

Dependence of Decontamination Performance on Co distribution in Test Pieces in Dry Surface Decontamination with Low-Pressure Arc Plasma

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We have been studying dry surface decontamination technology with low-pressure arc plasma (LPAP). The dependence of the decontamination performance on Co distribution in the test piece was investigated. The Co removal ratio became lower when Co was distributed more deeply in the metal oxide film, although all the metal oxide film was removed. However, a ⁶⁰Co removal ratio exceeding 90% was eventually achieved by repeated LPAP treatment.

Keywords: low-pressure arc plasma, dry surface decontamination technology, decontamination performance, cobalt, corrosion product film

1. Introduction

A clearance level [1] system for radioactive waste was standardized on December 1, 2005 in Japan. Therefore, it is becoming vital to reduce the radiation dose level of this waste to the clearance level by decontamination.

Some researchers have been studying various kinds of decontamination technology using plasmas [2-4]. We have also been studying dry surface decontamination technology with low-pressure arc plasma (LPAP) for the corrosion product films formed in the cooling water system of an atomic power plant. LPAP is a transferred-type DC arc plasma operated under reduced pressure. One of the advantages of LPAP is the fact that the cathode spots formed inside LPAP can eliminate the metal oxide film on the metal substrate without significant damage to the metal substrate when an object to be treated is set as a cathode [2,5]. This generates small amounts of secondary radioactive waste because no chemical solution is utilized. These advantages suggest the strong potential for practical decontamination technology. To realize this technology, the applicability should be investigated from various viewpoints. However, the dependence of decontamination performance on the Co distribution in the depthwise direction of the object to be treated remains unclear. The Co distribution in real radioactive waste differs in each case, because it depends on the contamination process, for example the formation of a radioactive corrosion product film under a cooling water system at an atomic power plant or the adhesion of radioactive nuclides to the tools etc. Therefore, in this report, we investigated the dependence of the LPAP

decontamination performance in the case of different Co distributions in a depthwise direction inside the metal oxide film.

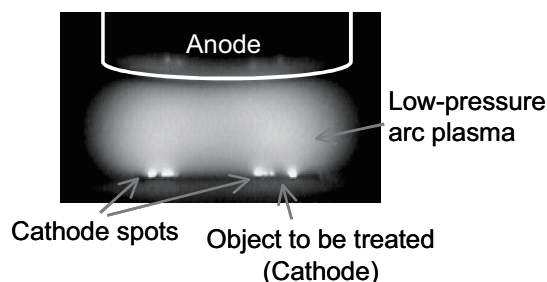


Fig. 1 Photograph of LPAP.

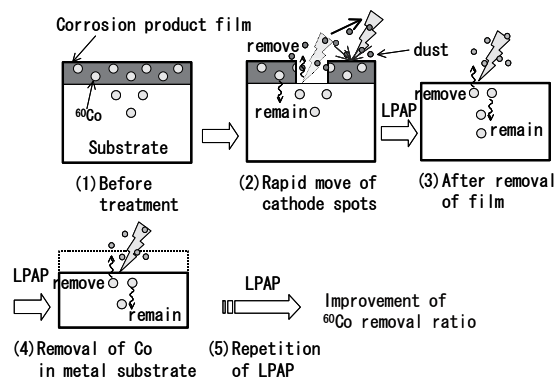


Fig. 2 Schematic process of removing Co by LPAP.

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2. Experimental Method

2.1 Principle of LPAP decontamination

Figure 1 shows a photograph of LPAP, in which we can see illuminating cathode spots.

Figure 2 shows the schematic process of removing Co. The metal oxide film on the metal substrate can be melted and evaporated due to the heat flux from the cathode spots. When the film is removed and the metal surface is exposed, the cathode spots move and rapidly find a new area that is still covered with the metal oxide film ((2) in Fig. 2) [2,5]. By repeating this process, the entire metal oxide film on the metal substrate can be removed. One of the reasons for this may be the fact that the work function of the metal covered with the metal oxide film is lower than that of the metal without the film. However, the details of these phenomena have not been completely clarified to date [2,5]. It is noteworthy that cathode spots can be formed, even on metal substrate, after all the metal oxide film has been removed, as shown in (3), (4) and (5) of Fig. 2.

2.2 LPAP Decontamination System and Experimental Conditions

A schematic diagram of an LPAP decontamination system is shown in Fig. 3. The system comprises an anode and cathode set in a chamber, a DC power supply system (no-load voltage: 200 V, load voltage: 100V). The water-cooled anode is made of copper.

