Laser Etching Characteristics of Metal Oxide Films Prepared under Nuclear-Reactor-Water-Simulated Conditions

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Laser etching characteristics of the stainless steel corrosion (oxide) films prepared under the nuclear-reactor-water-simulated conditions have been revealed. A Q-switched Nd:YAG laser of 12 ns pulse width was used to induce ablation processes. The laser beam was line-focused with a cylindrical lens and irradiated the traveling sample at different laser fluences. The etched surfaces were analyzed with a surface profiler, a scanning electron microscope, and an X-ray photoelectron spectrooscope. It has been shown that the oxide films can be efficiently removed with a relatively low energy, 1064-nm laser pulse of 50 mJ (2.3 - 2.9 J/cm²). No metallic-elements-enriched layers were observed on the laser irradiated surfaces. The effects of the laser wavelength on etching characteristics was also investigated with the 2nd harmonics (532 nm) and the 3rd harmonics (355 nm) laser beams. It has been found that for the unoxidized samples (the bulk surface of the stainless steel) the etching efficiency increases with decreasing the laser wavelength. By contrast, no clear wavelength dependence of the etching efficiency was observed for the oxidized samples, an effect which may be attributed to relatively flat response of the absorption coefficient to the laser wavelength for the oxide films surfaces.

Keywords : Laser etching, Metal oxide films, Nuclear reactor, Decontamination, Q-switched Nd:YAG laser

1. INTRODUCTION

Surface layers of materials can be removed by applying laser ablation processes. Such applications of ablation processes in industry include micromachining, surface cleaning, and paint stripping. To clean or decontaminate radioactively contaminated materials, surface removing processes are considered to be attractive options because most of such materials are only contaminated in their surface layers. Chemical and electrochemical processes have, so far, been applied to decontamination for nuclear facilities, but large amount of chemical solvents used accumulate as hazardous liquid-phase secondary wastes. The activation of the metal surfaces is another discouraging issue because it leads to rapid recontamination. Although an abrasive jet method has been applied as an alternate decontamination method, but it has disadvantages inducing surface deterioration due to mechanical forces. On the other hand, a laser etching is a method free of the above-cited disadvantages because it is a dry process and no liquid wastes are produced. The secondary waste produced in the laser process is only a trace of ablated particles which can be easily collected by a conventional filtering technique. In addition, the process can be applied not only to metals but also to organic contaminants such as oils and other chemicals. Potential function of surface modification by the laser irradiation is an additional attractive issue which could enhance the resistivity to corrosion and radiation of the cleaned surfaces.

The application of laser process for decontamination is not a new idea, but experimental investigations started rather recently. Because there reported few data on the applicability of the process to the real nuclear reactors (light water reactors), we prepared the metal corrosion films under the nuclear-reactor-water-simulated conditions and revealed their etching characteristics by laser ablation process.

2. EXPERIMENTS

To obtain an efficient ablation process, a high intensity laser beam is required. A pulsed Nd:YAG, an excimer, and a TEA (Transversely-Excited Atmospheric-pressure) CO₂ lasers may be candidates. But in the present study, we chose a pulsed Nd:YAG laser because of its compactness, durability, and possible beam delivery through optical fibers. A diagram of the experimental setup is shown in Fig. 1. A commercial, pulsed-flashlamp-pumped, Q-switched Nd:YAG laser (Spectra-Physics...
GCR-14) with a pulse width of 12 ns (FWHM) and a pulse repetition rate of 10 Hz was used. The laser beam was line-focused with a cylindrical lens of 100-mm focal length and irradiated the samples which were traveled linearly on a computer-controlled x table. An absorption-type neutral density filter was introduced before the lens to control the laser energy without changing the laser pulse waveform. Neither pulse-to-pulse change in the laser fluence nor change in the focused beam profile was observed presumably because of the limited thermal distortion in the filter due to the relatively short pulse width and the low repetition rate of the laser used. Before the laser irradiation tests the laser beam characteristics were measured with a beam profiler (Coherent Beamcode 6.2). The intensity distributions and the focused beam width as a function of the position are shown in Fig. 2. No beam homogenizer was used in this experiment, but the line-focused beam exhibits an acceptable uniform intensity distribution around the beam core region to investigate the etching characteristics. At the focal point the beam is focused to a width of less than 100 μm, a parameter which is independent on the laser energy. Shielding gas was supplied to the interaction region from a slit nozzle and the gas carrying ablated particles was exhausted from the nozzle. Those particles were collected with a set of Teflon-FEP (fluorinated ethylene propylene)-bound glass fiber filters.

