Pulse electrodecontamination of the surface of steel

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Abstract Electrochemical decontamination is a new technology for removing heavy metal from the surface of conductor. The optimum parameters are explored by studying the working mode with pulsed power supply. For testing and verifying advantages of this technology, we have made an experment on removing uranium pollution from metal surface of a polluted equipment, which has been used for over 20 years. A good decontamination result has been obtained even if a lower current density is supplied.

Keywords Uranium, Surface, Decontamination, Electrochemistry

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1 Introduction

Nuclear industries bring about environment pollution, although they have many advantages. For instance, US Department of Energy (DOE) reported there are over 4,000 radioactive pollution sites.[1] Therefore it is important to develop methods to prevent radioactive materials from polluting our environment. Now decontamination methods are divided into two types: physical and chemical.[2-4] For example, scrubbing,[4] stripping,[5] ultrasonic cleaning[6] and plasma decontamination[7] belong to physical method. On the other hand, chemical methods include those by using acid or other chemical solution to remove pollution. In 1996, Los Alamos National Laboratory reported that they got good result in removing plutonium pollution from metal surface by electrochemical decontamination method.[8] Not only is the equipment of electrochemical decontamination simple, but also it has obvious advantages in reducing waste and final cost, etc.[9,10]

Electrochemical decontamination technologies include electrolysis, electrophoresis and electroosmosis technology.[2,11] When this method is used to remove pollution on the surface of metal, the pollution leaves the surface and is dissolved by electrolysis.[12,13] The polluted part is linked with the anode, and the cathode is soaked in the solution. Then low voltage DC or pulsed power is supplied. In fact, this is a kind of process, in which the anode is dissolved. During this process, some controlled pollution moves to solution after leaving surface. This method can be used to clean up radioactive pollution in glove box and to replace the organic or acid solution methods because of its high decontamination efficiency. If pH value in the solution is controllable, radioactive or poisonous elements can be easily separated from the solution.

It is found that the working efficiency is affected obviously by the solution's pH value and current density. In this paper, the working solution is 200g/L $NaNO_3$ (pH~9) for reducing corrosion in electrolysis process and for keeping high working efficiency. Current density in DC electrolysis process is 0.10~0.20A/cm^2.[12-15]

2 Experimental

Most of reagents are of chemical purity including sodium nitrate, sodium borate, sodium oxalate, potassium permanganate, sodium hydroxide, absolute alcohol, and acetone. The specimen of stainless steel is 1Cr18Ni9Ti.

The distance between positive electrode and neg-

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ative electrode can be easily adjusted in the apparatus (Fig.1). Distance between the cathode and anode is 0.9cm, temperature of the solution is 25℃, and working solution is 200g/L $NaNO_3$ (containing 20g/L sodium borate and 2g/L sodium oxalate, pH~9). In this work, the specimen and steel sheet work as the anode and cathode, and the reference electrode is calomel electrode. Pollution on the surface of specimen is determined by X-ray fluorescence analyzer, or α/β-ray detectors. The size of specimen is 1.0mm× 1.5mm.

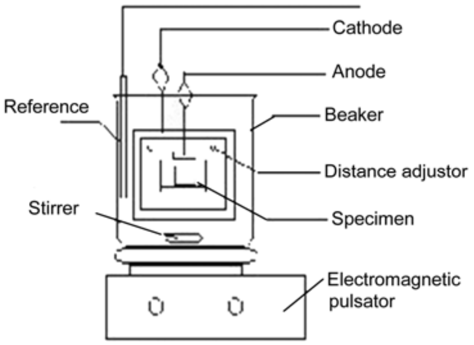

Fig.1 Apparatus for electrochemical decontamination

After the treated specimen is sent into KYKY1010B scanning electron microscope, its surface photo is taken firstly (working voltage of 3kV). Then, element contents are determined by NORAN X-ray spectrometer (single crystal Si detector, accelerating voltage of 20kV, angle of 43°, current of 100μA).

