Preparation of spherical WC–W₂C composite powder via noble metal-free catalytic electroless nickel plating for selective laser melting

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Abstract
In this present work, Nickel-coated tungsten carbide powder was prepared by high concentration electroless nickel plating without noble metal catalysis and the WC–W₂C based composites were successfully prepared by Selective laser melting (SLM). The Ni layers covering on tungsten carbide particles were controlled by the reagent type of complexing agent, stabilizing agent, and surfactant. When Trisodium citrate is used as a complexing agent, it has a well complexing effect on metal ions, but the other complexing agent is poor effect. Compared with ordinary electroless plating, it is not suitable to use stabilizers for high concentration electroless plating. When Polyvinyl Pyrrolidone is used as surfactant, a dense coating layer can be obtained and the coating surface is relatively smooth. Nickel-plated cast tungsten carbide powder as the main raw material, SLM prepared tungsten carbide-based composite materials with uniform microstructure distribution and high relative density. The hardness of the composite increases as the energy density increases. When the energy density is 1000 J m⁻¹, the density can reach 13.183 g cm⁻³ and the relative density is 96.8%, which will help to pave the way for the application of ceramic composites in SLM.

1. Introduction
Cemented carbides are usually fabricated by tungsten carbide particles and a minor amount of Co, Ni, and other metal binder phase, have been widely applied in drills, mold’s inserts and wear-resistant parts which require superior mechanical properties [1–3]. Generally, cemented carbides with complex geometry manufactured by the traditional process are costly [4]. Therefore, how the cemented carbides are used for the reduction in the cost of manufacturing of parts with complex shapes have been one of the central themes in engineering.

Selective laser melting is an additive manufacturing technique has attracted widespread attention due to its advantage of fabricating parts with complicated geometric structures easily. Thus, SLM is a promising process for the rapid preparation of complex cemented carbide parts by using the CAD software to sculpt the shapes and program to produce custom suitable objects [5]. However, the mechanical properties of ceramic parts fabricated by the SLM are significantly deteriorated due to cracks and spheroidized structure formed during the SLM process, thereby limiting their widespread applications [6]. Metal-ceramic specimens fabricated by SLM had the demerits as follow: inhomogeneity of chemical composition, phase segregation and high porosity, which largely attributed to the composite powder of uneven composition [7]. However, it is difficult to obtain metal–ceramic composite powders with the uniform structure by the traditional production process. To date,
metal-ceramic composite powders have been successfully synthesized via a variety of methods: mechanical mixing, ball grinding, sol-gel method, thermal reduction, electroplating, and electroless plating. Among them, the electroless plating technique has attracted the broadest attention. Great effort has been devoted to date to the fabrication of Ni-coated WC composite powders and Co-coated WC composite powders by electroless plating with the noble metal catalytic, and demonstrated that metal coating with uniform thickness and composition covered on the surface of the ceramic particles by electroless plating technology which can prevent ceramic particles from growing during the sintering process [1, 8].

WC–W2C and other ceramic particles need to be pretreated by noble metal such as Palladium, Tin, Gold, Silver to increase sensitization and activation before electroless plating owing to their low surface catalytic activity [9–12]. The adoption of precious metals will cause a sharp rise in costs, and the treatment of heavy metal-containing waste liquid is also a thorny problem. Electroless plating with noble metal free technology has attracted a great deal of attention recently. As for fabrication of Ni-coated WC powders, combining surface etching treatment and ultrasonic treatment were applied to enhance the surface catalytic capacity [13]. The problem of this method is the treatment of strong acid which is dangerous. Some novel methods have been reported that with the surface modification by polydopamine, the inactive material such as ceramics and glass was successfully loaded with metal by electroless plating [14–16].

Here, we applied a new technology of electroless nickel plating with chitosan on ceramics without noble metal catalysis aiming to fabricate the metal coated the ceramic powders with uniform thickness and composition for SLM economic and environmentally friendly.

2. Experimental method

The spherical casting tungsten carbide powder (purity over 99%, size of 15–45 μm) and air atomized copper-tin alloy powder (size of 15–45 μm) was prepared. All chemical reagents were of analytical grade and used with no further purification.

