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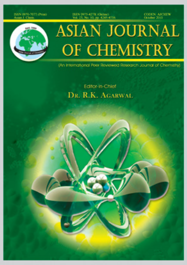

Study on the Laser Decontamination of Metal Surface at 1064 and 532 nm†

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Type 304 stainless steel is contaminated with $CsNO_3$, $Co(NH_4)_2(SO_4)_2$, CeO_2 and Eu_2O_3. We present the experimental results on decontamination of contaminants attached to type 304 stainless steel surface by coherent light of 1064 nm wavelength and its second harmonic generation occurring at 532 nm derived from a Q-switched Nd:YAG laser. The surface morphology and the relative atomic molar per cent of the specimen surface have been investigated by SEM and EPMA. The decontamination behaviour has been investigated for the variables such as a number of laser shots and fluence. The decontamination behaviour at 532 nm by varying the irradiation angle has also been investigated. The optimum laser fluence at 1064 nm wavelength is found to be 57.3 J/cm^2 and 97.7 % of Cs^+ ion is removed during 40 laser shots. The optimum application condition at 532 nm wavelength is found to be 13.3 J/cm^2 and 30º, respectively. The order of decontamination efficiency at 1064 nm is $CsNO_3 > Co(NH_4)_2(SO_4)_2 > CeO_2 > Eu_2O_3$ and at 532 nm is $CsNO_3 > Co(NH_4)_2(SO_4)_2 > Eu_2O_3 > CeO_2$.

Key Words: Decontamination, Q-Switched Nd:YAG laser, Ablation, Second harmonics, Irradiation angle.

INTRODUCTION

A number of laboratory study using lasers have focused on the possibilities of surface treatments such as removal of crust from archaeological iron artifacts[1], cleaning of metal traces on circuit boards[2], investigation of single shot imaging capability for OH radical distributions[3], investigation of efficiency of concrete removal[4] and investigation of the effect of wavelength and the material removal mechanisms for removing copper oxide from copper[5]. The preparation of metal oxide films on the material by laser chemical vapor deposition was also reported[6].

Lasers are being recognized as an attractive decontamination tools in the nuclear industry. Radioactive material is generated during the operation of a nuclear facility. Laser decontamination means the removal of radioactivity from the radioactively contaminated surface by the laser beam. Khalil *et al.*[7] presented an experimental and theoretical study of pulse laser ablation of stainless steel target. Various parameters, such as laser power, pulse duration, enthalpy and heat capacity were used. The evaluation of software for the ablation processes was done. They reported that the ablation process induced by lasers is a collective phenomenon that basically involves two phenomena: the laser radiation-with matter interaction and the dynamic of the ablation plume. Kameo *et al.*[8] reported that the decontamination efficiency could be improved by employing an acid containing sodium silicate gel on to a contaminated metal surface before a laser application. To understand the role of laser irradiation on chemical reactions, chemical states of O and Fe in the oxide layer before and after decontamination were analyzed by X-ray photoelectron spectroscopy. They concluded that the contaminated layer was dissolved by the acid and combined with the gel under a laser irradiation condition. Rafique *et al.*[9] studied the XRD and SEM analysis of a laser irradiated cadmium. They used a pulsed Nd:YAG laser (10 mJ, 12 ns, 1064 nm). From the test results, they reported that the hydrodynamic effects were apparent with a liquid flow which formed a recast material around the periphery of the laser focal area. Dimogerontakis *et al.*[10] studied a thermal oxidation induced during a laser cleaning of an aluminum-magnesium alloy. They used a Q-switched Nd:YAG laser unit with a pulse duration of 10 ns and a wavelength of 1064 nm. For the surface analyses of the treated samples, an X-ray photoelectron spectroscopy (XPS) and a secondary ion mass spectroscopy were used. They found that a thermal oxidation took place on the alloy during the irradiation in air

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with a laser energy range from 0.6-1.4 J/cm^2. The effect of nitrate and hydroxyl ions on the laser ablation of Cs^+ ion was investigated using SEM, EPMA and XPS[11]. The tested light source was a Q-switched Nd:YAG laser. It was suggested that the reactive oxygen generated from the decomposition of nitrate ion enhanced the removal of Cs^+ ion.