The test procedure is as follows. First, the air in the chamber is replaced with argon gas after setting the test piece as the cathode. Next, LPAP is ignited after filling up the gas to a set pressure. The main conditions of LPAP are listed in Table 1.

The arc voltage was almost 20 V, while the in-chamber pressure was set at a value whereby the best decontamination performance was obtained within the range from a few Pa to several hundred Pa [6].

2.3 Test Pieces and Evaluation of the Co Depth Ratio

The specifications of the test pieces in the experiments are listed in Table 2. Two kinds of test pieces, namely corrosion product film and the metal oxide film by thermal oxidation are used. ^{60}Co is one of the typical radioactive nuclides in low-level radioactive waste generated from an atomic power plant.

It was decided that the shapes and surface areas of the two test pieces were sufficiently large to make significant measurement of Co contained inside. Details of the measurement methods of Co are described in section 2.4.

A corrosion product film was formed on its surface by immersing the metal substrate in the water. The

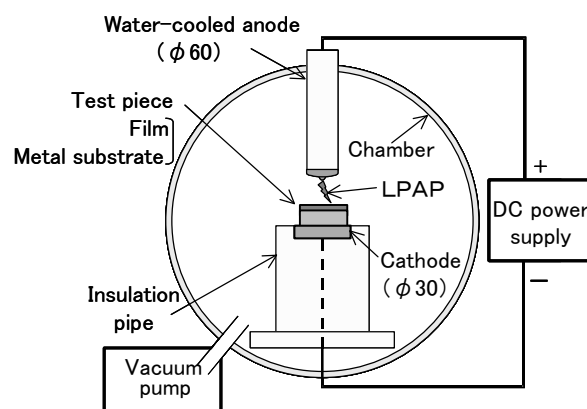


Fig. 3 Schematic diagram of the LPAP decontamination system.

Table 1 Main LPAP conditions.

Parameter	Value
Arc current	60 A
Gap length	2 mm
Pressure	50 Pa
Type of gas	Ar
Treatment time	1-4 s

Table 2 Specifications of test pieces.

Type of test piece	Corrosion product film containing ^{60}Co	Metal oxide film formed by thermal oxidation with non-radioactive Co
Shape of metal substrate	16*16*8 ^t (mm)	30*30*1 ^t (mm)
Concentration of Co	about 0.1(kBq)*	about 40 (μg/cm ²)
Main chemical compounds	Fe ₂ O ₃ , FeCr ₂ O ₄ , etc.	FeCr ₂ O ₄ , Cr ₂ O ₃ etc.

* ^{60}Co distributed both in the corrosion product film and metal substrate at a ratio of 70:30. ^{60}Co distributed at a depth of about 20 μm from the surface of the metal substrate.

Table 3 Production methods of metal oxide film test pieces with varying Co depth ratio in the film.

No.	Making method	Co depth ratio (%)
1	(i)Apply known weight of Co solution to the metal substrate. (ii)Oxide film is formed on its surface at a temperature of 1000°C for 1h in electric furnace by thermal oxidation.	43 - 61
2	(i)Oxide film is formed on metal substrate's surface at a temperature of 1000°C for 1h in electric furnace by thermal oxidation. (ii)Known weight of Co solution is applied to them. (iii)Organic solvent holding Co is vaporized at 600°C for 1h in electric furnace.	19 - 21
3	(i)Oxide film is formed on its surface at a temperature of 1000°C for 1h in electric furnace by thermal oxidation. (ii)Known weight of Co solution is applied to them. (iii)Organic solvent holding Co is vaporized under vacuum for 12h.	5 - 8

conditions of this water imitated those of the coolant water of an atomic power plant.

In the case of metal oxide film by thermal oxidation, an MOD Type Dip coating solution, Co-03 (Kojundo Chemical Laboratory Co., Ltd.) was used as a cobalt source. Three production methods are applied to vary the Co distribution in the depthwise direction of the metal oxide film shown in Table 3 (The word 'Co depth ratio' is used from now on.). The thickness of the metal oxide film itself is almost 1-2 μ m. The Co depth ratio in the metal oxide film was measured and evaluated by GDS (Gas Discharge Sputtering) analysis. Figure 4 shows an example of the GDS measurement result of the test piece made using the No. 1 method in Table 3. It represents the distribution of each component (O, Fe and Co) in the depthwise direction from the surface of the test piece.

