Research on the wettability of pulse electrochemical machining GCr12 substrates

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Abstract. Based on mold steel (GCr12), the relationship between pulse electrochemical machining (PECM) parameters and surface for wetting characteristics was explored. The groove structure with the depth of 0.5mm has been machined on the surface of the steel casting GCr12 by impulse electrochemical machine. Under the best processing parameters, the hydrophobic angle can reach 161.8°. The microstructure, elementary composition, and wettability of the sample were characterized and analyzed by scanning electron microscope (SEM), ultra-depth-of-field microscope, EDS energy spectrum, and contact angle measuring instrument. Single factor experiments are used to explore the influence of pulse electrochemical machining voltage and pulse time on the surface wettability of mold steel (GCr12).

1. Introduction
Wettability is one of the important features of the surface of the material that is characterized by the static contact angle. The main factors influencing wettability are the chemical composition and microstructure of the material surface and mainly by surface modification and surface micro modeling to modify the wettability of materials. The wettability has been directly applied to production and life; the construction of super-hydrophobic surfaces and intelligently controllable wettability surfaces is a research hotspot at this stage, which is of great significance in the fields of architecture, painting, biomedicine, etc.[1]. The construction of a super-hydrophobic surface on the metal substrate can effectively solve the problems of metal materials that are not resistant to corrosion and easy to coat ice during use. At the same time, it is given special functions such as self-cleaning [2, 3], oil-water separation [4, 5], lubrication, and drag reduction [6, 7], which has extremely high application value and market prospects. Mold steel is one of the most important materials for producing mold products with high precision, high complexity, high consistency, and high productivity at a very low cost [8]. With the rapid growth of the steel and mold industries, research into the processing performance of steel castings has become increasingly important. Consequently, in view of the industrial background of mold steel. The preparation of microstructure on the surface of mold steel has important industrial significance.

At present, researchers have used different micro-nano processing methods to prepare micro-nano structure devices with special wettability on the surface of the material[9]. Electrodeposition, photolithography, chemical corrosion, brush plating, wire EDM, and laser processing have been studied...
However, there are limits to these methods of preparation to some degree. For example, some methods have overly complicated processing steps, some have high processing costs, some are limited to the processing of particular materials, and some methods are inflexible. The laser processing method is a modern technical method that uses a laser beam to process various materials into different products according to requirements. When the laser beam is irradiated on the surface of the material, the processed part can heat up, melt, vaporize, or fall off in the small area, to achieve the purpose of processing. But in the process of processing, the workpiece will produce irregular burrs and melts. The chemical etching method refers to the metal material corroding the surface of the material through a chemical reaction. This method can prepare a large area of wettability surface, and the speed is relatively fast, but this method cannot prepare a complex surface. Exploring simple and practical methods that can prepare complex microstructures on the surface of materials to adjust their wettability is one of the main development directions in the field of material wettability research.

In this paper, the microstructure of die steel was prepared by pulse electrochemical machining. Tool wear will not occur in this process, and it has the technical characteristics of wide machining range, high machining efficiency, low machining cost, no residual stress, no burr, and so on so that the electrochemical machining technology has high precision and high stability. Therefore, it has been widely used in the preparation of micro-nano structures of various difficult-to-machining materials, and electrochemical machining of hydrophobic materials has become a hot spot in the wettability of micro-nanostructures. Electrochemical machining is a special machining method that uses the principle of electrochemical anodic dissolution of metal in the electrolyte to shape the workpiece. While processing, the piece is connected to the positive pole of the DC power supply, and the tool is connected to the negative pole, keeping a small space between the two poles. The electrolyte flows through the gap between the electrodes to form a conductive path between the two electrodes, and generates current under the power supply voltage, thereby forming an electrochemical anode dissolution. Based on the NaNO₃ solution used in this study, the electrochemical reaction between the cathode and the anode is as follows:

\[
\begin{align*}
M & \rightarrow M^{2+} + 2e^- \quad \text{Reaction 1} \\
2H_2O + 2e^- & \rightarrow H_2 + 2OH^- \quad \text{Reaction 2} \\
2H^+ + 2e^- & \rightarrow H_2 \uparrow \quad \text{Reaction 3} \\
M^{2+} + 2OH^- & \rightarrow M(OH)_2 \quad \text{Reaction 4}
\end{align*}
\]