During the refurbishment of hot cells, decontamination work is necessary because it reduces the occupational exposure to workers and the burden for the safe management of radioactive wastes. Korean Atomic Energy Research Institute has operated the DFDF (DUPIC Fuel Development Facility) since 2000. All the DUPIC (Direct Use of PWR spent Fuel in CANDU) processes are executed in hot cells under a dry condition. As the operation age increases, the need to repair these hot cells increases. The radioactivity of the hot cells in the DUPIC Fuel Development Facility is presumed to be high and the predominant radionucleide is Cs-137. And also, the surface of a wall is contaminated with spent fuel particles. Before the refurbishment of the hot cells, the application of a remotely operated decontamination technique is required. The merits of a laser decontamination technique are a remote application, a high decontamination factor, the generation of a small amount of secondary waste and a negligible occupational exposure to workers.

The objective of the study is to optimize the removal parameters of a Q-switched Nd:YAG laser system on the type 304 stainless steel contaminated with $CsNO_3$, $Co(NH_4)_2(SO_4)_2$, CeO_2 and Eu_2O_3, respectively. Especially, the effect of laser fluence and laser shot numbers on the removal of contaminants was emphasized. The effect of laser irradiation angle on the removal of contaminants was also investigated at 532 nm.

EXPERIMENTAL

Specimen preparation and analysis: Type 304 stainless steels were cut into a rectangular form for experimental specimens. They were polished with abrasive papers and washed with water and ethyl alcohol. Four kinds of specimens have been used for laser decontamination tests. The experimental specimens were prepared as follows: Eu_2O_3 powder (Aldrich Chemical Company, Inc.) and CeO_2 powder (Aldrich Chemical Company, Inc.) diluted with distilled water were slowly dropped onto the surface of stainless steel specimen by injection separately and then dried in a room temperature. Two kinds of $Co(NH_4)_2(SO_4)_2$ and $CsNO_3$ solutions were also dropped onto the specimen surfaces, respectively and then dried for the tests. The relative atomic molar per cent of the metal surface elements before laser irradiation was analyzed by EPMA as given in Table-1. After laser irradiation, the relative atomic molar per cent of the affected zone was also analyzed by the same process. The three points in a spot were investigated and averaged for one data point. The content of carbon atom was excluded in the surface composition.

Laser irradiation apparatus: Q-Switched Nd:YAG laser (Brilliant b, Quantel Co.) with pulse duration of 6 ns and maximum repetition rate of 10 Hz emits a fundamental wavelength at 1064 nm and maximum pulse energy determined from energy meter was 870 mJ/pulse. A second harmonic generation of a Q-switched Nd:YAG laser with pulse duration of 5 ns and a wave length of 532 nm was used. Fig. 1 shows a schematic diagram of the experimental apparatus. Surrogate specimen was mounted on a X-Y stage. An articulate mirror was used for a transfer and a convergence of a laser beam at the target point. Laser fluence was calculated from measuring the pulse energy with an energy meter and from estimating the beam diameter.

