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Laser-assisted surface cleaning of metallic components

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Abstract. Removal of a thin oxide layer from a tungsten ribbon and ThO_2 particulates from zircaloy surface was achieved using a pulsed Nd:YAG laser. The removal mechanism of the oxide layer from the tungsten ribbon was identified as spallation or sublimation depending on the wavelength and fluence of the coherent radiation. The oxidized and cleaned surfaces were analysed by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDS) and atomic force microscopy (AFM). Laser-cleaned tungsten ribbons were used in a thermal ionization mass spectrometer (TIMS) to determine isotopic composition of neodymium atoms. The fundamental (1064 nm) and the third harmonic (355 nm) radiations were found to be the most effective in removing ThO_2 particulates from the zircaloy surface. Decontamination efficiency was found to be critically dependent on the wavelength of the coherent radiation and number of exposures. The mechanism of cleaning of ThO_2 particulates from the zircaloy surface at different wavelengths of the incident radiation has been explained qualitatively.

Keywords. YAG laser, oxide layer, contamination, cleaning.

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1. Introduction

The use of lasers to clean surfaces has generated considerable interest in recent years as it has major advantages over conventional methods. It is an environmentally friendly and dry cleaning process and generate very little secondary wastes. The process can be done remotely without any manual intervention. The laser parameters can be tailored to remove contaminants (either particulates or deposited layers) selectively without causing any damage to the underlying substrate. These advantages have enabled laser-based surface cleaning technology to be employed in many areas of engineering and science, e.g. nuclear industry, art restoration work and semiconductor industry. In this paper we report our work on laser cleaning of a thin oxide layer from tungsten ribbon and radioactive particulate removal from metallic surface. Our work is discussed in detail in the following paragraphs.

The utility of tungsten and its alloys in different industries is well known. Tungsten is an attractive choice for thermionic emission because of its high emissivity, high thermal and chemical stabilities. When fresh tungsten is exposed in ambient atmosphere, an oxide film (WO_3) is spontaneously formed on its surface [1]. Presence of tungsten oxide on tungsten causes problem in some material characterization instruments, e.g. thermal ionization mass spectrometer (TIMS) and scanning tunnelling microscopes (STM), where tungsten is used as filaments and tips respectively. TIMS is used primarily for accurate measurement of isotopic ratios of different elements. In TIMS a thin ribbon of tungsten is used as sample and ionization filament. Removal of the native oxide layer from the tungsten ribbon is mandatory for TIMS sample preparation as the native oxide layer sublimates at around 700°C [2]. In a STM, tungsten is used as tips. The presence of oxides causes unstable tunnel current in STM tips resulting in tip damage. The most common method for cleaning these components is by wet chemical cleaning with hydrofluoric acid. We have been successful in removing the oxide layer by irradiating the ribbon with short pulses obtained from an Nd:YAG laser, the results of which will be discussed in the next section.

The other application of laser-based surface cleaning we have carried out is the removal of radioactive particulates from metallic surface. This application is very relevant pertaining to nuclear industry in the field of nuclear fuel fabrication and radioactive waste management. As we know, India is persuading a three-stage nuclear power programme for effective utilization of uranium and thorium reserves to fulfill the ever growing need of energy [3]. The third stage of this programme is based on advanced heavy water reactor (AHWR) to be operated with thorium-based fuels. AHWR will utilize (Th,U-233)O_2 as the fuel and zircaloy 2 as the clad material. The fuel for AHWR; needs to be fabricated inside heavily shielded glove boxes or inside a hot cell owing to very high dose rate normally associated with it. Operations involving fuel fabrication thus need to be mechanized with minimum manual intervention. Following the loading of the fuel elements with MOX fuel pellets, the outer clad surface gets contaminated with loosely attached radiotoxic particulates necessitating their cleaning before they can be removed from the glove box/hot cell for further processing. We envisage the laser-assisted surface decontamination to play an important role as the laser beam can be readily transported inside the glove box or hot cell offering the prospect of cleaning of AHWR fuel elements in a remote and dry manner. To this end, we have undertaken a study to understand the mechanism of laser-assisted removal of ThO_2 particulates off the metal surface and present here results of some precursory decontamination experiments carried out in this direction.