2. Experiments

2.1 Experimental steps
Use 800#, 1000#, 1500# sandpaper to polish the mold steel to remove the oxide film on the surface, and then use acetone, absolute ethanol, and deionized water in the ultrasonic cleaner (BG-01) to clean for 300s and then blow dry. Finally, the workpiece is placed on a high-precision pulse electrochemical machining machine for electrochemical machining. Then observe the microscopic morphology with a scanning electron microscope (SEM), and finally measure the contact angle of water droplets on each sample surface with a hydrophobic angle measuring instrument 5 times, and take the average value to observe its hydrophobicity.

2.2 Experimental conditions
The experimental parameters and value ranges are shown in Table 1.
Table 1. Main experimental parameters and value ranges.

| Experimental conditions | Value range or name |
|-------------------------|---------------------|
| Electrode parameters    |                     |
| Electrolyte composition | 25% NaNO₃           |
| Electrolyte temperature | 25°                 |
| Experimental parameters | Processing voltage  | 7.8 V, 7.9 V, 8.0 V, 8.1 V, 8.2 V |
|                         | Pulse time          | 1.5ms, 2ms               |
|                         | Cathode specimen size | Φ20 mm×5 mm            |
|                         | Cathode material    | Mold steel(GCr12) (Fe:84.5%, Cr:12.8%, Other: 2.7%) |
| Electrode parameters    | Anode specimen size | Φ20 mm×5 mm              |
|                         | Anode material      | Pure copper electrode sheet |

2.3 Sample characterization

Besides, the high precision pulse electrochemical machining machine (PECM-800S, Germany) used in the fabrication of microstructure experiments can be equipped with up to 10 generator modules, the voltage can reach thousands of volts, the maximum current can reach 1200A, the machining precision can reach 2-5um, the roughness of rough machining can reach Ra < 0.5 um, and the finishing machining can reach Ra < 0.1um. After the surface microstructure was prepared by electrochemical machining, the micro / nano-scale morphology of the surface was studied by scanning electron microscope (SEM, ZEISS, Germany) and ultra-depth-of-field microscope (ZEISS, Germany). The chemical element composition of the surface was analyzed by X-ray energy dispersive spectrometer (EDS), and the wettability of the workpiece surface was measured by contact angle measurement.

3. Results and analysis

3.1 Micromorphology

Figure 1 shows the microstructure diagram of the mold steel surface magnified 100x and 5000x under different processing parameters. As shown in Figure 1, as the voltage increases gradually, the microstructure in the image changes greatly. Figure 1b shows the surface microstructure machined under the 7.9V 2ms parameters, with a hydrophobic angle of 161.8°. Compared with Figure 1a (7.8V 2ms), some uneven structures are relatively added on the surface. Also, more sub-micron and nano-scale fractured particles are formed. Figure 1e and f are the surface microstructure under 8.2V 2ms and 8.2V 1.5ms processing parameters. When the voltage is constant, the pulse time increases, and the electrochemical reaction takes longer during the machining process, resulting in more corrosion effects on the same part. As can be seen from the figure, Figure 1e forms more nanostructures than Figure 1f. It can be seen from the overall trend of image changes in Figure 1 (a-f). From the overall trend of the image change in Figure 1 (a-f), it can be seen that with the increase of voltage, the electrochemical reaction becomes more intense, and the corrosion effect on the grain boundary becomes more intense, resulting in a large number of micron particles on the surface being broken, and more nano-scale sunken structures are formed on the surface.
Figure 1. Microstructure images of different processing parameters. 
(a) 7.8V 2ms processed image (b) 7.9V 2ms processed image (c) 8.0V 2ms processed image (d) 8.1V 2ms processed image (e) 8.2V 2ms processed image (f) 8.2V 1.5ms processed image

Figure 2. Surface groove structure of the workpiece

3.2 Characterization of the groove profile
Figure 2 shows the three-dimensional image obtained by an ultra-depth-of-field microscope after pulse electrochemical machining. As shown in the figure, it is the three-dimensional view of the surface groove and the schematic diagram of the groove width under 7.9V 2ms parameter processing. With the increase of voltage, the electrochemical effect is gradually enhanced, and the material removal increases at the same time, so the width of the groove gradually becomes larger. Figure 3 is a line chart showing the change of groove width under the parameters of pulse time 2ms and voltage from 7.8V to 8.2V. Figure 4 is a curve of the roughness of the groove surface machined at different voltages.