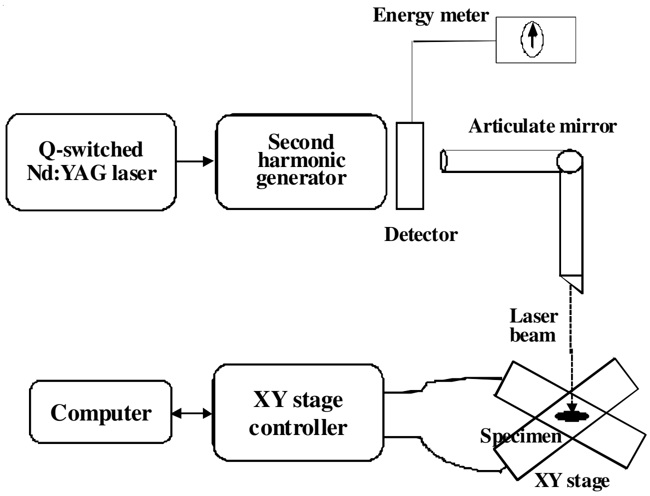

Fig. 1. Schematic diagram of the experimental apparatus

RESULTS AND DISCUSSION

Effect of laser wavelength: Fig. 2 shows the remaining portion (X_f/X_o) of cobalt and cesium ions on type 304 stainless steel specimens against the number of laser shots at 12 J/cm^2 under two wavelength conditions. X_f and X_o are, respectively, the residual and initial relative atomic molar per cent of contaminants. The remaining portion of Co^{2+} and Cs^+ ions is decreased with the increase of the number of laser shots at 1064 nm. The remaining portion of Co^{2+} and Cs^+ ions, however, is drastically decreased at 532 nm. For the two wavelength conditions, ablation plasma is clearly visible when the surface is irradiated. At 1064 nm wavelength condition, Cs^+ ion is more easily removed than Co^{2+} ion.

Fig. 3 shows the remaining portion of cerium and europium ions against the number of laser shots at 12 J/cm^2 under two wavelength conditions. At 532 nm, Eu^{3+} and Ce^{4+} ions are also drastically removed by the laser. Eu^{3+} ion is more easily removed than Ce^{4+} ion in the early stage of laser irradiation.

TABLE-1
RELATIVE ATOMIC MOLAR PERCENT BEFORE LASER IRRADIATION

Element	N	O	Ni	S	Cr	Fe	H	Ce	Eu	Cs	Co
$Co(NH_4)_2(SO_4)_2$	2.0	10.7	6.9	0.2	18.0	59.1	Trace	–	–	–	3.1
$CsNO_3$	4.5	25.4	5.9	–	13.6	45.7	–	–	–	5.2	–
CeO_2	–	11.3	6.0	–	17.2	58.5	–	7.0	–	–	–
Eu_2O_3	–	30.6	7.7	–	10.1	45.7	–	–	5.9	–	–

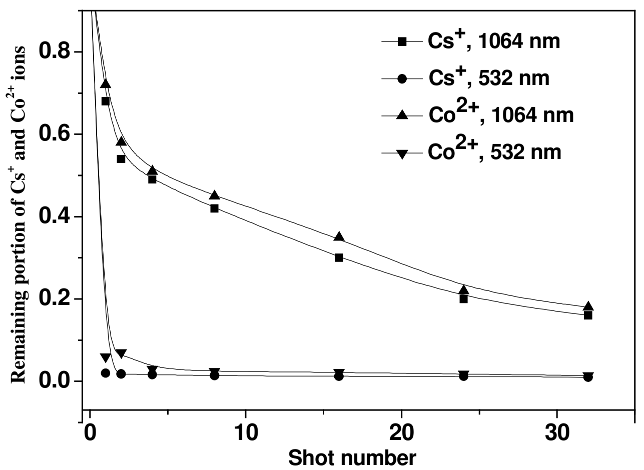

Fig. 2. Remaining portion of cesium and cobalt ions against the number of laser shots (12 J/cm^2 and 10 Hz)