The nuclear-reactor-water-simulated corrosion (oxide) films were prepared by using an autoclave with a high-pressure, high-temperature water circulating system. 304 stainless steel (SUS304) pieces, whose dimensions were 2-mm-in-thickness, 15-mm-in-width, and 50-mm-in-length, were put into the autoclave. Table 1 shows the PWR (Pressurized Water Reactor)-simulated water conditions for the sample preparation. An early study showed that the physical and chemical properties of the oxide films prepared under such simulated conditions were
very similar to those of the real corrosion films of the reactors. Therefore, etching characteristics of the real oxide films can be explored by using such simulated samples. It was also confirmed that for SUS304 the oxide film growth rate was saturated in a water exposure time of approximately 2000 h. In this experiment, therefore, the test pieces were exposed for 2000 h to simulate not only the physical and chemical properties but also the thickness of the corrosion films.

The laser irradiated the samples under the various experimental conditions: different laser fluences, defocused distances, traveling speeds, and shielding gas types. The etched surfaces were analyzed with a surface profiler, a Scanning Electron Microscope (SEM), and an X-ray Photoelectron Spectroscope (XPS). The ablated particles were also analyzed to get information on the size distribution and the chemical compositions of the particles. The effects of laser wavelength on the etching characteristics were also investigated with the 2nd harmonics (532 nm) and the 3rd harmonics (355 nm) laser beams in addition to the fundamental wavelength beam.

3. RESULTS AND DISCUSSION

The appearances of the samples before and after the laser irradiation are shown in Fig. 3 (a) and (b) respectively. In (b), it is seen that the black surface layer (oxide film) is removed by the laser irradiation and the glossy surface of the base metal appears. Figure 4 (a) and (b) show the SEM photographs of the sample surfaces before and after
Fig. 6. Depth profiles of oxygen concentration measured with an XPS for various samples: the oxidized (○) and the unoxidized (●) samples without laser irradiation, and the oxidized samples irradiated by a 50-mJ (□) and a 150-mJ (Δ) laser pulses. For the laser irradiated samples (□, Δ), the focused beam width is 1200 μm and traveling speed is 0.25 mm/s. He shielding gas is used.

Fig. 7. Dependence of etch depth on the focused beam width for the PWR-simulated SUS304 samples. The laser energy is 50 mJ and the traveling speed 0.25 mm/s. He shielding gas is used.

Fig. 8. Depth profiles of Cr, Fe, Ni, and O measured with an XPS for the PWR-simulated SUS304 samples. The fluence is 1.7 J/cm² and the traveling speed is 0.25 mm/s. He shielding gas is used.

the laser irradiation respectively. In (a), scattered several-μm-sized particles and densely-formed submicron-sized particles are observed. In an earlier study, the laser Raman spectroscopy measurements showed that these particles were dominated by the chromium ferrous oxides (FeCr₂O₄). For the real radioactively contaminated materials in the reactors, the radioactive contaminants exist only in the oxides in most cases. Some linear digs also observed in Fig. 4 (a) were formed when the SUS304 bulk sample surfaces was polished before forming the oxide films. From these observations, the maximum thickness of the films appears to be the order of several μm. In (b), i.e., the surface after the laser irradiation, neither oxide particles nor digs are observed any more, presumably because of an evaporation process caused by the laser irradiation. But the smooth surface indicates that the surface would be melted to a certain extend and then resolidified. Both an evaporation and a melting processes seem to take place under the present experimental conditions.

Figure 5 shows the macroscopic cross section of the SUS304 bare sample after the laser irradiation. In this case the laser irradiation was very strong, i.e., 50 shots at 10 Hz with a fluence of 19 J/cm² under the static sample conditions. But neither fusion zone nor heat affected zone is seen in this observation, which indicates the molten layer is extremely thin. This is presumably due to the very low mean laser power (only 4 W) input to the work. This is another advantage of using this type of high-peak-power laser for the decontamination process.

For the PWR-simulated samples, we measured the oxygen concentration at the surfaces by an XPS to reveal how the oxide films are removed. Figure 6 shows the depth profiles of oxygen concentration of the different samples: the oxidized and the unoxidized samples without laser irradiation, and the oxidized samples irradiated by a 50-mJ and a 150-mJ laser pulses. It is shown that for the
50-mJ (0.8 J/cm²) laser irradiated sample, most of the oxygen remains, while for the 150-mJ (2.3 J/cm²) laser irradiated sample the oxygen concentration is reduced to a level as low as that for the unoxidized sample. At the laser fluence of 2.3 J/cm², the oxide film seems to be almost fully etched. It is difficult to measure the etch depth directly with a surface profiler because of very high roughness of the oxide film surfaces. We define the oxide film thickness in arbitrary units as the depth at which the oxygen concentration corresponds to 50% of its maximum value at the top surface. The etch depth is then defined as the difference of the oxide film thicknesses before and after the laser irradiation. The etch depth can therefore be normalized by the film thickness before the laser irradiation, so unity corresponds to full etching of the oxygen-included layer. Based on these, normalized etch depths are plotted in Fig. 7 as a function of the focused beam width which was changed by changing the defocused distance while keeping laser energy constant at 50 mJ. It is clear that the etch depth increases with decreasing beam width, and hence increasing laser fluence. For a beam width of 300 μm, almost full etching is obtained with a relatively low laser energy of 50 mJ, the corresponding laser fluence being 2.9 J/cm². The etching characteristics were also explored as a function of the traveling speed in a range of 0.25 - 5 mm/s, but it was shown that the etch depth did not much depend on the traveling speed. This may be due to the fact that the films are fully etched with the first single laser shot at the given laser fluence in this experiment.