3 Results and discussion

3.1 Effect of frequency

In 200g/L (pH~9) $NaNO_3$ solution, specimen mass was measured after processed by different frequency (95:5 occupied to empty pulse proportion), the results are shown in Fig.2. It is obvious that the working efficiency is higher in 100~1000Hz power supply than in 5000Hz. So 100~1000Hz frequency is chosen as the working frequency range.

3.2 Effect of pulse proportion

Specimen mass was determined in different positive to negative pulse proportions (95:5 occupied to empty pulse proportion) in 200g/L (pH~9) $NaNO_3$ solution while the working frequency is 100Hz. It was found that high working efficiency can be got by using high positive to negative pulse proportion when working in low current density, but it was on the contrary in high current density, as shown in Fig.3. So 75:25 is chosen as the working pulse proportion.

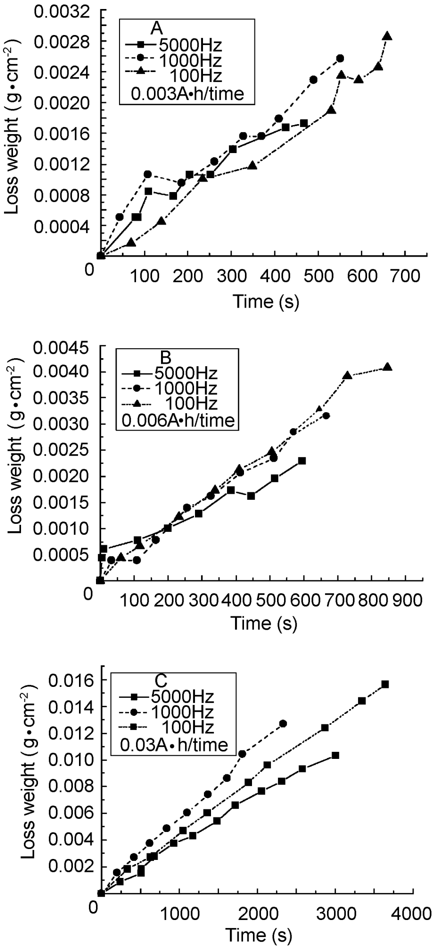

Fig.2 Effect of frequency in electrolysis process

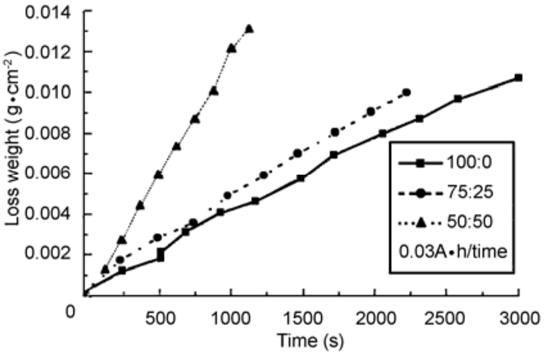

Fig.3 Effect of positive to negative pulse proportion

3.3 Effect of electrolysis on surface

Specimens were analyzed by SEM (shown in Fig.4) after electrolyzed for 2 min in 4V voltage pulsed power with 75:25 positive to negative pulse proportion and 95:5 to 100:0 occupied to empty pulse proportion that equals to 0.2 A·cm^{-2} DC power. It is difficult to distinguish SEM photos of the specimens electrolyzed in 100Hz or 1000Hz but we can easily distinguish between original specimen and electrolyzed ones. The effect of electrolysis is sharper in 8V than in 4V and this effect is more obvious in 1000Hz than in 100Hz when cell voltage is 8V.