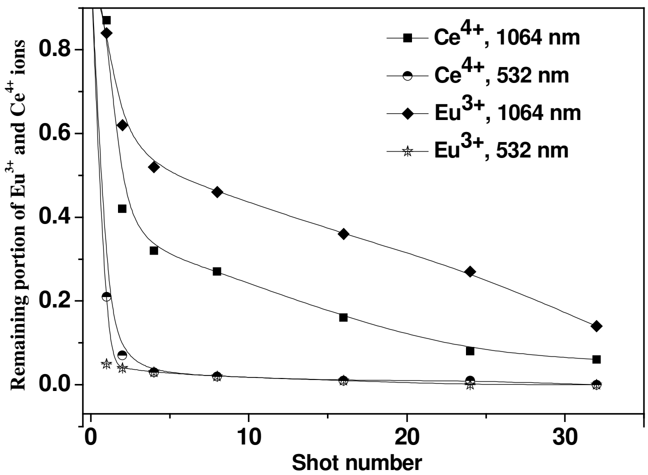

Fig. 3. Remaining portion of europium and cerium ions against the number of laser shots (12 J/cm^2 and 10 Hz)

At 1064 nm, the two ions are not so drastically decreased. Laser removal efficiency of Ce^{4+} ion, however, is better than Eu^{3+} ion at 1064 nm. The order of removal efficiency at 1064 nm is $CsNO_3$ > $Co(NH_4)_2(SO_4)_2$ > CeO_2 > Eu_2O_3 and at 532 nm is $CsNO_3$ > $Co(NH_4)_2(SO_4)_2$ > Eu_2O_3 > CeO_2. Consulting the test results of Figs. 2 and 3, it is found that laser fluence of 12 J/cm^2 is not sufficient to remove contaminants during the 32 laser shots at 1064 nm.

A proper explanation of thermal and photochemical laser ablation would require a detailed knowledge of the fundamental interactions between the laser light and matter. The term photochemical is used if the laser induced ablation proceeds mainly non-thermally[12]. The wavelength effect on the laser removal of contaminants can be explained by comparing the physical property of contaminants. Melting point and boiling point of contaminants are listed in Table-2. At 1064 nm, the order of removal efficiency is inversely related to the melting and boiling point of contaminants. In other words, contaminants of low melting and boiling point show better removal efficiency. Considering the wavelength of 1064 nm is in the IR region, the ablation of contaminants is predominantly caused by a thermal activation. At 532 nm, the order of removal efficiency between Eu_2O_3 and CeO_2 is reversed. This shows that the photochemical activation of contaminants by 532 nm wavelength also affects the removal efficiency.

TABLE-2
MELTING POINT AND BOILING POINT OF CONTAMINANTS

Chemicals	Melting point (ºC)	Boiling point (ºC)
$Co(NH_4)_2(SO_4)_2$	1,495	2,927
$CsNO_3$	414.0	849.0
CeO_2	2,400	3,500
Eu_2O_3	3,722	4,118

Fabbro *et al.*[13] reported that laser ablation rate is inversely proportional to the laser wavelength and is proportional to the laser fluence. They obtained the experimental mass ablation rate m:

$$m \approx 110\left(\frac{\phi}{10^{14}}\right)^{\frac{1}{3}} \lambda^{-\frac{4}{3}} \quad (1)$$

where ϕ is the laser fluence and λ is the laser wavelength. Comparing the removal efficiency of individual element in Figs. 2 and 3, all the test elements are effectively removed at 532 nm wavelength laser in a given laser fluence.

Effect of laser fluence: The removal efficiency of Cs^+ was measured as a function of number of laser shots for 1064 nm Q-switched Nd:YAG radiation of stainless steel specimen. Fig. 4 shows the remaining portion of Cs^+ ion on type 304 stainless steel specimens under various laser fluence conditions. The remaining portion is decreased with the increase of the number of laser shots. For the 57.3 and 229.3 J/cm^2 of laser fluence conditions, Cs^+ ion on the surface is drastically decreased during the first 10 shots. For the 6.4 and 14.3 J/cm^2 of laser fluence conditions, however, Cs^+ ion on the surface is not so drastically decreased. Consulting the test results, the applicable laser fluence for the removal of Cs^+ ion on type 304 stainless steel at 1064 nm is found to be 57.3 J/cm^2.