Figure 3. Groove width under different voltages.

Figure 4. Roughness corresponding to different voltage and pulse times.

Figure 4 shows the corresponding roughness under different voltage and pulse times. Under the processing parameters of 7.9V and 2.0ms, the corresponding roughness is the lowest, and the corresponding hydrophobic angle is also the largest with the increase of voltage, the roughness increases gradually, and the corresponding hydrophobic angle decreases. When the pulse time is 2ms, the roughness and the hydrophobic angle show a linear corresponding trend.
3.3 Chemical composition analysis

Figure 5 is the EDS map of different processing parameters of the mold steel surface. Figure 5 and Table 2 show that the original surface mainly contains two elements of Fe and Cr and some other minor elements. After electrochemical action, the main elements did not change, compared with the original GCr12, the content of C increased significantly, and a large amount of O appeared. This may be due to the carburization and oxidation of Fe and Cr during machining, resulting in an increase in C and O content on the machined surface.

![Figure 5](image)

**Figure 5. Change the diagram of the original surface and machined surface elements.**

| Table 2. Surface element content of GCr12 in different processing processes. |
|------------------------------------------------|
| Element | Fe | Cr | C  | O  | Other |
| Original surface (%) | 84.5 | 12.8 | 1.6 | 0.4 | 0.7 |
| Machined surface (%) | 79.8 | 11.3 | 6.2 | 1.9 | 0.8 |

3.4 Effect of electrolytic machining parameters on the hydrophobic angle

In this experiment, the effects of different processing morphologies on the hydrophobic angle under 7.8V to 8.2V 1ms and 2ms parameters were studied. The contact angle of water droplets on the surface of each sample was measured 5 times and the average value was taken. Figure 6 shows the size of the hydrophobic angle corresponding to different parameters.

![Figure 6](image)

**Figure 6. Influence of voltage and pulse time on the hydrophobic angle**

Figure 6 shows the effect of mold steel (GCr12) on the hydrophobic angle under different voltages and pulse times, as well as a comparative image of the hydrophobic angle. It can be seen from the figure that when the pulse time is 2ms and the voltage is 7.8V, the hydrophobic angle is 145.62°. When the voltage was 7.9V, the curve reached the peak value and the hydrophobic Angle reached the maximum.
value, which was 161.8°, becoming the superhydrophobic surface. When the voltage increases to 8.0V and 8.1V, the hydrophobic angle decreases gradually, but the decrease is small, and the contact angle is still more than 150°, keeping the super-hydrophobic surface. When the voltage reaches 8.2V, the decreasing trend of the hydrophobic angle increases, and the hydrophobic angle is 141.6°. When the pulse time is 1.5ms, under the voltage of 7.9V-8.2V, the hydrophobic angle decreases with the increase of the voltage, and the overall trend of the hydrophobic angle in this range is smaller than that when the pulse time is 2ms. This is because at the same voltage, the longer the pulse time is, the longer the duration of the electrochemical reaction is, which will lead to the increase of material removal rate and the formation of relatively more micro-nano structures on the surface, thus affecting the micro-surface of the groove. Under the same pulse time condition, as the voltage increases, the electrochemical reaction becomes very intense.

4. Conclusions
The hydrophobic surface of the mold steel GCr12 binary micro/nanostructure was prepared by pulsed electrochemical machining (PECM). With a voltage of 7.9 V and a pulse time of 2ms, the maximum hydrophobic angle is to be obtained.

The microstructure and chemical composition were studied by SEM, EDS, and depth-of-field microscope shows that the rough structure of the surface of the workpiece has a great influence on the hydrophobic angle. The appropriate amount of recessed microstructure on the surface of the workpiece has a great influence on the hydrophobicity. The results shows that it is not that the more nanostructures, the better the hydrophobicity. With the increase of voltage, the electrochemical action is enhanced, and the formation of too many nanoscale sag structures reduces the hydrophobicity.

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