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Development of electrolyte filtration system for ECM taking into account removal of chromium (VI) ions

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ABSTRACT

During the ECM process, the metal workpiece is dissolved and turns into sludge which contaminates the electrolyte. To realize precise ECM with high cost-effectiveness, an electrolyte treatment system which can realize reuse of the electrolyte and maintain the electrolyte quality constant is significantly important and essential. Especially, in the ECM of alloys containing a certain level of chromium, it is very likely chromium dissolves to the toxic carcinogen Cr(VI). Therefore, an electrolyte filtration system is required for removing not only the sludge but also residual toxic ions in the electrolyte for health and environment conservation reasons. In this study, activated carbon and scrap iron, which are low cost and easily available materials, were newly utilized to reduce and remove toxic Cr(VI) ions. Experiments clarified that use of activated carbon has no influence on the machining ability of NaNO₃ aqueous solution serving as the electrolyte. By adjusting the pH of the electrolyte to acidic, activated carbon can remove Cr(VI) from the NaNO₃ aqueous solution electrolyte to a concentration of less than 0.1 mg/L. On the other hand, scrap iron generated from metal cutting processes can be used to reduce Cr(VI) to non-toxic Cr(III). By mixing HNO₃ into the electrolyte solution, the reduction efficiency of scrap iron on Cr(VI) improves significantly.

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Nomenclature

Abbreviations

ECM	Electrochemical machining
AC	Activated carbon
Cr(III)	Trivalent chromium
Cr(VI)	Hexavalent chromium
CrO ₃	Chromium trioxide
NaNO ₃	Sodium nitrate
HNO ₃	Nitric acid
NaOH	Sodium hydroxide
SEM	Scanning electron microscope
C _b	Cr(VI) concentration before treatment
C _a	Cr(VI) concentration after treatment

1. Introduction

Electrochemical machining (ECM) [1,2], as schematized in Fig. 1, is a machining process based on the principle of electrolysis. In Fig. 1, by applying a voltage between two electrodes which are placed in an electrolyte solution, the anode material decomposes into ions through electrochemical reaction. In the decomposition process, the workpiece material, which is the anode, is removed. The generated ions will remain in the electrolyte or react with other ions in the electrolyte and turn into precipitate. In addition, hydrogen gas bubbles are generated on the cathode surface. Both the precipitate, referred to as sludge in ECM, and bubbles as shown in Fig. 1, have a significant influence on the current flow in the working gap between the tool and workpiece. Therefore, clean electrolyte with no sludge and bubble is required to realize ECM precisely. Ideally, the clean fresh electrolyte should constantly be supplied to the gap during machining. However, this is not realistic given that it will require a significant volume of electrolyte. For this reason, in ECM technology, an electrolyte treatment system for purifying and recycling used electrolyte should ideally be equipped to the ECM machine.

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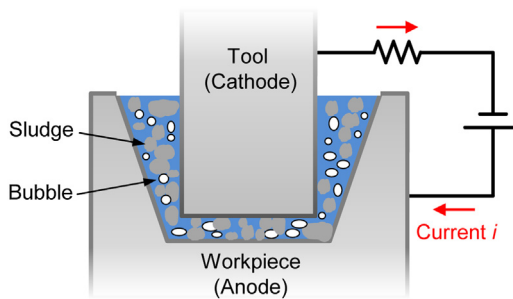


Fig. 1. Schematic diagram of electrochemical machining.

On the other hand, in the ECM of alloys containing chromium (Cr) such as stainless steel, the chromium dissolves into ions in the electrolyte with two states which are characterized by markedly different chemical behavior and toxicity: trivalent chromium ion Cr(III), and hexavalent chromium ion Cr(VI). While Cr(III) is an essential nutrient for many organisms and has low toxicity, Cr(VI) is known to be an extremely toxic and carcinogenic matter which poses a serious threat to the environment and human health [3]. The maximum contaminant level of chromium for drinking water is, as per the World Health Organization (WHO) set standard, 0.05 mg/L [4]. Therefore, in ECM, in addition to sludge, Cr(VI) must be removed from electrolyte before it is reused for machining or disposed, as shown in Fig. 2.