The cast tungsten carbide powder was immersed in sodium hydroxide solution for 10 min to remove the oil, the powder was soaked with HNO3 solution for 10 min and washed with distilled water, and dried at 60 °C in air. The treated powder was poured into the mixture solution of chitosan (2 g l−1) and acetic acid (2 ml l−1) for surface modification, by stirring 10 min, and then dried at 60 °C for 60 min. After drying, the surface modified powder was immersed in a solution of nickel sulfate hexahydrate (NiSO4·6H2O) at 40 °C for 10 min. The solution in sodium borohydride (NaBH4) solution was then added to the solution of nickel sulfate hexahydrate at 35 °C for 20 min, rinsed, and dried.

Composition of electroplating solution is as follow: NiSO4·6H2O solution (320 g l−1), NaH2PO2·H2O solution (320 g l−1) as reducing agent; C20H4N2 and KSCN (10 mg l−1) as stabilizing agent; C6H8O7·2Na, Na3C6H5O7·2H2O, CH3COONa·3H2O (240 g l−1) as complexing agent, PVP and C18H29NaO3S (10 mg l−1) as brightener. The pH value of solutions was adjusted to 12.5 ± 0.5 by adding NH3·H2O solution. The surface activated ceramic powder was poured into the electroless plating solution, which was stirred with a magnetic stirrer in the water bath at 85 °C for 60 min. Different from ordinary electroless plating, this experiment adopted a separating funnel to add a reducing agent. Then the electroplated powders were harvested, cleaning with ultrasonic and reducing in a hydrogen atmosphere at 500 °C. The schematic diagram of surface modified electroless nickel plating is shown in figure 1.

A certain amount of the electroplated powders and copper-tin alloy powders (15 wt%) were put into a V-blender to mix for 1 h. The mixed powders were composited by SLM equipped with a 250 W fiber laser device. The parameters of laser forming are as follows: laser power was 100–200 W, laser beam spot scanning speed was 160–220 mm s−1, scanning spacing was 100 μm. The thickness of the layer was 30 μm, and the dimension of specimens was 10 mm × 10 mm × 5 mm.

The microstructure and thickness of electroplated WC–W2C powders were characterized by field emission scanning electron microscope (FE-SEM SU-8010) and the elemental distribution of Nickel layer was obtained by using energy-dispersive x-ray spectrometer (EDS). The phase of the electroplated WC–W2C powders was identified by x-ray Diffractometer (XRD) (Bruker Co., Massachusetts, USA) using Cu Ka radiation (λ = 1.54060 Å), x-ray photoelectron spectroscopy (XPS) was carried out on an XSAM800 multifunction ESCA system (Kratos Analytical Limited, UK) using Al Ka radiation (hn = 1486.8 eV). Hardness was measured by HB-3000 hardness tester with a 30 kgf. The density of tungsten carbide based composite was characterized using Archimedes principle.
Figure 1. The schematic diagram of surface modified electroless nickel plating.

Figure 2. XRD pattern of the original WC–W₂C and Nano-nickel coated WC–W₂C composite powder.
3. Results and discussion

3.1. Non-noble metal surface activation

To determine the phase structure of the synthesized particles, we performed XRD analyses, as shown in figure 2. From the figure, the typical XRD spectrum can be indexed as that of WC–W2C with the hexagonal crystal structure of the original WC–W2C powders and the plated WC–W2C composite powders. The diffraction peak of amorphous nickel emerges in addition to those of the WC–W2C powders, indicating that cast tungsten carbide was successfully activated by nickel (figure 2(b)). Figure 3(b) shows an SEM image of the surface modified particle, where one can see that the chitosan coating is indeed formed on the surface of the WC–W2C powders, while the texture of initial powder’s surface is clear (figure 3(a)). Figure 4 shows the morphology of the composite powder activated by nickel, where nanoparticles covering larger spherical WC–W2C powders are readily seen. Further EDS analysis on the surface of the coating reveals that the nickel signal is detected, thereby confirming that the ceramic particles are successfully covered by nickel.

The XPS pattern of the chitosan coated WC–W2C powder and nano-nickel activated WC–W2C powder is shown in figure 5. The C1s spectral peaks of the chitosan coated WC–W2C particles were detected at the binding energy of 284.2, 286.15 eV, corresponding to the -C-O and -C-O-C- which could be consistently indexed as that of chitosan. In addition, the spectral peaks of C1s at 287.7 eV is also visible, belonging to -C(=O)-NH-. The functional group was mainly formed by the combination reaction between the hydroxyl group of acid treated WC–W2C particles’ surface and the amino group of chitosan and enhanced the interfacial bonding strength between the chitosan layer and the substrate [17]. The N1s spectrum absorption peaks of WC–W2C powder activated by Nano-Nickel is 401.25 eV, while the –NH3 of chitosan coating is 399.35 eV, suggesting that the nickel atoms have chelated with the nitrogen atoms which had a couple of isolated electrons, and the binding
energy was increased. Therefore, the adhesion strength between Ni and chitosan coating fabricated by chemical adsorption method are enhanced.

