



NANO MATERIALS & PROCESSES INC.

3D (ADDITIVE) PRINTING

REDUCE PRINTER NOZZLE WEAR AND IMPROVE DEPOSITION ACCURACY

Problem Statement

Additive manufacturing can take several forms. The most commonly available method of additive manufacturing is the fused deposition manufacturing process being generically called 3D printing. A large percentage of additive manufacturing or fused deposition manufacturing (FDM) is accomplished by extruding plastic through a nozzle. Plastics by themselves, do not pose any great difficulty to the equipment.

The mechanical characteristics of the base plastic can be altered with filler material. Such materials are wood, carbon fiber, fiberglass, Kevlar, and various metals. Filler materials that have the properties necessary to improve or alter the base plastic carry with them abrasive characteristics which, over time, produce damage by erosion of the extrusion orifice of the nozzle. This erosion changes the diameter of the extrusion orifice. Once the diameter of the extrusion orifice has changed it is no longer possible to continue additive manufacturing at the precision or performance level desired.

In addition to erosion, filler materials can cause clogging of the nozzle when printing at fine resolution. This may cause the printer to cease printing.

It is possible to manufacture the nozzles from materials which can withstand the abrasive characteristics of the filler material. Materials that can withstand the abrasive characteristics also carry with them negative properties which cannot be easily overcome. For example:

- A nozzle made from stainless steel or tungsten carbide will withstand abrasives, but the thermodynamics are negatively impacted by a factor of as much as 8-10X negative. This means that printing requires more energy to maintain the proper temperature. This increases the cost of equipment needed to support the tungsten carbide tip. In addition, tungsten carbide is expensive due to manufacturing difficulty and material cost.
- A synthetic ruby tip nozzle also increases cost. The synthetic ruby costs approximately 50% more than tungsten carbide and requires additional equipment (although different from that needed for tungsten carbide).
- Nozzles made from either brass or aluminum, have excellent thermodynamic characteristics, but will erode quickly when using abrasive media. Unprotected, failure usually occurs after depositing 100-200 grams of material.

Resolution

Nano Materials and Processes, Inc. (NANOMPI) has a proven process for protecting metals used in high stress applications. It adds a MOH=10 surface of nanodiamonds (“ND”) to the metal. This has been highly successful when combined with chrome and nickel plating for forming dies and metal cutting tools. Application of the ND modified chrome increased the life of

the tool by 10 fold. This translates to 1200-1400 hardness using the Vickers HV scale in kg/mm. This compares to 865-1076 for tungsten carbide. Nanodiamond is a 38.7% improvement over tungsten.

Forming, stamping, and extrusion dies are used with metal (not plastic) and undergo significantly more abuse in the harsh manufacturing process than that which occurs in the extrusion nozzle of an FDM robot machine.

3D printing nozzles have two different inside diameters, one at the inlet and one at the outlet. At the inlet the nozzles can be 2 mm or 3 mm and at the outlet the opening can be as small as 0.2mm or as large as 0.6 mm. Due to the confined nature of the nozzles inner path, it is not possible to chrome this path. Therefore, two different coating technologies were used on the first article prototype 3D printing nozzles. Both coatings derive their performance from the abrasion resistance characteristics offered by the diamond and from the thin film mechanics that permits the formation of a very thin film that is infused with the *nanodiamond*.

Six sets of nozzles have been provided to independent users for evaluation. The users print with filled materials and some use extreme fills of as high as 30% carbon.

Initial results from 3 users were as follows:

1. After 1500g of 30% carbon filled PETG no noticeable degradation
2. Other users have run 20% filled materials with the same results
3. Improved flow characterized by no clogging following use of three (3) spools of low quality PLA and with no need for cleaning
4. Excellent thermo-stability and heat-up of the nozzle characterized by minimal temperature drift and overshoot on heat-up
5. Nozzle cleans-up easily when hot by simply wiping with paper towel.

