Mechanical Properties of Carbon Fiber Reinforced Nanocrystalline Nickel Composite Electroforming Deposit

Abstract: In order to obtain higher strength fiber reinforced composite electroforming deposit, carbon fiber reinforced nanocrystalline nickel composite electroforming deposit was prepared by electrodепositing with pulse current and a flexible wheel was applied to rub and extrude the electroforming deposit. Results shown that when the grains of the carbon fiber reinforced nickel composite electroforming deposit were refined from micron to 80nm at room temperature, the microhardness increased from 230Hv to 740Hv, and the tensile strength increased from 1025MPa to 1472MPa. With the further refinement of the grains of the electroforming deposit, the tensile strength decreased significantly due to the decrease of the bonding strength between the carbon fiber and the nickel matrix, while the microhardness still increased to 758Hv. At 200°C, the carbon fiber reinforced nanocrystalline nickel composite electroforming deposit still showed high strength. When the temperature rose to 400°C, the influence of nanocrystalline on the tensile strength of the carbon fiber reinforced nickel composite electroforming deposit was no longer significant, due to the rapid growth of crystal grains and the precipitation of interfacial brittle substances.

Keywords: nanocrystalline; carbon fiber; tensile strength; microhardness; medium temperature; nickel

Electroforming is a special processing technology for manufacturing metal parts by using the principle of metal ion cathodic electrodeposition. It has been successfully applied in high-tech fields such as precision molds, aerospace, weapons and micro-nano manufacturing [1-3]. Tensile strength is an important performance of electroforming deposit. Increasing the tensile strength of electroforming deposit is one of the hot-spots in electroforming technology. Some scholars have proposed that the high-strength fiber can be applied to reinforce electroforming deposit, which significantly improves the strength of electroforming deposit [4-5]. For example, Suchentrunk [4], a member of the European Aerospace Defense & Space (EADS), used boron fiber, silicon carbide fiber and other lightweight high-strength fiber to reinforce the nickel, copper and aluminum by electroforming, and the composite shown high tensile strength.

According to the formula of the mix rule, the strength $\sigma_c$ of the composite electroforming deposit in the direction of fiber reinforcement can theoretically be calculated. The formula is as follows:

$$\sigma_c = \sigma_f V_f + \sigma_m V_m = \sigma_f V_f + \sigma_m (1 - V_f)$$

In the formula, $\sigma_f$ is the strength of the reinforcing fiber, $\sigma_m$ is the strength of the matrix metal, $V_f$ is the volume fraction of the fiber, and $V_m$ is the volume fraction of the matrix metal.

It can be known from formula (1) that increasing the volume fraction of reinforcing fiber can increase the tensile strength of the composite electroforming deposit. It is the research hotspot which most scholars have focused on. However, it is found that a large amount of pores will be generated inside the composite electroforming deposit when the volume fraction of the fiber is too high, which can reduce the strength of the electroforming deposit [6-7].

It can also be found from the formula (1) that the tensile strength of the fiber reinforced composite electroforming deposit is not only related to the strength and volume fraction of the fiber, but also closely related to the tensile strength of the matrix metal. Existing research by many scholars has shown that the performance of electroforming
deposit can be significantly improved by changing the electroforming process. For example, Lei et al. [8] used high-frequency narrow pulse width pulse current for high-speed liquid electroforming, and obtained the nickel electroforming deposit with the tensile strength of 1160MPa. Urb et al. [9] refined the electroforming deposit grains by adding saccharin to the electroforming solution, which greatly improved the tensile strength and microhardness of the nickel electroforming deposit. Zhu [10] used insulating ceramic microbeads to rub the surface of the cathode during electroforming, which could remove hydrogen and refine crystal grains, and increased the tensile strength of electroforming nickel from 605MPa to 1410MPa.

In this paper, the method of refining the grain size to nano-scale, was proposed to fabricated composite electroforming deposit with higher tensile strength composite and carbon fiber reinforced nanocrystalline nickel composite electroforming deposit was taken as an example to study the effect of nanocrystalline on the tensile strength and microhardness of composite electroforming deposit.