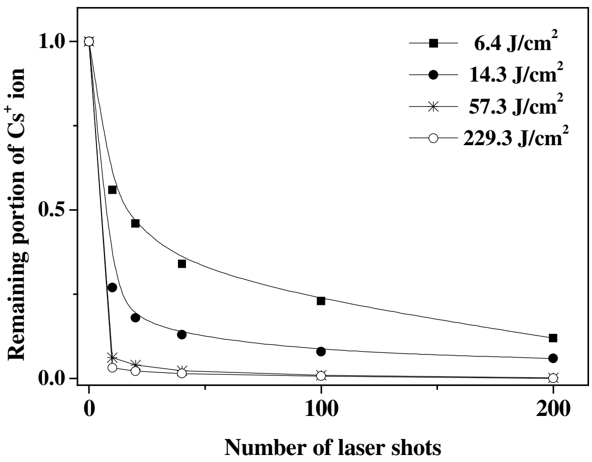

Fig. 4. Remaining portion of Cs^+ ion against the number of laser shots (1064 nm)

Removal efficiency of the four contaminants on the type 304 stainless steel specimen was investigated against the laser fluence at 10 laser shots. The results are given in Fig. 5. It shows that all the test ions are removed rapidly for the fluence increase up to about 13.3 J/cm^2. The increase of removal efficiency is negligible when the laser fluence exceeds the 13.3 J/cm^2.

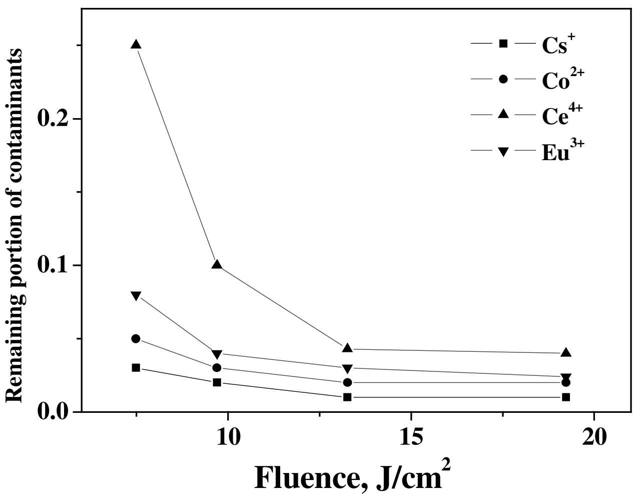

Fig. 5. Remaining portion of contaminants against the fluence for the 4 kinds of contaminants (10 shots, 532 nm)

Laser fluence applied to the decontamination of contaminated specimen is much different according to the types of laser and to the kinds of substrate. Fukui *et al.*[14] reported that the metal ions on the stainless steel were satisfactorily removed by the application of more than 4 laser shots at the laser fluence of 5.3 J/cm^2 in their laser decontamination study with a Q-switched Nd:YAG laser. Delaporte *et al.*[15] studied the decontamination of radioactive inconel specimens by using an excimer laser and reported that the decontamination rate appears to be very efficient for the removal of contaminants loosely adhered on the surface during the first few hundred of shots and that it is impossible to remove entirely the dense oxide layer adhered on the inconel surface at 3 J/cm^2 as the oxides are trapped into the material cracks. Although the contaminants are removed continuously for a fluence increase up to about 20 J/cm^2, considering the removal efficiency slope, the laser fluence of 13.3 J/cm^2 is determined as an appropriate condition for the decontamination of type 304 stainless steel.

