Advanced materials for additive manufacturing

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Abstract. Additive manufacturing (AM), especially known as 3D printing, depends on materials. If we do not have the appropriate materials, it can only be making bricks without straw even with the advanced 3D printer. Therefore, the main development direction of additive manufacturing, such as 3D printing, is using new special consumables materials. 3D printing is relatively easy to metals and difficult to high strength alloys, 3D printing is relatively more difficult to some ceramics, and may be harder to the nano ceramics. To solve the problems of 3D printing materials, such as limited properties and applications, some new nano modifier 3D printing materials are prepared. Scanning electron microscopy (SEM), microhardness and friction and wear tests are used to characterize the obtained NiCrAlY, WC-10Co-4Cr and ceramic powders and coatings. The results show that the optimized process can be used to prepare the nano modifier materials successfully. The coatings have high bonding strength and good wear resistance. Nano-modification and nanostructured spherical particles powder makes it possible for the preparation of high strength alloy materials even nano ceramic materials through 3D printing.

1. Additive manufacturing —must break the bottleneck of materials

As an additive manufacturing technology, 3D printing will profoundly affect the future of manufacturing, and it has become a new economic growth point in the future. In fact, additive manufacturing technology may date back to rather early time, some coating technologies in the field of materials and surface engineering are the most typical, such as laser or electron beam deposition coating technology, thermal spraying technology, and hard facing technology, etc. Then it is developed into the rapid prototype manufacturing technology or free form fabrication technology, and it is used in the fields of the mold manufacturing, industrial design for the manufacture of the models.

Additive manufacturing is based on the materials. The industry believes that the development of 3D printing currently encounter material bottlenecks. If we do not have the appropriate materials, it can only be making bricks without straw even with the advanced 3D printer. It is no wonder that using new special consumables materials is the main development direction of 3D printing.

3D printing is relatively easy to metals and difficult to high strength alloys, 3D printing is relatively more difficult to some ceramics, and may be harder to nano-ceramics. Fortunately, recent research let us see the hope that nanostructured spherical particle powders can be prepared through regulating microstructures of powders. And the nanostructured spherical particle powders can be used as the raw materials of 3D printing, which makes it possible for 3D printing the nano-ceramic materials.
2. Thermal spraying and 3D printing with high-strength super alloys

MCrAlY (M=Ni/Co/Ni+Co) alloy is presently considered as one of the most important the engine turbine blades and other components of high-temperature protection, because of its good high temperature oxidation resistance, good hot corrosion resistance, good plasticity, similar to the thermal expansion coefficient of the matrix, small effect on the capabilities of the matrix, and adjustable composition, etc. MCrAlY coatings can be used as a bond coating of thermal barrier coating, or as a protecting coating that is applied to aircraft engine and gas turbine, or can be used directly as a high temperature thermal barrier working coating around 1000 °C, and can be used to resist high temperature oxidation, sulfidation corrosion, erosion and other damage under the conditions of 800 ~ 1100 °C. These coatings can extend the life of superalloy components.

Nano-modification technology is applied to the preparation of MCrAlY alloy powder materials. The thermal sprayed MCrAlY coating made by using the modified alloy powder materials has more excellent high temperature performance. High strength and high temperature alloy products with the alloy powder materials can also be obtained by 3D printing. The following gives the relevant findings:

The flowability and density of powder feedstocks that is used for thermal spraying will affect the deposition rate of the spraying operation and the performance of the coating. Adding nano modifier into NiCrAlY alloy when vacuum smelting, and then powder feedstocks for thermal spray is prepared through ultrasonic gas atomization technology. Then, different nano modified NiCrAlY coatings is prepared by using HVOF [1-4].

2.1. The characterize of NiCrAlY powders

Figure 1 shows the morphologies of the NiCrAlY powders with and without addition of nano modifier. The powders prepared by ultrasonic gas atomization had a smooth and dense surface, exhibiting good sphericity. Some powders had adhered satellite particles with diameter of around 30μm. The NiCrAlY powders were evidently refined after modifier addition. The average particle sizes of the powders with 0 and 0.3 wt.% nano modifier were about 33.6μm (Figure 1(a)) and 16.8μm(Figure 1(c)), respectively.

![Figure 1](image)

**Figure 1.** The morphology of NiCrAlY powders: (a),(b) non-modified; (c),(d) modified.

2.2. The surface morphology and properties of NiCrAlY coating

As we can see from the Figure 2, the surface of coating without nano modifier is relatively coarse, and the surface of coating with nano modifier is smoother. And, cracks and porosity of the coating without nano modifier are larger, poor in conjunction with the matrix. The coating with nano modifier is
apparently dense, preferably is in conjunction with the matrix. Table 1 shows that the average microhardness and bonding strength of NiCrAlY coating. Visibly, the average microhardness and bonding strength of NiCrAlY coating are significantly improved by nano-modification.

