



# High plasticity and anodic behavior of electroformed nickel without chloride ion



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## ABSTRACT

A new process to prepare the electroformed nickel without chloride ion activating the anode in the solution is employed in this study, where the sulfur nickel is used as anode. The concentration of nickel sulfamate and boric acid and the pH value were measured during the electroforming process, as well as the anodic passivation curve. The microstructure was observed by means of optical microscope (OM), transmission electron microscope (TEM), and the mechanical property was investigated by tensile experiment. The results show that the concentration of nickel sulfamate and boric acid remains stable with the values of 425 g/L and 35 g/L respectively during the process of electroforming while the pH value keeps stable. The electroforming process could continue without chloride ion as the activator of the anode. The grains of electroformed nickel are very fine and their average size is 5  $\mu\text{m}$ . The elongation of electroformed nickel without annealing treatment reached up to 20%, and the tensile strength was 460 MPa. In this case, electroforming without chloride ion as the activator of the anode is an outstanding method for the electroformed nickel with the excellent mechanical property.

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## 1. Introduction

Electroforming is a metal forming process where the metal could be prepared through electrodeposition or electroplating on the surface of cathode metal [1]. Compared with other basic metal forming processes, such as casting, forging, stamping, deep drawing, machining and fabricating, electroforming is very effective. It is a near-net shaped method used to prepare the metal parts with high precision [2]. In addition, electroformed metal is extremely pure and its property is superior to wrought metal, due to its refined and uniform grains. Therefore, it has been widely used in electronics, automobile, weapons, and other fields in recent years [3–8]. The electroforming technique has also been widely used in weapon manufacture. It is the main method adopted to fabricate nickel liners of shaped charges based on the research at present [9,10]. According to the theory of penetration fluid dynamics, the jet formed from the nickel liners of shaped charges should be of high density and high extension properties [11]. As a result, the electroformed nickel needs a higher plasticity.

In the conventional preparation method of electroformed nickel, the electrolytic nickel used as anode is easy to passivate, and therefore it needs some chloride ion as an anode activator [12]. The anodic dissolving can be promoted by chloride ion, and the passivation of the electrolytic nickel can be avoided. The chloride ion can also improve the

electrical conductivity of the electroforming solution and the dispersion of the solution. However, the internal stress of the coating will increase with the addition of chloride ion [13], which decreases the toughness of the coating, even leads the embrittlement of the coating.

In order to eliminate the internal stress caused by chloride ion, some sulfur-containing compounds, such as saccharin, need to be added into the electrolyte. The sulfur-containing compounds not only can eliminate the internal stress, but also refine the grains, which can improve the plasticity of the electroformed nickel [14,15]. However, as the sulfur-containing compounds are added, some inclusions forming near the grain boundaries occurred, which increases the brittleness of the electroformed layer [16].

Luo has prepared electroformed nickel by high speed electroforming in the absence of any sulfur-containing additives. However, due to the presence of chloride ion, the electroformed nickel sheet is of greater brittleness and the plasticity of the electroformed nickel increases slightly [17].

In this work, the sulfur nickel was used as anode and the electroformed nickel was prepared without sulfur-containing additives and chloride ion. In this experiment, the concentration of the components in the solution was detected by titration and the value of pH was measured, of which the purpose was to make sure whether the electroforming process could continue. The passivation mechanism of the anode was investigated through the anodic passivation curves. The elongation and tensile strength of the electroformed nickel were measured, and the influence of the microstructure on the mechanical property of the electroformed nickel was investigated. These results indicate that electroforming method without chloride ion and sulfur-

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containing additives can be used to prepare electroformed nickel with excellent mechanical properties.

## 2. Experimental procedures

### 2.1. Preparation of electroformed nickel

The electroformed nickel was deposited from a sulfamate bath by direct current (DC). During the depositing process, sulfur nickel (nickel content  $\geq 99.96\%$ , sulfur content  $\leq 0.04\%$ ) was used as anode, which was cleaned with distilled water and alcohol respectively. Stainless steel plate with the dimensions of 100 mm  $\times$  50 mm  $\times$  1.5 mm was chosen as cathode materials. The thickness of the deposition with the substrate was measured per 16 h, every time 5 values need to be got by using the propeller micrometer. At last, the thickness of the electroformed nickel was obtained by calculating the average thickness and minusing the thickness of original substrate. In order to separate the electroformed nickel from the cathode substrates, the stainless steel was mechanically polished, cleaned and dried carefully before deposition. The electroformed nickel was prepared from the sulfamate baths, which contained nickel sulfamate ( $\text{Ni}(\text{SO}_3\text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$ ) 450 g/L, boric acid ( $\text{H}_3\text{BO}_3$ ) 40 g/L, WT-400 1 ml/L as a low bubble wetting agent. WT-400 needs to be added constantly in order to make the electroforming solution stable during the depositing process. The electroforming solution temperature was kept at 323 K, and the cathode current density was 4.0 A/dm<sup>2</sup>. The pH of the bath was adjusted to 3.6 before depositing and then rise up slowly to 5.5 during the experiment process.