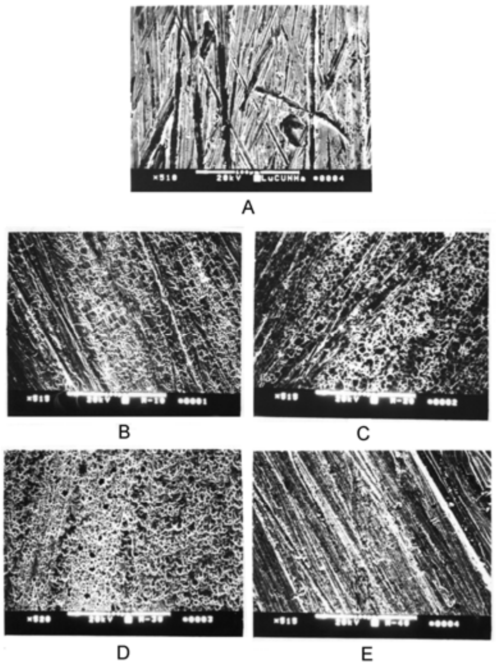

Fig.4 SEM photos of decontaminated specimen
A-original specimen; B-4V voltage; 100Hz frequency; C-4V, 1000Hz; D-8V, 100Hz; E-8V, 1000Hz.

3.4 Decontamination effect

For verifying and testing the electrochemical decontamination of stainless steel, we electrolyzed the specimen in 0.2A·cm^{-2} with pulsed power then determined the effect every 2 min until the pollution reached the detection limit. Decontamination factors (DF) are calculated according to Eq.(1), and they are compared with the result obtained by DC power electrolysis. As shown in Fig.5, it is obvious that pulsed power is better than DC, and working effect at high voltage is better than at low voltage.

Electrochemical decontamination effect is compared with classical chemical decontamination technologies, including alkaline permanganate (AP, 3mol/L NaOH+10%wt KMnO$_4$) and nitric acid permanganate (NP, 1mol/L HNO$_3$+10%wt KMnO$_4$) (Fig.5B). Electrochemical method is as good as NP and better than AP, but NP is rarely used in decontamination of nuclear facilities because it is strongly corrosive. So electrochemical method is a new good decontamination technology especially using pulsed power supply.

$$\mathrm{DF}=\frac{\text{Oringinal dose of pollution}}{\text{Dose of pollution after decontamination}} \qquad (1)$$

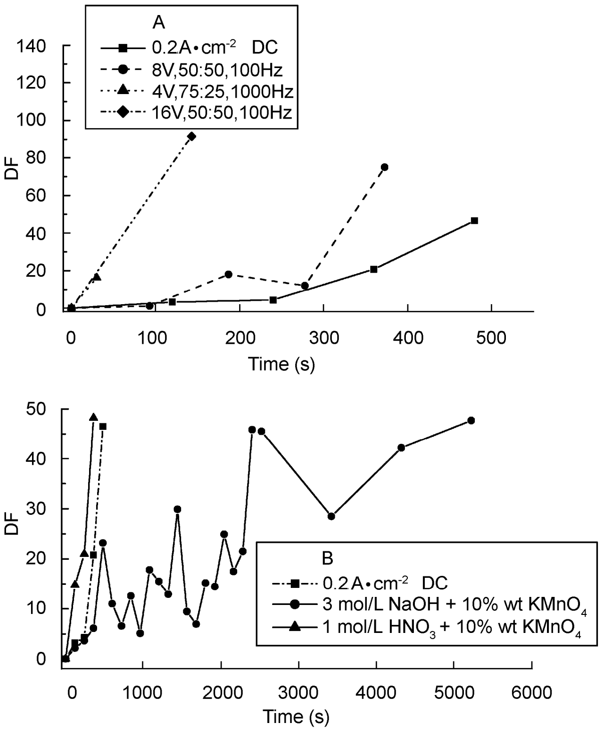

Fig.5 Decontamination effect
A—Pulsed power supply, B—DC power & chemical decontamination.

