ductile metallic particles used to form the nanostructure could be larger than the V-groove. This is valuable in terms of manufacturing cost, as the micro-sized Sn particles could be sprayed to form nanostructures without requiring the high cost of nano-sized materials.

Unlike Sn metallic nanostructures, the TiO₂ nanostructures in the V-grooves had a porous structure, even though the size of TiO₂ particles was much smaller than the FIB-milled pattern width.

3.2 Nanoscale Welding

Nanoscale welding was implemented through the following procedure: (1) a 5-mm-wide pattern was milled on Si substrate by FIB; (2) Sn particles were deposited on the FIB-milled area; and (3) FIB-milling of both Si and Sn was used to shape a Si-Sn-Si cantilever.

Fig. 3 shows the nanoscale welding result obtained using an NPDS assisted by an FIB. The thickness (t) of the cantilever was 100 nm, the length (l) was 350 nm, and the widths of Si₁, Sn, and Si₂ were 10, 6.3,

and 6.3 mm, respectively, as shown in Fig. 3a-c. The FIB milled more material at both the Si_1/Sn and the Sn/Si_2 interface. Therefore, the length of the welded part was only around 175 nm (dotted circles in Fig. 3c). In this region, the contact area between the Sn and Si was only 0.017 mm^2 . It is noteworthy that the NPDS could create a freestanding nanostructure with multi-materials at room temperature with no thermal process such as high-temperature sintering. This could be used for many applications, particularly in flexible membrane structures.

4. Conclusions

This paper described how the environmentally friendly dry particle spray method could be scaled down to the nanoscale manufacturing regime. As a demonstration, a solvent-free NPDS, which is a dry particle spraying method, was utilized along with an FIB. First, we showed that there was no significant nanoscale substrate damage due to particle impacts. Then, we proposed two different types of nanomanufacturing processes, nanoscale patterning and joining, and used an NPDS to illustrate how a dry particle spray could be applied to a nanomanufacturing process. The NPDS created metallic sub-100-nm nanostructures inside V-grooves. We also fabricated a freestanding nanostructure with a very small welded area of 0.017 mm^2 .

Future research is planned to determine the mechanism of nanoscale particle packing and adhesion as well as the manufacturing resolution and aspect ratio limits of this process.

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