1 Experiments

According to the metal electrodeposition principle [11], the grain size of the deposition mainly depends on two factors, which are the growth rate of the crystal nucleus and the crystal grains. If the growth rate of the crystal nucleus is greater than the growth rate of the crystal grains, the crystal grains are many and small, and the grains of the deposition are fine and dense. The cathodic polarization overpotential is the driving force of electro-crystallization. The larger overpotential will lead to smaller nucleation radius, higher growth rate and finer crystal. The advantage of pulse current over direct current is that it generates high peak current at the same average current which makes electrodeposition performed at a higher overpotential. As a result, finer grains are deposited [12]. Sulfonimide additives can directly inhibit the growth of crystal grains, increase the difficulty of crystallizing, and increase the cathode overpotential [13]. Both the pulse current and the additive were applied in this experiment. The pulse power supply used was produced by Shanghai Riyi Technology Co., Ltd., the current ranges from 0A to 30A, the voltage ranges from 0V to 30V, the duty cycle ranges from 0% to 100%, and the frequency is 2kHz. The output waveform is a square wave, as shown in Figure 1, where \( T \) is the pulse period; \( t_{on} \) is the pulse width; \( t_{off} \) is the intrapulse; \( i_{m} \) is the average current density.

The entire experimental apparatus is shown in Figure 2. The circulating heating filter system mainly consisted of a liquid storage tank, a heating pipe, a thermocouple, a magnetic pump and a filter, which could ensure the cleanness of the electroforming solution and the constant of the temperature. The carbon fiber winding system mainly consisted of carbon fiber, a filament storage tube, a rotation motor, a horizontal axis, and a cathode. The carbon fiber was taken out from the filament storage tube and fixed on the surface of the cathode. The motor rotated to drive the carbon fiber entangle on the cathode, and the controller drove the carbon fiber to reciprocate in the horizontal direction, so that the carbon fiber gradually covered the entire surface of the cathode. After the power was turned on, metal nickel was continuously deposited on the surface of the cathode and the carbon fiber and the carbon fiber was gradually wrapped therein. The volume fraction of carbon fiber was determined by the current density, the rotational speed of the motor, and the moving speed of the horizontal axis.

A flexible wheel was arranged to be in close contact with the cathode. During the electroforming process, the flexible wheel continuously squeezed and rubbed the carbon fiber and the deposited nickel, which could improve the compactness of the composite electroforming deposit and improve its mechanical properties. The core of the flexible wheel was PVC plastic which wrapped with the felt cloth, as shown in Figure 3.

The type of the carbon fiber used was T300B-1K produced by Toray Industries, and the diameter of the monofilament was about 8 to 10 μm. As shown in Table 1, the carbon fiber has excellent electrical conductivity and high specific strength. In order to improve the bonding performance between carbon fiber and electrodeposited nickel, carbon fiber should be pretreated before electroforming, such as degreasing, degumming and roughening.
The low-stress sulfamate electroforming solution whose composition shown in Table 2 was selected as the solution. All the reagents used were analytically pure and prepared by deionized water. The pH value and the temperature of the solution were maintained at 4.5 and 43°C separately during the whole reaction.

The high purity sulfur-free nickel beads from Canadian INCO Metals Co., Ltd., were employed as the anode. In order to prevent the slag from oozing out, the nickel beads were wrapped with polyester cloth after being degreased and cleaned, and placed in an electroforming tank.

The cathode was a cylindrical hollow aluminum rod with an outer diameter of 15 mm, and the actual electrodeposited area was estimated to be about 0.47 dm². After being subjected to degreasing, polishing, weak etching and so on, it was placed in the electroforming tank.

By changing the peak current density and controlling the electric quantity, carbon fiber reinforced nanocrystalline nickel composite electroforming deposit with different grain sizes and the same thickness of 150μm were prepared. The carbon fiber was completely buried in the nickel electroforming deposit, and the structure of the deposited layer was dense with no pinholes. Since the carbon fiber has strong electrical conductivity, the surface of the deposits where the wire was laid had protrusions.

The surface was leveled on a lathe where the excess nickel was removed. The composite electroforming deposit was cut into ring-shaped pieces with 9 mm width.
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by WEDM (wire electrical discharge machining). And then, the pieces were tested for tensile strength.

The microhardness of the carbon fiber reinforced nanocrystalline nickel composite electroforming deposit was tested by HVS-1000A digital microhardness tester with a load of 500g and a holding time of 10s. The hardness value was measured at 5 points on the surface, and the average value was taken as the microhardness of the composite electroforming deposit.

The method of filament pull-out was employed to test the bonding strength of carbon fiber-nickel interface at different conditions.