The peaks of Ni$_{2p3/2}$ and Ni$_{2p1/2}$ emerge in XPS pattern of activated WC–W$_2$C powder, and the binding energies of those two peaks are 852.2 and 869.4 eV, respectively (figure 5(b)), thereby confirming that Ni (0) was successfully formed on the surface of chitosan-coated cast tungsten carbide after the reduction of sodium borohydride solution, which shows high catalytic performance in the electroless plating process.

3.2. Effect of complexing agent on electroless nickel plating
One of the key factors that influence the morphology and quality of the coating in the electroless plating process rests with the choice of the complexing agent [18]. Figure 6 shows the morphologies of the nickel plating of WC–W$_2$C powder by using different complexing agents. The surface of the powder is relatively smooth and small clasts are also observed when using Na$_3$C$_6$H$_5$O$_7$·2H$_2$O as complexing agent (figure 6(a)). In addition, the coating on the particles is relatively uniform with an average thickness of ~8 μm (figure 6(b)). The coating prepared by the complexing agent Sodium EDTA covered the particles with a more rough surface and thinner thickness, but some particles have bald spots on the surface without coating (figure 6(c)) and the coating is discontinuous (figure 6(d)). When CH$_3$COONa·3H$_2$O was adopted as a complexing agent, the nickel-coating covered the tungsten powder was non-uniform, at the same time, some small nickel particles were found (figures 6(e) and (f)). Figures 6(g) and (h) reveal that complexing agent C$_4$H$_7$O$_6$KNa is beneficial to the improvement of coating quality, although there are minor defects in the surface finish and density of the coating.

Figure 5. XPS pattern of the chitosan coated WC–W$_2$C powder and Nano-nickel activated WC–W$_2$C powder.
3.3. Effect of the stabilizing agent on electroless nickel plating

The stabilizing agent also plays a key role in preparing the nickel coating by an electroless plating method. Some anode ion stabilizers, such as sulfides, arsenides, and iodide ions, inhibit the deposition of nickel by adsorbing on the catalytic sites on the metal surface [19]. However, the decrease of electroplating speed of the coating is due to the toxic effect of excessive adsorption of stabilizer on the coating or substrate surface. C_{10}H_{8}N_{2} and KSCN were applied to investigate how the stabilizing agent affects the morphology of the coating deposited by electroless nickel plating. The morphologies of the prepared composite powders are quite different as shown in figure 7.

Figure 6. SEM images of effect used different complexing agents: (a), (b) Na_{3}C_{6}H_{5}O_{7}·2H_{2}O, (c), (b) C_{10}H_{16}N_{2}O_{6}, (e), (f) CH_{3}COONa·3H_{2}O, (g), (h) C_{6}H_{4}O_{6}KNa.

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The composite powders with rough surface were obtained by using 2–2 pyridine as a stabilizer and the fragments of the coating are also observed (figures 7(a) and (b)), which is different from those prepared by general electroless plating due to the addition of a large amount of the reducing agent and the substantial consumption
of the inhibitor. Although the composite powders prepared with the KSCN as the stabilizing agent has a smooth surface and a thinner coating, (figures 7(c) and (d)), the coating is too thin. From the above results, the inhibitor is unsuitable for high concentration electroless nickel plating as a whole.

3.4. Effect of surfactant on electroless nickel plating
Surfactant is often used as an additive affected the deposition rate, structure and corrosion resistance of coating in the electroless plating process and the primary function is to reduce the surface tension between the hydrogen and liquid interface by adsorbing the active agent on the hydrogel surface, so as to accelerate the removal of the residual bubbles on the surface of the coating and improve the quality of the coating, subsequently [20, 21]. The WC–W2C particles were covered by coating with a rough surface and low density prepared by the absence of surfactant. At the same time, a lot of debris was also produced (figures 8(a) and (b)). Figures 8(c) and (d) reveal that it is beneficial to improve the surface finish and density and prevent the formation of debris by using the surfactant Polyvinyl Pyrrolidone. However, not all surfactants are favorable for coating quality. From figures 8(e), (f) it can be seen that the surface roughens and the porosity of the coating increases when surfactant C18H29NaO3S is added.