3.5 Effect verificantion and test

To verify and test the effect of electrochemical decontamination technology, some parts of nuclear facilities are electrolyzed in 0.013 A·cm^{-2} current by pulsed power supply with 100Hz frequency, 75:25 positive to negative pulse proportion and 95:5 to 100:0 occupied to empty pulsed proportion, then their effects are determined every 2 min until the pollution can not be detected by the inspector. The result shown in Fig.6 indicates a good decontamination effect using electrochemical decontamination even if the working current is smaller than the optimum. The size of the steel part of furnace is 456 mm × 305 mm × 4 mm. Pictures of the part (Fig.7) show that the specimen's surface became smoother and brighter after decontamination than the original one.

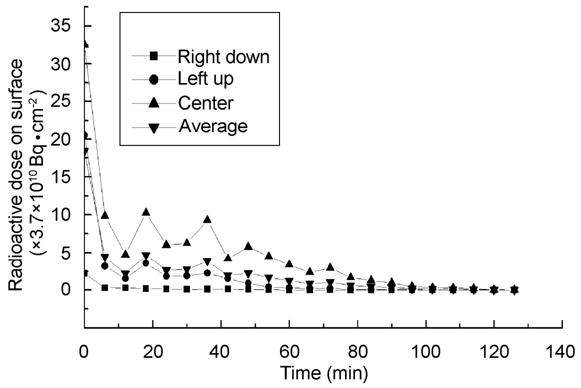

Fig.6 Verifying and testing the decontamination effect

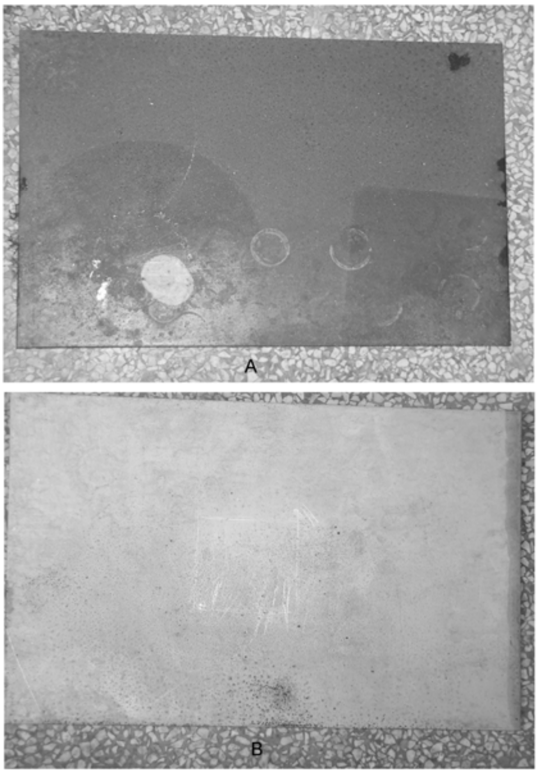

Fig.7 The part's appearance
A—Original part; B—Part after decontamination

4 Conclusion

Electrochemical decontamination methods can get better results and efficiency than AP technology. In the testing and verifying work, we not only found good effect obtained in very low current as working time increased, but also found this method to be suitable for the decontamination of other materials such as graphite and some porous materials.[16] Electrochemical decontamination is more economic than other chemical decontamination technology because it produces less waste than other chemical methods, and its solution can be reused after filtering and adding electrolyte. This electrochemical technology can clean surface of the part with irregular shape and inner surface. Meanwhile, it is proved that the anti-corrosion ability of materials has not been affected.[17] In shorts, electrochemical decontamination method is a new good technology for removing pollution from the surface of conductor. It will be widely used in more fields in the future.

Electrochemical decontamination produces better effect by using pulsed power supply than using DC power, especially in raising efficiency and saving power. Current relaxation is used to raise activity of the electrode and reduce polarization of the solution near the anode in pulsed power supply. Empty time makes solution around the anode return to equilibrium concentration and makes some compounds desorbed from the anode. This is probably the true reason why high efficiency can be obtained by pulsed power supply. Negative pulse can desorb compounds (including oxygen, hydrogen, etc.) and reduce inactivation of electrode on the surface of the anode, so reducing positive to negative pulse proportion.

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