Ethical approval: The conducted research is not related to either human or animal use.

2 Results and discussions

2.1 Microstructure of carbon fiber-nanocrystalline nickel composite electroforming deposit

Figure 4 is the transmission electron microscope (TEM) images of the carbon fiber reinforced nanocrystalline nickel composite electroforming deposit obtained at different peak current densities with the duty cycle of 10% and frequency of 2 kHz. It can be seen from the figure that as the peak current density increases, the average grain size of the composite electroformed layer decreases significantly. When the peak current density increases from $15 \text{ A/dm}^2$ to $120 \text{ A/dm}^2$, the average grain size of the composite reduces from 200nm to 40nm which means the grain size is remarkably refined.

2.2 Microhardness

Figure 5 is a graph showing the change of the microhardness of the carbon fiber reinforced nanocrystalline nickel composite electroforming deposit with grain size, and the carbon fiber volume fraction is 40%. It can be seen from the figure that when the grain size of the carbon fiber-nickel composite electroforming deposit is refined from $15 \text{ A/dm}^2$ to $120 \text{ A/dm}^2$, the average grain size of the composite reduces from 200nm to 40nm which means the grain size is remarkably refined.

Table 1: The properties of the carbon fiber.

| Properties       | Elastic modulus /Gpa | Tensile strength /Mpa | Density /kg m$^3$ | Specific strength | Average diameter (μm) | Resistivity (μΩ cm) |
|------------------|----------------------|-----------------------|-------------------|-------------------|-----------------------|--------------------|
| Values           | 230                  | 3530                  | 1.76×10$^3$       | 2                 | 8-10                  | 1.6×10$^3$         |

Table 2: The composition of the solution.

| Content  | Nickel sulfamate | Boric acid | Nickel chloride | Sodium dodecyl sulfate |
|----------|------------------|------------|-----------------|------------------------|
| g/L      | 500              | 30         | 15              | 0.05                   |

Figure 4: TEM images of the composite electroforming deposit at different peak current densities.

(a)$=15\text{A/dm}^2$ (b)$=60\text{A/dm}^2$ (c)$=90\text{A/dm}^2$ (d)$=120\text{A/dm}^2$
the nanocrystalline has a great improvement effect on the hardness of the composite.

2.3 The Influence of nanocrystalline on the tensile strength of composite electroforming deposit

The tensile strength of composite electroforming deposit with different grain sizes and the same 40% carbon fiber volume fraction was tested, and the grain size–tensile strength curve is shown in Figure 6. From this figure, it can be found that when the grain size of the composite electroforming deposit is refined from 200nm to 40nm, the tensile strength of carbon fiber - nanocrystalline nickel composite electroforming deposit first rises and then decreases. When the grain size is 80nm, the tensile strength of the composite material reaches up to 1472 Mpa while the tensile strength of the composite is only 1238 Mpa and 1198 Mpa when the grain is 40nm and 200nm respectively. According to the experiment, the tensile strength of the carbon fiber – micron-crystalline nickel composite electroforming deposit with the same volume fraction is only 1023 Mpa. It can be seen that nanocrystalline can obviously improve the tensile strength of carbon fiber reinforced nickel composite electroforming deposit.

According to the law of Hall-Petch, the change of strength properties $\sigma$ with the grain size $d$ in ordinary polycrystalline metal materials is usually in accordance with the following relationship:

$$\sigma = \sigma_0 + Kd^{-\frac{1}{2}}$$

(2)