As described above, it is evident that the oxygen atoms can be very efficiently removed by the laser irradiation. But the real contaminants are not the oxygen atoms but the radioactive metallic elements such as 60Co. Because it is known that in some cases, there would occur a selective ablation of the specific elements, we need to check how the metallic elements are removed. Figure 8 shows the depth profiles of Cr, Fe, and Ni as well as oxygen for the sample irradiated at a fluence of 1.7 J/cm². If the selective etching occurred for oxygen, we should observe the metallic-elements-enriched layer in the oxygen depleted region. But such layers are not observed, which indicates that the selective etching may not be dominant in this case.

The effects of the laser wavelength on etching characteristics were investigated for both the unoxidized and oxidized samples. Figure 9 shows the dependence of the surface profiler-averaged etched depths of the unoxidized samples on the laser fluence for the different laser wavelengths. For this measurement a surface profiler could be used because of the relatively small roughness of bare metal surfaces. It is shown that the shorter wavelength results in the deeper etch depth and the lower etching threshold fluence. This is most probably due to the higher Fresnel absorption at the shorter wavelength even though the plasma absorption (inverse bremsstrahlung absorption) and/or the beam scattering by the ablated particles may also affect the etching characteristics. Figure 10 shows analogous results obtained with the oxidized samples but the wavelength dependence of the etch depth is not clear in
this case. From this, the absorption coefficient of the oxide films seem to have a relatively flat response to the wavelength in the range tested in this study. The reason for the saturated etch depth seen at fluences of around 1 J/cm² in the case of the 355-nm light etching is not clear. But this may be attributed to the influence of the Rayleigh scattering by the ablated particles. Because the scattering loss of the laser energy is inversely proportional to the 4th power of the wavelength, the loss becomes higher at shorter wavelength. (10) Therefore, with the shorter wavelength laser the saturation of the etch depth may occur at lower fluences. It is also shown in Fig. 10 that the threshold fluences needed to etch oxide film are very low (lower than ~0.2 J/cm²). From the surface morphology of the oxide films, it is considered that the Fresnel absorption of the films would be higher and the thermal conductivity of the films would be lower when compared with those of the base metal. These two factors may result in much lower threshold fluences for the films than for the base metals. Such large difference in the threshold fluences between the oxide film and the base metal constitutes an opportunity for selective etching of oxide films without deteriorating base metal surface, if the fluence is adequately chosen.

4. SUMMARY AND FUTURE WORKS

In summary, it has been demonstrated that nuclear-reactor-water-simulated corrosion films of stainless steel can be very efficiently etched by applying a Q-switched Nd:YAG laser ablation process. Full etching is obtainable with a 1064-nm laser pulse energy of only 50 mJ (2.3 - 2.9 J/cm²). The process creates no defects at the surfaces of the base metal because of the extremely low average laser power (~0.5 W) applied. The data reported in this paper are for the PWR-simulated samples but it has also been confirmed that the process is applicable to the corrosion films of the another typical reactor: BWR (Boiling Water Reactor).

Future works include evaluation of microscopic recontamination (redeposition, etc.) and corrosion resistivity of the laser treated surface, and fiber-optic-based processing demonstration. We have already confirmed that a laser energy of 50 mJ can be delivered with a large-core-diameter (1200 µm) quartz fiber, but the fluence of the transmitted laser beam in this case is lower than needed. To increase the fluence, a multiplexing fiber delivery system is now under investigation. Although the processing speed is limited in the present study because of the limited repetition rate of the laser used, the speed can be simply scaled with the repetition rate and the output energy of the laser. Recently, 100-Hz, high-energy Q-switched Nd:YAG lasers are commercially available, the use of which could realize significant enhancement in the processing speed. But we consider that the application with highest potential for this process is "hot spot decontamination", where the processing speed is less important than for large-area decontamination. (Manuscript received Jan. 27, 1997, revised May 14, 1997)

REFERENCES

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