3.5. Optimization of the electroless plating solution
In light of the aforementioned analysis of the influence of each reagent on the coating quality, we optimized the ratio of electroplating solution and the test parameters through experiments (table 1). The nickel-coated WC–W2C composite powder prepared by using the optimized process is shown in figure 9. As can be seen from figure 9, the carbide surface is deposited with a dense coating with low roughness and uniform thickness of about 5 μm. Further chemical analysis was performed using an energy dispersive x-ray spectroscopy (EDS), as shown in figure 9, where only the nickel and phosphorus signal are detected, suggesting that the nickel-phosphorus layer is of high purity. Figure 10 shows the XRD pattern, from which the diffraction peaks are identified as nickel and cast tungsten carbide. Furthermore, Ni-P peaks are also visible due to the addition of reducing agent inevitably [22], confirming that the WC–W2C particle is successfully coated with a nickel-phosphorus layer and no other impurity phases.

3.6. Structure and performance of WC–W2C based composites
It is well-known that WC–W2C acts as one of the most important hard alloy materials for laser manufacture. The XRD patterns of WC–W2C based composite materials prepared via selective laser melting (SLM) technology is shown in figure 11 using the different linear laser energy densities (η = P/V). The diffraction...
peaks corresponding to WC–W2C with a hexagonal crystal structure and Cu(Sn), Cu_{0.81}Ni_{0.19} possessed of the face-centered typic cubic structure do not have changed obviously with different linear laser energy densities. The cross-section morphology of WC–W2C based composite material is shown in figure 12, there are plenty of molten cast tungsten carbide (gray) and some Cu-based binder phases (black), meanwhile, large pores (marked by blue circles) are found in the composite materials by using a lower $\eta$ of 450 J m$^{-1}$ (figure 11(a)). As the linear laser energy density increased, the relative density of the coating increased from 90% (450 J m$^{-1}$) to 96.8% (1000 J m$^{-1}$) due to the disappearance of pores from figure 13. However, the cracks are also observed on the surface of composite materials by using a lower $\eta$ of 700 J m$^{-1}$, but when the line energy density reaches 1000 J m$^{-1}$, the crack disappears due to the fluidity and the elasticity is improved at high temperature, which effectively inhibits the release of the internal stress by producing cracks [23]. The hardness for the composite materials are shown in figure 14, where one can see that the line energy density has a great influence on the hardness. The hardness of the composite materials fabricated by the line energy density of 450 J m$^{-1}$ is 69 HRA. The hardness of composite materials is enhanced by the line energy density of 1000 J m$^{-1}$, having an average value of 75.74 HRA. However, the hardness of WC–W2C drops slightly at $\eta = 700$ J m$^{-1}$, which may be caused by long cracks when the thermal stress rises [6]. Srivatsan et al also found...
that due to the presence of residual cracks in the microstructure, the hardness of TiB$_2$–B$_4$C composite revealed a slight decrease [24].

4. Conclusion

A new electroless nickel plating technique is applied to prepare the nickel coatings on the surface of cast tungsten carbide without noble metal catalysis, and tungsten carbide-based composite materials are fabricated via SLM technology. The Nano-nickel surface activated precursor is prepared by surface modification of chitosan, and Nano-nickel successfully covered with the surface of cast tungsten carbide to utilize the chelation of chitosan. The dense and uniform core–shell structured WC–W$_2$C–12wt%Ni composite powder was obtained by electroless nickel plating by the optimized plating process at 85 °C for 60 min. The optimized electroplating solution formula as follows: NaH$_2$PO$_2$ as reducing agent, Na$_3$C$_6$H$_5$O$_7$·2H$_2$O as complexing agents, and PVP as
a brightener. The tungsten carbide-based composite materials prepared by SLM exhibit the good structure and hardness of the parts which is benefited from the coated composite powder. The densification behavior of cast tungsten carbide based parts is controlled by adjusting the laser energy density.

Figure 11. XRD pattern of tungsten carbide-based materials by different linear laser energy densities.

Figure 12. SEM images of section morphology of tungsten carbide-based materials by different linear laser energy densities. (a) 450 J m$^{-1}$, (b) 630 J m$^{-1}$, (c) 700 J m$^{-1}$, (d) 1000 J m$^{-1}$; EDS pattern of Nickel-coating WC–W$_2$C composite powder.
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