In Fig. 4, point P_O is the mid-point of the maximum and minimum values of O signals' intensity. The arrow was drawn from the surface to P_O , with its length defined as A_O . A_{Fe} and A_{Co} are similarly defined. The thickness of the metal oxide film was defined as the average of A_{Fe} and A_O . The Co depth ratio (%) is defined by the ratio of A_{Co} relative to the thickness of the metal oxide film.

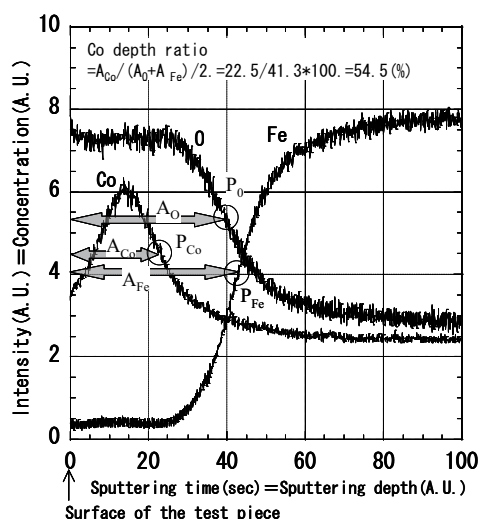


Fig. 4 Distribution of each element's concentration.

2.4 Evaluation Method of Decontamination Performance

The Co removal ratio when only the metal oxide film was removed, a_0 , is defined as,

$$a_0 = (1 - \Gamma_0/\Gamma_F) \times 100 (\%) \quad (1)$$

where Γ_F is the amount of Co in the film before LPAP treatment. And Γ_0 is the amount of Co remaining in the surface of the metal substrate after removing only the metal oxide film.

Additionally, the Co removal ratio when Q (A · s) of LPAP treatment was applied, a_Q , is defined as,

$$a_Q = (1 - \Gamma_Q/\Gamma_N) \times 100 (\%) \quad (2)$$

where Γ_N is the amount of Co in the test piece before LPAP treatment and Γ_Q is the amount of Co remaining in the test piece after Q (A · s) of LPAP treatment.

For radioactive test pieces, Γ were evaluated from the radiation dose level of the test piece with a Ge semiconductor detector (SEIKO EG&G). For non-radioactive test pieces, Γ_F was evaluated from the weight of the Co solution applied to the metal substrate when the forming metal oxide film shown in Table 3. Γ_0 was evaluated as follows: The surface of the metal substrate, including Co, was dissolved in the solution by electrolytic polishing. Subsequently, the concentrations of Co and Fe in the solution were measured by ICP (Shimadzu, ICPS-7500). Based on this measurement result of Fe concentration in the solution, the polished depth of the metal substrate can be evaluated. The measurement results of the Co concentration mean the total weight of Co included in the polished metal substrate. 2 to 3 times of electrolytic polishing of 1-2 μ m deep, was repeated, because Co in the metal substrates decreases with the depth of the metal substrate. The electrolytic polishing method can polish only metal, and cannot polish and dissolve metal oxides.

a_0 and a_Q were used to evaluate the decontamination performance of LPAP.

3. Results and Discussion

3.1 Removal of Corrosion Product Film

First, we investigated whether LPAP can remove metal oxide film.

Figure 5 shows the photographs and SEM photographs of the corrosion product film test pieces (a) before and (b) after LPAP treatment. Photographs of Fig. 5 (a), (b) correspond to ‘(1)’, ‘(3)’ in Fig. 2 respectively.

Before LPAP treatment, a brown-colored corrosion product film covers the surface of the test piece. In contrast, a surface with metallic luster is observed after LPAP treatment. In SEM photos, the grain boundary of metal substrate is clearly observed on the surface of the test piece before treatment, although no such boundary can be observed after LPAP as shown in (b).