### 2.2. Electrochemical measurements

The electrochemical measurement was performed with an electrochemical station (CHI660) at 323 K by linear potential sweep method. The counter electrode and reference electrode were a graphite sheet electrode and a saturated calomel electrode, respectively.

The working electrode was prepared as the following. First of all, the specimens were cut into 10 mm  $\times$  10 mm  $\times$  3 mm, and welded with Cu wires to keep conductive. Then it was sealed in a PVC cylinder by a layer of epoxy resin, leaving the other end of the rod exposing to the solution. Finally, the specimens were polished before measured.

There were two kinds of solutions in this work, as shown in Table 1. They were the same as the electroforming solution except the content of nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ). One of them involved nickel chloride 5 g/L, while the other contained no nickel chloride. The electrolytic nickel and sulfur nickel were used as anode respectively.

### 2.3. Measurement of the component content and the pH value during the electroforming process

Nickel ions would form complexes with EDTA quantitatively in the alkaline condition. The murexide was used as an indicator to measure the concentration of nickel sulfamate. 2 ml electroforming solution was added into the 250 ml conical flask. And then 60 ml deionized water, 5 ml ammonia, 1 g ammonium fluoride were added into the conical in sequence. As follow, a little of murexide was added as the indicator. After the solution became homogeneous, the standard titration solution with 0.05 mol/L EDTA dissolving in it was added into the solution until the solution turned purple from brown. The concentration of the nickel

sulfamate could be calculated from the volume of the standard titration solution.  $\text{H}_3\text{BO}_3$  is a kind of weak monoprotic acid, and it is not easy to be detected by acid–base titration directly. However,  $\text{H}_3\text{BO}_3$  could combine with mannitol polyols, which would enhance the ionization constants. This made it realizable to measure the concentration of  $\text{H}_3\text{BO}_3$  by acid–base titration [18]. In order to eliminate the difference in the pH of the bath, methyl red was added into the electroforming solution as indicator, and then standard titration solution with 0.1 mol/L sodium hydroxide was added until the solution turned green from yellow, of which the pH was about 6.2. The metal ions in the solution were masked by potassium oxalate. Then, the mannitol polyols was added so as to enhance the ionization constants of the boric acid. At last, the standard titration solution was added into the solution until the solution turned to red. The concentration of the boric acid could be calculated from the volume of the standard titration solution. The pH was measured by a miniature pH sensor (LIDA220) at 323 K.

### 2.4. Microstructure observation and tensile test

The specimens were cut from the electroformed nickel with a thickness of 0.6 mm as shown in Fig. 1. The specimens were mounted by epoxy resin and ethylenediamine. After the epoxy resin solidified, the specimens were mechanically polished in the direction of grain growth vertically, and then wiped with concentrated nitric acid. Optical microscope (OM) of Olympus DP-70 and transmission electron microscope (TEM) of TECNAI F20 were used to investigate the microstructure of the electroformed nickel. The mechanical property was measured on the material testing machine of CMT4105 and the tensile speed was 0.3 mm/min.

## 3. Results and discussion

### 3.1. The anodic behavior

The pure nickel is easy to passivate in the electroforming solution, especially when the electric current goes through the nickel [19]. As shown in Fig. 2, there is obviously passivation range in the three anodic passivation curves. In the nickel sulfamate solution without chloride ion, the corrosion potential  $E_{\text{corr}}$  of the electrolytic nickel is about  $-0.13$  V which is the highest among the three curves. The corrosion current density  $i_{\text{corr}}$  of it, which is about  $10^{-8}$  A cm<sup>-2</sup>, is so low that no activation range is observed. This indicates that the corrosion resistance of the electrolytic nickel is quite high. The electrolytic nickel could only dissolve in the initial stage, and the passivation film forms on the surface of the anode quickly, which leads that the surface become insulative. Therefore, the electroforming could not continue. When the anode potential increases to 1.2 V, the transpassivity occurs. The passivation film on the surface of electrolytic nickel became loose, and then dissolved. This leads the current density increases. When chloride ion is added into the electroforming solution, as shown in Fig. 1, the corrosion potential  $E_{\text{corr}}$  decreases to about  $-0.26$  V and the corrosion current density  $i_{\text{corr}}$  is about  $10^{-7}$  A cm<sup>-2</sup>. An apparent activation–passivation range is observed. The initiating passivation

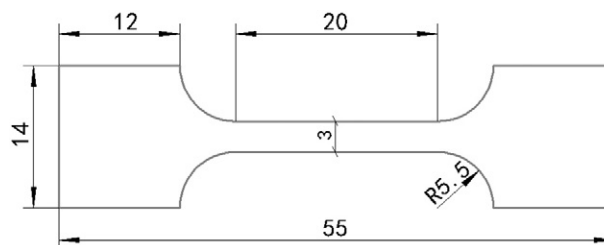


Fig. 1. Sketch of the specimen used for tensile test.

Table 1  
Three kinds of anode and the electrolyte.

No.	Working electrode	Solution
I	Electrolytic nickel	Without $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
II	Electrolytic nickel	With $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
III	Sulfur nickel	Without $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

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