COMPARISON OF NOZZLE MATERIALS

Comparing printer tip cost to durability in grams of material deposited before the need for printer tip replacement:

Type of Tip (MK8)	Typical Unit Cost	Material Used	Grams Deposited Before Failure	Tip Cost/Gram Deposited
Brass, non-coated	\$4-6	20% carbon fill	100	\$0.04-0.06
Brass with twin clad XT Coating	\$15 to 25€			
Stainless Steel or Hardened Tool Steel	\$25-30		200-300	\$0.10-0.125
Chrome Coated	\$25-30			
Tungsten Premium Alloy (post machined)	49€			No data available
Ruby Tip ¹	\$85			
ND Coated ³	\$17	30% carbon fill PETG ²	1500 g and still going	< \$0.011

Notes: 1 – Ruby tips may fracture

2 – Currently considered the most abrasive printing material

3 – Actual end-user experience (third-party)

The reason for the durability of nanodiamond coated 3D printer tips can be seen by comparing test results of nanodiamond coatings to those of known tungsten/chromium carbide coatings.

Non-cosmetic, mechanical coatings using nanodiamonds with a coating metal, custom developed and optimized for 3D printer nozzles provides these benefits:

- Increased mechanical surface strength
- Increased surface lubricity
- Increased surface life
- Reduction or elimination of unfavorable reactions between fluids and base materials
- Increased life for continuous stamping dies

Micro-hardness of the plating, Vickers HV, kg/mm	1200-1400
Recommended plating width on the working detail surface, Microns	5-20
Increase of the service life with plating	2-15 X

PERFORMANCE OF COATINGS

Tungsten/Chromium Carbide Coatings

Carbidex Series	Rockwell Hardness (HRC)	Alloy Composition	Vickers Hardness (HV)
C1000	68-71 HRC	Formulation of Tungsten Carbide, Cobalt Matrix Key Characteristics: Ultimate abrasion resistance with moderate corrosion resistance	940-1076 HV
C1000Ni	68-71 HRC	Formulation of Tungsten Carbide, Nickel Matrix Key Characteristic: Ultimate abrasion and moderate to good corrosion resistance	940-1076 HV
C1000-17	66-68 HRC	Formulation of Tungsten Carbide, Cobalt Matrix Key Characteristic: Ultimate abrasion and moderate corrosion resistance with ductility	865-940 HV
C1000Cr	69-70 HRC	Formulation of Tungsten Carbide, Cobalt, 69-70 HRC Chrome Matrix Key Characteristic: Ultimate abrasion and good to excellent corrosion resistance	1044-1076 HV
C4000	55-60 HRC	Formulation of Carbon, Chromium, Nickel Matrix Key Characteristic: Moderate corrosion and abrasion resistance with high temperature performance	620-740 HV
C5000 (CPR)	58-62 HRC	Proprietary Formulation of Carbides within a Nickel Chrome Cobalt Matrix Key Characteristic: Moderate wear, extreme corrosion resistance, economical	690-790 HV
C6000	58-62 HRC	Proprietary Formulation of Carbon, Chromium, Tungsten, Nickel Key Characteristics: Moderate wear, extreme corrosion, economical	690-790 HV
C9000	68-71 HRC	Formulation of Tungsten Carbide (micron & nanometer particles), Cobalt Matrix. Key Characteristic: Excellent wear resistance and good corrosion resistance specially formulated for fine particle abrasion	940-1-076 HV

% Improvement HV: ND Coating vs Tungsten Carbide Combinations				
<i>Material</i>	<i>Low</i>	<i>High</i>	<i>Low %</i>	<i>High %</i>
Nanodiamond Coated	1200	1400		
C1000	940	1076	27.7%	30.1%
C1000Ni	940	1076	27.7%	30.1%
C1000-17	865	940	38.7%	48.9%
C1000Cr	1044	1076	14.9%	30.1%
C4000	620	740	93.5%	89.2%
C5000 (CPR)	690	790	73.9%	77.2%
C6000	690	790	73.9%	77.2%
C9000	940	1076	27.7%	30.1%

Product Availability

NANOMPI Diamondized™ 3D printer tips with nanodiamond thin film coating are currently available in the following configurations and output orifices:

- E3D V5, 0.2 mm (can substitute for V6 with adjustment)
- E3D V5, 0.4 mm (can substitute for V6 with adjustment)
- MK8, 0.2 mm
- MK8, 0.4 mm

SPECIAL ORDERS

Non-stock nozzle types and orifice sizes can be special ordered. For consumer grade 3D printers the minimum order is ten (10) pieces.

Commercial 3D printer nozzle coating is available for customer owned items and is quoted on request.

CONTACT INFORMATION

Email: info@nanmpi.com

Call: 248-529-3873