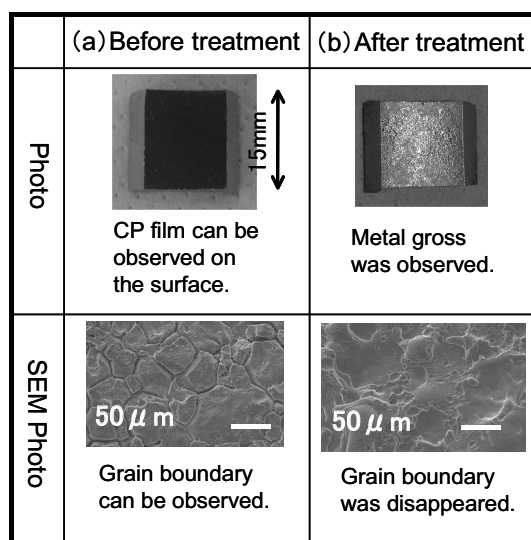


Fig. 5 Photographs of test pieces (a) before and (b) after LPAP treatment.

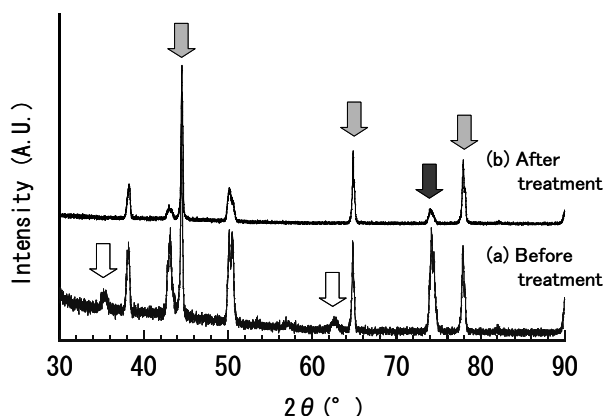


Fig. 6 X-ray diffraction spectra of test pieces (a) before and (b) after LPAP treatment.

⇩ : Corrosion product film (Magnetite (Fe_3O_4), Fe_2O_3 , FeCr_2O_4 etc.)

⇩ : Metal substrate (Kamacite (Fe,Ni)),

⇩ : Metal substrate (Fe-Cr)

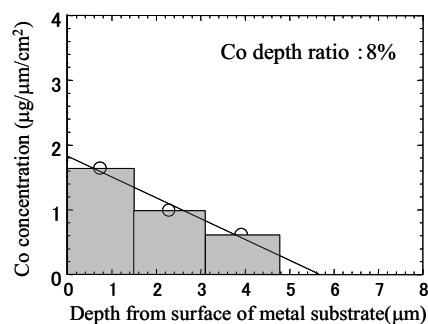
The X-ray diffraction method is also used for surface analysis of the test piece. XRD spectra (a) before and (b) after LPAP treatment are shown in Fig. 6. In the X-ray diffraction pattern, peaks for the corrosion product film have disappeared and the intensity of the peaks from the substrate increased after LPAP treatment. These surface analyses show that the corrosion product film was removed by LPAP.

3.2 Effect of the Co Depth Ratio in Metal Oxide Film

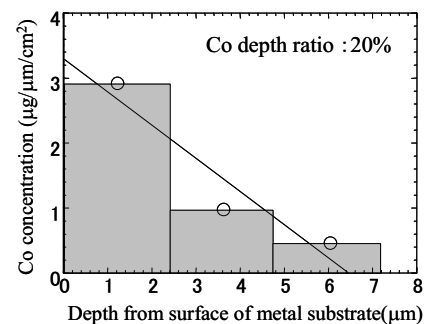
In the previous section, we confirmed that the metal oxide films (thermal oxidized and corrosion product films) were removed by LPAP treatment. In this section, we would like to describe details of the removal of Co.

Figures 7 (a) and (b) show the examples of Co distributed within the metal substrate after removing the metal oxide film. Y-axis is the weight of Co per unit depth per unit area of the metal substrate, in other words, the Co concentration per unit volume of the metal substrate. (a) and (b) are shown with Co depth ratios of 8% and 20%, respectively.

The thickness of each bar means the depth of the metal substrate polished by one-time electrolytic polishing, while the height of each bar means the average Co concentration in this polished metal substrate. The symbol ‘○’ was plotted at the middle of the thickness of each bar, while the straight line was drawn as a minimum square approximation for these symbols.



(a) Co depth ratio:8%



(b) Co depth ratio:20%

Fig. 7 Co distribution in the depthwise direction after LPAP treatment.