In this formula, $\sigma_0$ is constant, $K$ is elastic coefficient, and $d$ is grain size. In theory, with the grain refinement, the strength of the metal matrix should always increase. According to formula (1), it is concluded that the fiber reinforced composite materials should always increase with the grain refinement, but it is inconsistent with the actual results. The reason is that the strength of fiber reinforced composite materials is not only related to the strength of fiber and metal, but also related to the bonding strength of both. Therefore, the bonding strength between carbon fiber and nanocrystalline nickel matrix was tested by the method of filament pull-out, and the result is shown in Figure 7 - the change of bonding strength with grain size is not constant. When the grain size is larger than 80nm, the bonding strength increases with the decrease of the grain size. This is because nanocrystalline not only reduces the porosity, but also increase the density of the electroforming deposit. The nickel atoms, which reduced by the nickel ions, accumulated on the surface of the rough carbon fibers, filled the rough pits in the surface of the carbon fibers and gradually wrap the carbon fibers to form an interface. Compared to the micron-crystalline, the refined grains make the fibers tightly hooped therein. When the carbon fibers were peeled off from the nickel matrix, the high interfacial density significantly increased the difficulty of destruction, which exhibited high bonding strength in a macroscopic manner. Therefore, when the grain size was in this interval, the tensile strength of the carbon fiber - nanocrystalline nickel composite electroforming deposit increased remarkably as both the bonding strength and the matrix strength.
increased. When the grains were lower than 80nm, the bonding strength began to show a very significant downward trend. This is because the finer nanocrystalline was obtained by increasing the peak current density in this experiment. As the peak current density increased, a large amount of hydrogen was adsorbed on the surface of the carbon fibers, causing the electroforming deposit to generate pinholes around the carbon fibers. While the nanocrystalline interface was so sensitive that small defects will cause a significant drop in performance. As a medium for transferring and dispersing the load from the matrix to the fibers, the interface must have a high bonding strength. Otherwise, once the interface is destroyed or debonded in a large area, the material will be broken in advance [14, 15], which means the tensile strength will far below the value calculated according to formula (1). Therefore, when the grain was refined to below 80nm, the tensile strength of the carbon fiber-nanocrystalline nickel composite electroforming deposit began to decrease.

2.4 Strength properties at medium temperature

Since nickel matrix materials are mainly used in higher temperatures, the tensile strength at medium temperature is particularly important. Figure 8 shows the relationship between grain size and tensile strength of carbon fiber reinforced nanocrystalline nickel composite electroforming deposit at 200°C and 400°C. The volume fraction of carbon fibers was 40% in the composite electroforming deposit.

It can be seen from the figure that the tensile strength of the carbon fiber reinforced nanocrystalline nickel composite material at 200°C was above 1000MPa, while the tensile strength of the carbon fiber reinforced micron-crystalline nickel composite electroforming deposit at 200°C was only 923 MPa from the other test. Furthermore, the tensile strength of carbon fiber reinforced nanocrystalline nickel composite material with 80nm grain size was up to 1258MPa. Therefore, nanocrystalline can significantly improve the tensile strength of the carbon fiber reinforced composite electroforming deposit at 200°C. Comparing Figure 7 and Figure 8, it can be found that the influence of grain size on the composite electroforming deposit at 200°C was basically consistent with the influence at room temperature.

According to Figure 8, the tensile strength of the nanocrystalline composite electroforming deposit was approximately from 710MPa to 750MPa at 400°C, comparing to the tensile strength of 623 MPa which shown by the micron-crystalline composite electroforming deposit. Therefore, the nanocrystalline showed little influence on the tensile strength at 400°C. The main reason is that the electrodeposited nanocrystalline began to grow up rapidly after 250°C, and also the thermal stability of the deposited layer decreased. As the temperature increased further, the grain growth of the deposited layer became more and more obvious, and the ability of the deposited layer to resist external force deformation was weakened, and the tensile strength was significantly reduced [16]. Second, carbon fiber and nickel will reflect at a high temperature of 400°C, which reduced the strength of carbon fiber. In addition, the reaction product precipitated rapidly at the interface, resulting in a significant increase in brittleness and a sharp deterioration in plasticity, leading to a
significant decrease in strength [17]. Therefore, at 400°C, the refinement of grain size had little effect on the tensile strength of the composite electroforming deposit.

3 Conclusions

1. When the grain size of the carbon fiber-nickel composite electroforming deposit was refined from micron to 40nm, the microhardness increased from 230 Hv to 758 Hv.

2. The tensile strength of the carbon fiber-nanocrystalline nickel composite electroforming deposit first increased and then decreased with the grain refinement, reaching a maximum value of 1472MPa when the grain size is 80nm.

3. The bonding strength between carbon fiber and nickel matrix had an important influence on the tensile strength of composite electroforming deposit. When the grain size was refined from 80nm to 40nm, the tensile strength of the composite electroforming deposit was also significantly reduced due to the decrease in bonding strength.

4. At 200°C, the tensile strength of nanocrystalline on carbon fiber-nanocrystalline nickel composite electroforming deposit still had obvious enhancement effect. But at 400°C, due to the rapid growth of crystal grains and the precipitation of brittle substances on the interface, the influence of nanocrystalline on the tensile strength of composite electroforming deposit was no longer significant.

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