2. Experimental

The schematic of the experimental set-up is shown in figure 1. A Q-switched 6–8 ns pulsed Nd:YAG laser capable of emitting at 1064, 532 and 355 nm wavelengths was used as the coherent source for carrying out the cleaning studies. The laser emits a multimode beam of $\sim$1 cm^2 cross-section. Energy of each pulse was measured by directing a small

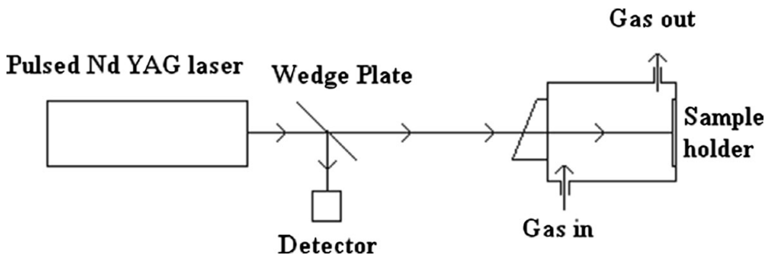

Figure 1. Schematic of the experimental set-up.

fraction of the beam to a pyroelectric Joule meter with the help of a wedge plate. The samples (tungsten ribbon, thoria-contaminated zircaloy metal) were irradiated inside a chamber, the ends of which were sealed with the sample holder on one side and a LiF Brewster window on the other.

The chamber was pre-purged with argon gas and a continuous flow of gas was maintained during the experiment. The samples (tungsten ribbon: 50 mm (length) $\times$ 2.5 mm (width) $\times$ 0.030 mm (thk.), contaminated metallic samples: 15 mm $\times$15 mm) were appropriately mounted on the sample holder. During the experiment the laser was operated in single-shot mode. The samples were irradiated at all the three wavelengths under varying fluence conditions. For each wavelength and fluence a new sample was used in the experiment.

3. Results and discussion

3.1 *Removal of tungsten oxide layer from a thin tungsten ribbon*

SEM analysis of the oxidized tungsten ribbon showed the thickness of the oxide layer to be $\sim$1–2 μm and the layer was not continuous but full of fine cracks. Several experiments were carried out by varying the laser fluence aiming to find out the threshold fluence for oxide removal. It was found that beyond the threshold, oxide removal was achieved at all wavelengths for a wide range of fluence values. Single-shot removal of the entire oxide layer was found to occur above 0.2 J/cm^2 for 1064 nm, 0.15 J/cm^2 for 532 nm and 0.10 J/cm^2 for 355 nm. In case of 1064 nm and 532 nm, it was found that the removal mechanism was predominantly spallation when smaller value of fluence was used (0.20–0.46 J/cm^2 for 1064 nm and 0.15–0.21 J/cm^2 for 532 nm). Peeling off the oxide layer in the form of chunks of few millimetres was visually observed. However, higher fluence resulted in sublimation of the oxide layer. In case of 355 nm, spallation was not observed at all and the removal process was sublimation over the entire fluence range. Figure 2 shows the oxidized and laser-cleaned portion of the tungsten ribbon. The image revealed that removal occurred without any melting of the substrate. In order to understand the interaction between the oxidized tungsten surface and the laser radiation at different wavelengths, the knowledge of absorptivity of the oxide layer to the incident radiation was necessary. This was determined by measuring the absorptivity of a clean tungsten ribbon and a ribbon with the oxide layer using an integrated sphere. The absorptivity of the tungsten oxide layer was found to be 15% at 1064 nm, 18% at 532 nm and