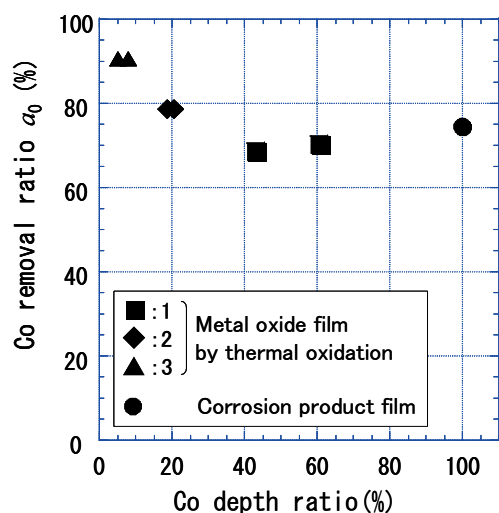


Fig. 8 Dependence of the ^{60}Co removal ratio on the Co depth ratio.

Some Co remained in the test piece, although all metal oxide film was removed as shown in Figs. 5 and 6. Co remained and was distributed at a depth of almost 5–7 μm from the surface of the metal substrate. The concentration of Co decreases with the depth of the metal substrate. With a shallower Co depth ratio (Fig. 7 (a)), less Co remained in the metal substrate, and vice versa (Fig. 7 (b)). It could be estimated that Co at the boundary between the metal oxide film and metal substrate are prone to remain in the metal substrate during LPAP treatment.

The area of the triangle means the total weight of Co per unit area remaining in the metal substrate and the Co removal ratio a_0 can be obtained from these results. Figure 8 shows the experimental results of the dependence of the Co removal ratio, a_0 , on the Co depth ratio, when only the metal oxide film is removed ((3) in Fig. 2). The numbers in the square in Fig. 8 indicate the method used to make the test pieces shown in Table 3.

Consequently, a_0 decreases with the Co depth ratio. With a Co depth ratio of 40% or more, only 70% of a_0 was

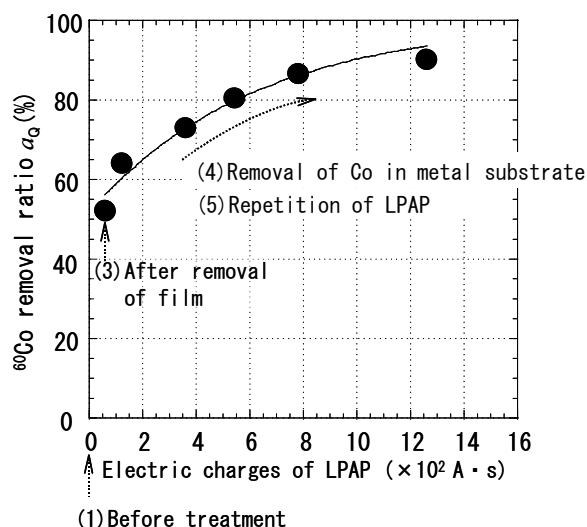


Fig. 9 Improvement of the ^{60}Co removal ratio.

achieved. Conversely, with a Co depth ratio of 10% or less, 90% of a_0 can be achieved after removing only the metal oxide film. The Co removal ratio a_0 is significantly dependent on the Co depth ratio.

To improve the Co removal ratio, a_0 , Co in the metal substrate not in the metal oxide film should be removed. Figure 9 shows the improvement in the ^{60}Co removal ratio, a_0 , by repeated LPAP treatment for the corrosion product film test piece. The numbers marked in Fig. 9, e.g. '(3) After removal of film', correspond to the process in Fig. 2 respectively.

After the removal of metal oxide film, Co remains in the surface of the metal substrate. However, Co in the surface of the metal substrate could be also removed by repeating the LPAP treatment shown in Fig. 9. Eventually, 90% of a_0 could be achieved by LPAP.

These experimental results mean that LPAP could achieve sufficient decontamination performance through repeating LPAP treatment, even in the case of a deeper Co depth ratio like for corrosion product films.

Almost $400 \text{ A} \cdot \text{s}/\text{cm}^2$ of electric charges per unit removed area of the test piece were required to achieve a 90% Co removal ratio. Several further times will be required for a Co depth ratio of 10%.

4. Conclusions

We investigated the dependence of the decontamination performance on the Co distribution in the test piece with low-pressure arc plasma (LPAP) decontamination technology. Consequently, the Co removal ratio when removing the metal oxide film became lower when Co was distributed more deeply in a metal oxide film, such as the corrosion product film. However, LPAP was finally able to achieve sufficient decontamination performance via repeated LPAP treatment, because LPAP could also remove Co in the metal substrate, as well as the metal oxide film. These experimental results would be useful when LPAP treated various kinds of contaminated objects.

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