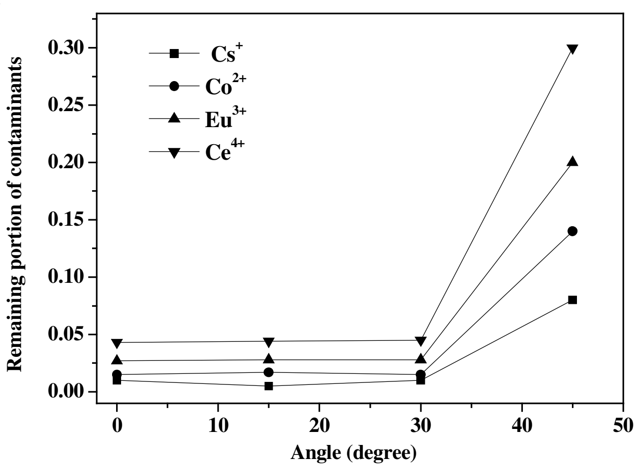

Fig. 6. Remaining portion of the contaminants against the irradiation angle (10 shots, 532 nm, 13.3 J/cm^2)

Effect of laser irradiation angle: Fig. 6 shows the removal behaviour of the contaminants on the stainless steel at various irradiation angles. The specimen was irradiated by changing position of angle at 10 laser shots. The angle of 0º means that the irradiation of laser beam is perpendicular to the specimen. The angle of 15º means that the specimen is inclined at 15º from the perpendicular of laser beam. It shows that the 3 kinds of specimen were effectively removed for the angle in the range between 0 and 30º. When the irradiation angle increases to 45º, however, the removal efficiency decreases suddenly. Therefore, the irradiation angles which are variable for ensuring decontamination performances were found to be in the range between 0 and 30º.

The exposed specimen morphologies were examined by SEM at a magnification of 50X. SEM micrographs of the specimens before and after the laser irradiation at the angles of 0, 15, 30, 45º are shown in Fig. 7. The surface of the specimen was contaminated with $CsNO_3$ (a), $Co(NH_4)_2(SO_4)_2$ (b), Eu_2O_3 (c) and CeO_2 (d), respectively. Also the numbers (1) (2) (3) (4) in the photos represent the laser irradiation angles of 0, 15, 30, 45º, respectively. From the SEM analysis it was found that Co^{2+}, Cs^+ ions exist in the form of a crystal as in (a) and (b). On the other hand, the Eu_2O_3 and CeO_2 on the specimen are dissipated in a powder form as in (c) and (d).

The formation of crater has already been studied by the other researchers. Khalil *et al.*[7] reported that a volume of about 20 mm in diameter and 4 mm in depth of type 304 stainless steel is removed by a combined sublimation and melting process at each pulse of Nd:YAG laser. They suggested that the relation between two ablating processes is determined by the pulse duration and effects the quality and efficiency of the manufacturing process. On the other hand, Rafique *et al.*[9] reported that the high laser heating rates turn significant amounts of target material area to be melted and this molten material infiltrates into the solid target by capillary action. The heat affected zone around crater shows that there is a variation in the pressure around the crater.

During the laser irradiation, the metal surfaces and contaminants are ablated and the craters of different shapes depending on the irradiation angles are formed as shown in (a-1, 2, 3, 4), (b-1, 2, 3, 4), (c-1, 2, 3, 4) and (d-1, 2, 3, 4). It can be seen that the circle form of crater changes to an ellipsoidal shape as the irradiation angle increases to 45º and the removal efficiency become worse.

Conclusion

Q-Switched Nd:YAG laser system is employed to perform a comparative study on the laser decontamination of type 304 stainless steel at 1064 and 532 nm. At 1064 nm, the order of laser removal efficiency is inversely related to the melting point and boiling point of contaminants. This implies that the laser ablation of contaminants in IR region is predominantly caused by a thermal activation. The order of removal efficiency between CeO_2 and Eu_2O_3 is reversed at 532 nm. This can be explained by the contribution of photochemical activation of contaminants by 532 nm wavelength. Thus, in conclusion, ablation mechanisms involved in the removal of contaminants from type 304 stainless steel surface at 1064 mn and 532 nm are found to combine both thermal and photochemical effects. Successful contaminant removal is achieved at 532 and 1064 nm wavelength above certain laser fluence.