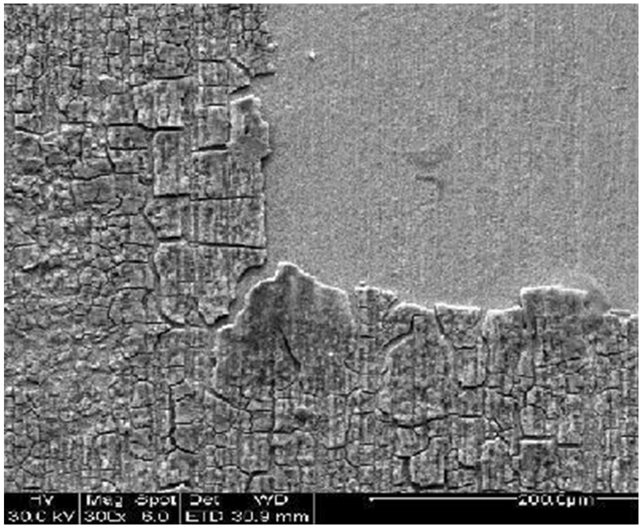

Figure 2. SEM image showing the oxidized and laser-cleaned portion of the tungsten ribbon.

85% at 355 nm while the absorptivity of tungsten was found to be 40% at 1064 nm, 48% at 532 nm and 58% at 355 nm.

At 1064 and 532 nm, the oxide layer was more transparent. As a result, most of the laser radiation was transmitted through the oxide layer and got absorbed at the tungsten substrate. The laser irradiation of the tungsten substrate generated stresses normal to the oxide/metal interface. The development of the stress field resulted in the fracture of the interface and spallation of the oxide layer. At higher fluence, the temperature of the oxide layer increased beyond its sublimation temperature resulting in the removal of the film by vapourization. The oxide layer was highly absorbing at 355 nm and large fraction of the incident laser radiation was absorbed by the oxide layer itself resulting in a rise of its temperature. It was observed that single-shot removal of the entire oxide layer by sublimation was possible when the fluence is more than 0.10 J/cm^2. The laser-cleaned and uncleaned surfaces were also examined by EDS. The EDS result showed significant reduction in oxygen percentage and increase in tungsten percentage after laser cleaning implying the removal of the oxide layer. The laser-cleaned and uncleaned tungsten ribbons were used as a sample filament in a TIMS for determining isotopic ratios of neodymium atoms. No ion current was obtained when the sample was deposited on a tungsten ribbon with oxide layer. This was due to the sublimation of the oxide layer before the vapourization of the neodymium sample. However, well-resolved peaks corresponding to different isotopes were obtained when the sample was deposited on a cleaned tungsten ribbon.

3.2 *Removal of ThO_2 particulates from zircaloy surface*

In this experiment the samples were prepared by smearing oxalate route derived milled ThO_2 powder taken along with a small quantity of isopropyl alcohol on the surface of

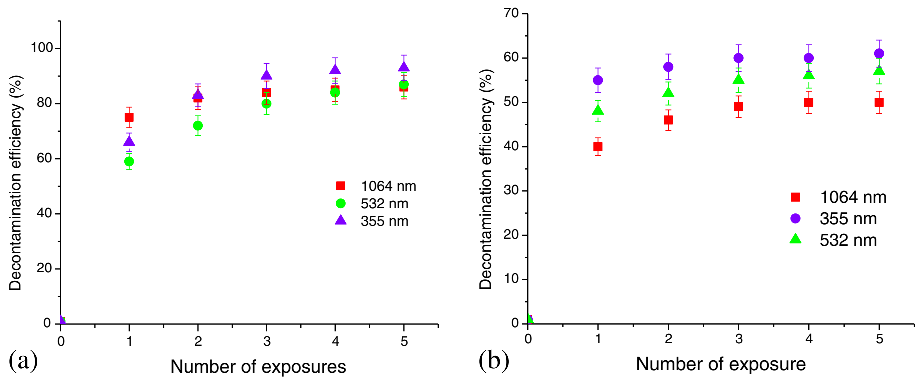

Figure 3. Variation of DE as a function of the number of shots. Substrate: (**a**) Zircaloy, (**b**) LiF. Contaminant: Milled ThO_2 powder, fluence: 0.2 J/cm^2.