Chemical precipitation is the most widely used method for removing heavy metals from industrial wastewater owing to its low cost and the simplicity of the operation [5]. However, unlike other heavy metals, Cr(VI) cannot be converted into hydroxide in aqueous solution because Cr(VI) exists mainly as highly soluble oxyanions [3,6]. On the other hand, Cr(III) is less soluble and readily precipitates as chromium hydroxide Cr(OH)₃ [7]. Therefore, in ECM it is usually necessary to dispose the waste electrolyte after machining with certain reduction agents such as NaHSO₃, FeSO₄ etc., which are capable of reducing Cr(VI) to non-toxic Cr(III). This is followed by adding an alkali agent such as NaOH to the electrolyte to convert Cr(III) into Cr(OH)₃, which can be removed as a precipitate. However, since a large amount of chemicals is required in this process and excessive amounts of sludge are produced, the process has poor economic efficiency in the collection and disposal of sludge.

Besides the precipitation method, there are many other depuration technologies for removing Cr from industrial wastewaters [5,8] such as membrane filtration, ion exchange, electro-deposition, activated carbon adsorption [9–12] and photocatalytic reduction of Cr(VI) [13,14] etc. The choice of treatment method depends on the characteristics of the effluent. However, none of these depuration technologies stated here have yet to be adopted in the treatment of used electrolyte by the current mainstream manufacturers of ECM machines.

2. New proposal of electrolyte treatment

In this study, a new filtration method is proposed to remove unwanted Cr(VI) ions in used electrolyte. The following are to be noted concerning this proposal:

1) According to Barakat [5], filtration is a low cost and easy operation method for removing heavy metal ions from industrial wastewater.

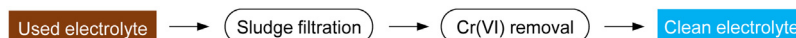


Fig. 2. Procedures for electrolyte treatment in ECM process.

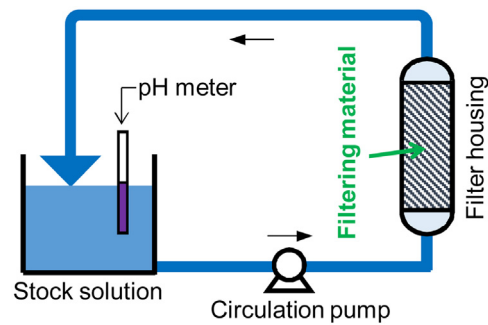


Fig. 3. Experimental setup: circulation filtration of electrolyte solution.

2) With the filtration method, no foreign ions are introduced into the electrolyte solution after treatment, which is considered a significant advantage of this method for the treatment of the electrolyte.

With regard to the filtering material, activated carbon (AC), a well-known adsorbent, is proposed for treating Cr-contaminated electrolyte in this study. Previous researches have shown that activated carbon possesses not only adsorption ability but also reduction effect for removing Cr ions from its aqueous solution [9–12]. However, so far no research have been conducted with regard to the removal of Cr(VI) in ECM electrolyte using activated carbon. Therefore, in this study, we aimed to clarify the applicability and characteristics of activated carbon for removing Cr(VI) when Cr ions exist in the electrolyte during ECM.

In addition to activated carbon, we also attempted the use of scrap iron (Fe) considering its low cost. According to references [15,16], scrap iron can function as an electron donor for reducing Cr(VI) to Cr(III). However, in their study, the solution was not the general electrolyte used in ECM. Therefore, in this study, we focused on investigating the feasibility of applying scrap iron for the reduction of Cr(VI) during the electrolyte filtration process.

3. Experiments

3.1. Stock solution & reagent

A stock of hexavalent chromium solution was prepared by dissolving the required amount of chromium trioxide (CrO₃) in distilled water. On the other hand, the simulated solution of used electrolyte was prepared by dissolving both sodium nitrate (NaNO₃) and CrO₃ in distilled water. NaNO₃ aqueous solution is the most widely used standard electrolyte for precision electrochemical machining. The desired concentration of the stock solution, ranging from 20–200 mg/L, was made by controlling the volume of dilution water. The solution pH was adjusted with aqueous solutions of nitric acid (HNO₃) and sodium hydroxide (NaOH), without introducing new ions into the NaNO₃ electrolyte.

3.2. Experimental method and setup

Fig. 3 shows a schematic diagram of the experimental setup. The stock solution containing Cr ions was circulated constantly by a pump through a home-made filter filled with activated carbon or scrap iron. The pH of the solution was monitored using a pH meter and adjusted as needed in the experiments. The effects of

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