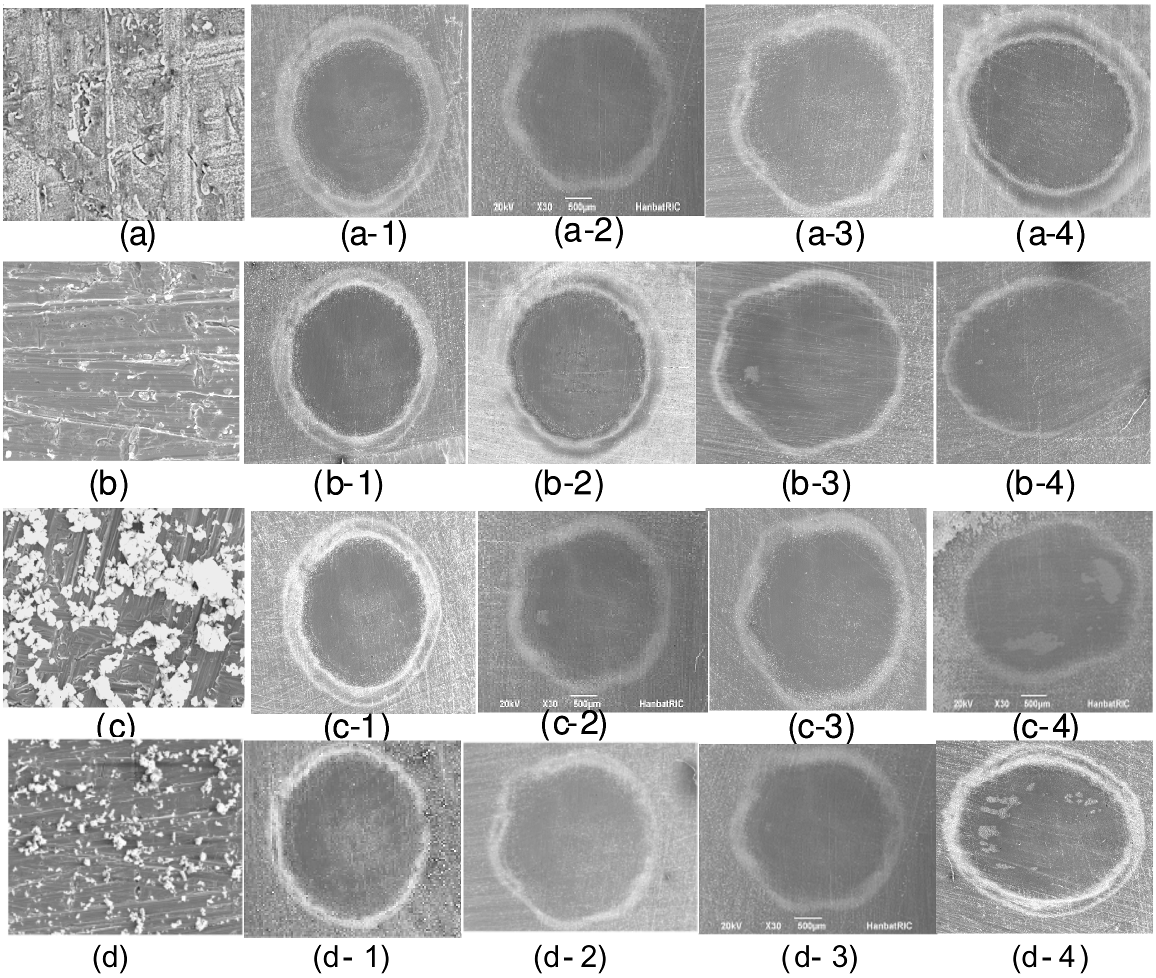

Fig. 7. SEM images of SUS 304 surface (50X) contaminated with (a) $CsNO_3$, (b) $Co(NH_4)_2(SO_4)_2$, (c) Eu_2O_3 and (d) CeO_2 before and after 8 laser shots of laser irradiation at (1) 0º, (2) 15º, (3) 30º, (4) 45º (532 nm)

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