zircaloy sheaths of 15 mm × 15 mm size. The laser beam always intercepted the entire contaminated portion of the sample thus avoiding the necessity of any scanning. A vacuum pump connected to the chamber through a HEPA filter was kept on during the experiment to avoid any airborne activity being released in the working area. The alpha activity of the samples was monitored with a ZnS (Ag) scintillation detector.

In the first set of experiments decontamination efficiency (DE), defined as the percentage removal of the initial activity, was studied as a function of the number of exposures for a fixed laser fluence of 0.2 J/cm^2 for all the three wavelengths. The dependence of DE when deposited on zircaloy is shown in figure 3a. It is seen that a very high decontamination efficiency was obtained within the first few laser exposures for all the wavelengths. To ascertain the contribution of the absorption by the particulates in the observed cleaning process, we performed the next set of experiments by depositing the milled thoria powder on an optical-grade LiF slab with no absorption over the entire range of wavelengths used here and the result is shown in figure 3b. The behaviour with respect to 1064 nm is in contrast with that when the powder was deposited on zircaloy surface. DE obtained here was always less for 1064 nm and maximum for 355 nm. In this experiment, the substrate does not play any role in the cleaning process as it was transparent to all the wavelengths under study. Minimum DE at 1064 nm points to the fact that the absorption of radiation at 1064 nm by the ThO_2 particulates is less in comparison to 532 nm and 355 nm. Actual absorption by the particulates was estimated by comparing the transmission of the laser beam through bare LiF and LiF with contamination. Under similar condition 1064 nm exhibited 30% absorption, 532 nm exhibited 45% absorption and 355 nm exhibited 59% absorption.

In the light of these observations, the mechanism of cleaning of the ThO_2 particulates from the zircaloy surface can be explained in the following manner: In the laser-assisted cleaning process, cleaning force is generated by the absorption of the incident radiation by both the particulates as well as the substrate. When the contaminant is transparent to the incident radiation, major contribution of cleaning force comes from the substrate absorption and when the contaminant is absorbing, maximum contribution comes from the particulates. In our experiment the very high decontamination efficiency obtained with 1064 nm points to the fact that absorption by the substrate plays a major role in generating the cleaning force as the study with LiF substrate clearly established that particulate contribution towards the cleaning process is minimum at this wavelength. The field-enhanced absorption due to the focussing effect caused by the semitransparent particulates further enhances the cleaning force. The very high DE obtained with 355 nm at higher fluence values is due to the contribution of the particulates in generating the cleaning force due to its high absorption to the incident radiation. In case of irradiation at 532 nm, the DE has been observed to be lower than 1064 nm and 355 nm even though absorption in both particulates as well as substrate contributes to the process of cleaning. Particulate absorption reduces the field-enhanced absorption and the substrate absorption is also less at 532 nm in comparison to 355 nm.

4. Conclusion

Removal of oxide from a thin tungsten ribbon was achieved using a pulsed Nd:YAG laser without any damage to the ribbon. Dependence of the cleaning mechanism on laser wavelength and fluence was experimentally studied. Laser-cleaned ribbons were successfully used as sample filaments in a TIMS for determining isotopic composition of neodymium atoms. Replacing the conventional technique of chemical cleaning with the laser process would be beneficial as it would eliminate chemical waste.

In the cleaning of ThO_2 particulates from zircaloy surface 1064 nm and 355 nm radiations are found to be the most effective. Cleaning of the clad tubes will be preferred with 355 nm radiation as particulates are highly absorbing here. Field-enhanced absorption on the substrate surface that is very significant in the case of radiation at 1064 nm can cause damage to the substrate by forming pits.

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