![Figure 2.](image1)

**Figure 2.** The surface morphology of the NiCrAlY powders: (a) non-modified; (b) modified.

**Table 1.** Microhardness and bonding strength of nano-modified NiCrAlY coatings.

| Modifier | non | 1#   | 2#   | 3#   |
|----------|-----|------|------|------|
| Hardness HV₀.₁ | 329.5 | 367.8 | 373.5 | 426.8 |
| Bonding strength(MPa) | 53.13 | 57.3 | 61.4 | 67.15 |
| Modifier B | non | 1# | 2# | 3# |
| Hardness HV₀.₁ | 290.5 | 327 | 336.3 | 390.3 |
| Bonding strength(MPa) | 53.13 | 56.70 | 63.14 | 59.34 |

After nano modification, the hardness of NiCrAlY coating can increase 30-40% , the bonding strength between the coating and substrate can increase 20-35%, the coating thermal shock resistance can increase 20-50%, and can make the coating has good high temperature oxidation resistance and the high temperature sulfide resistance of NiCrAlY coating, which are improved more than one time. This kind of NiCrAlY powder materials can be used as raw materials for 3D printing.

### 3. WC/Co based cermet materials for thermal spraying and 3D printing

#### 3.1. SEM image of WC-10Co-4Cr powder

This is a kind of important high performance ceramic coating. It is widely used in aerospace, automobile, metallurgy and electric power because of its hardness and good toughness, so as to enhance the wear resistance of the base metals. Figure 3 shows the SEM image of WC-10Co-4Cr powder.

![Figure 3.](image2)

**Figure 3.** SEM image of WC-10Co-4Cr powder.
3.2. The properties of WC-10Co-4Cr coating

In recent years, the WC/Co and WC/CoCr coating instead of the hard chromium plating layer is modified by rare earths, also receive good results [5-9]. Many researches indicated that the microhardness and bonding strength of WC-12Co coating is significantly increased by adding proper nano rare earths. And nano rare earths inhibit the decarbonization of WC particles, and refine microstructure effectively [10]. The hardness of coating increased by 42%, the wear volume of coating decreased by 43% when added 1.5wt% nano rare earths. Our recent research shows that with the increase of nano rare earths, the hardness and the friction and wear resistance of the WC-10Co-4Cr coating has been significantly improved, it is shown in Figure 4.

![Graph showing the hardness and wear of WC-10Co-4Cr coatings with different nano rare earths](image)

**Figure 4.** The hardness (a) and wear (b) of WC-10Co-4Cr coatings with different nano rare earths.

Recently, we have carried on the preliminary attempt on the 3D printing by using WC-10Co-4Cr power materials with nano rare earth modification. The results show that 3D printing products can be prepared by using this kind of powder materials.

4. Nano-ceramic materials are available for 3D printing

The current ceramic materials have two shortcomings: the prevalence of brittle and low thermal shock resistance and these shortcomings limits the use of ceramic materials. As the coating materials, the bonding strength between the ceramic coatings and the substrate materials and the compactness of the coatings themselves will be taken into account.

To solve these problems, nano modification technology was invented by Prof. Y. Wang and has produced the nano-ceramic coatings that have great superior toughness, wear and corrosion resistance, thermal shock resistance and good processability [11, 12]. Compared with the widely used commercial Metco 130 coatings, the wear resistance of nanostructured alumina/titania ceramic coatings has improved for 3-10 times, the corrosion resistance of the coatings has improved for 1 times, the bonding strength of the coatings has improved for 1-2 times and the thermal shock resistance of the coatings has improved for 5-10 times. The nanostructured thermal spraying coating technology, which is called a revolutionary advanced technology by the US Navy, has been widely used in the parts of hundreds of warships, submarines, minesweepers and aircraft carriers.

The nano-ceramic powders are spherical powders, which are convenient for using laser or electron beam to manufacture, and will form metallurgical bonding with the parent metal after cladding processing, and the cladding crack is small, the hardness is high, it will not shed under the impact action. Therefore, there is a hope that nano-ceramic materials can be formed by 3D printing because of its simplicity and applicability. That is to say, the nanostructured spherical particles powders can be used as the raw materials of 3D printing, and makes it possible for the preparation of the nano-ceramic
materials through 3D printing. Surface morphologies of nano-ceramic powder particles are shown in Figure 5.

![Surface morphology of nano-ceramic powder particles after plasma treatment: CPSP: (a) 275, (b) 300, (c) 325, (d) 341, (e) 363, (f) 391 (a’~f’) are magnification of (a~f).](image)

**Figure 5.** Surface morphology of nano-ceramic powder particles after plasma treatment: CPSP: (a) 275, (b) 300, (c) 325, (d) 341, (e) 363, (f) 391 (a’~f’) are magnification of (a~f).

### 5. Conclusion: The bright future of 3D printing

Nano-modified and nano structured spherical particles powders make it possible for the preparation of high strength alloy materials even nano-ceramic materials through 3D printing. I believe we can see a variety of metals, plastics, and ceramics, including nano-ceramic material products or parts will be produced by 3D printing in the near future.

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