SAND2020-7089C

Impact of Ionizing Irradiation on Surface Wettability: Fundamentals and Application in Engineering Superhydrophobic Surfaces

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INTRODUCTION

Understanding surface-to-coolant interfacial energy and mass transport is of paramount importance in understanding heat transfer and corrosion properties of nuclear materials. Interfacial transport processes are typically quantified in terms of surface wettability or surface energy [1]. Extreme environments in a nuclear reactor and ionizing irradiation of materials including gamma, alpha, and neutron radiation are known to affect these surface and interfacial properties in diverse ways. Specifically, the role of gamma irradiation on surface wettability/surface energy change by a process known as Radiation Induced Surface Activation (RISA) [2, 3] has been demonstrated by several researchers. Previously, the authors published their findings on the possibility of surface oxidation as a result of gamma irradiation which improved surface wettability and the Leidenfrost temperature on Zircaloy-4 surfaces [4].

However, a complete understanding on the mechanism responsible for the change in surface characteristics as a result of gamma irradiation is critical to address its impact on different surfaces exposed to ionizing irradiation, apart from understanding the role of total irradiation dose and rate of exposure. This requires the use of specialized gamma irradiation facilities along with comprehensive post irradiation examination such as surface energy measurements, surface morphology measurements, and surface chemistry analysis.

To achieve this goal, various surfaces (metallic and ceramic) were irradiated at the NSUF Gamma Irradiation facility (GIF) at Sandia National Laboratories (SNL) [5] followed by advanced post-irradiation surface characterization as part of a Rapid Turnaround Experiment (RTE). Based on the analysis, gamma irradiation was observed to cause local oxidation, pitting, and corrosion depending on the surface, even in the absence of corrosive reagents or extreme environments. The local oxidation appeared to increase with an increase in the cumulative dose, thereby increasing the surface energy and wettability of the surfaces. The corrosion on the surfaces was also captured through electrochemical potential (ECP) measurements.

Based on the obtained fundamental understanding on the impact of ionizing irradiation, the authors developed a technique that leverages the change in surface morphology as a result of irradiation-induced local oxidation along with chemical treatments using hydrophobic chemical reagents such as fluorosilanes to create superhydrophobic surfaces [6]. Superhydrophobic surfaces are known to have several applications in self-cleaning surfaces, corrosion resistant coatings, and condensation heat transfer [7]. The scalability of the developed technique as a result of large-scale gamma irradiation cells available commercially makes this a promising technique for the development of superhydrophobic surfaces.

In this paper, the authors provide a brief overview of their findings from the Rapid Turnaround Experiment conducted at the NSUF GIF facility at SNL on different surfaces, as well as provide more details on the engineering of superhydrophobic surfaces.

MATERIALS AND METHODS

Two different Co-60 gamma irradiators were used in the present work obtain a complete understanding on the effect of total dose and dose rates. The high dose rate NSUF GIF at SNL had a dose rate of 32 Gy/s, whereas the gamma cell facility at MIT provided a dose rate of 0.7 Gy/s. The maximum total dose on the samples was 19.2 MGy in the high dose rate facility and that in the low dose rate facility was 1.2 MGy. The dose rate was measured at the NSUF GIF using a calibrated Victoreen Model 550 ionization chamber with the Inovision Radiation Measurements Therapy Dosimeter Model 35040 electrometer. Surface energy measurement was also carried out at GIF, with SNL using a four-liquid approach through the determination of the polar (Lewis acid-base) and Lifshitz-van der Waals (includes Debye, Keesom, and London dispersion interaction) components of the surface energy. (Readers are requested to refer [8] for further details on surface energy measurement). Specifically, the four fluids used were deionized water, ethylene glycol, glycerol, and diiodomethane. A Zeiss Merlin Scanning electron microscope with a 15 kV high-resolution detector was used to understand surface morphology change and a PE Versaprobe II XPS was used for surface chemistry studies. ECP measurements were carried out with 0.1M H_2SO_4 using a Palmsens EMStat potentiostat with a saturated calomel reference electrode. Three metallic surfaces (Zircaloy-4, 110 Copper, 316 stainless steel) and one ceramic surface (high resistivity SiC) were irradiated.

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RESULTS AND DISCUSSION

Surface Wettability and Surface energy measurements

The surfaces exposed to both the gamma cells at SNL and MIT were covered with UHV foil to prevent the contamination of samples inside the gamma cells and isolate ECP changes that could occur between the sample and the surface of the gamma cell. Numerous samples of each kind were loaded and a sample of each kind was taken out for each exposure length during the total exposure time to carry out the contact angle measurement with different fluids to estimate surface energy. Fig. 1 and Table 1 show the contact angle (with deionized water for samples irradiated at both MIT and NSUF GIF) and surface energy change (for samples irradiated at NSUF GIF) respectively. The increase in surface energy with exposure can be observed for all the samples, confirming that the mechanism of RISA is applicable to both as-fabricated ceramics and metals. The increased surface wettability can be observed from Fig. 1 as a decrease in measured static contact angle with an increase in irradiation dose. Most of the samples showed very low contact angle after gamma irradiation with copper showing complete superhydrophilicity (not shown in the graph). Importantly, it could be observed that the decrease in contact angle was clearly a function of total dose and is similar for both the dose rates and hence the mechanism could be considered dose rate independent.

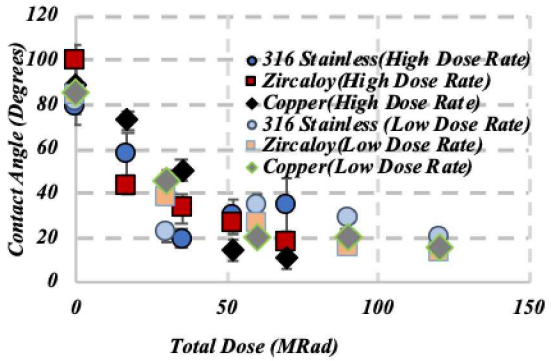

Fig. 1. Contact Angle decrease with Gamma irradiation.

TABLE 1. Surface Energy Measurements before and after Irradiation(Total dose 1920 MRad)

Sample	Sample Condition	Surface Free Energy (mJ/m^2)
Zircaloy-4	Before Irradiation	34.26
	After Irradiation	66.33
Copper	Before Irradiation	35.27
	After Irradiation	67.52
Stainless Steel	Before Irradiation	35.36
	After Irradiation	63.68
Silicon Carbide	Before Irradiation	30.60
	After Irradiation	66.21

The study also demonstrates an important conclusion not covered in the existing reports [2, 3]. So far, all the studies (at least to the authors' knowledge) considered wettability increase as a result of ionizing irradiation on *pre-oxidized surfaces*. The proposed mechanism in those studies was the photon induced anodic reaction between oxide layer and water molecules that leads to bond breaking of any organics adhering to the pre-oxidized surface. In the present case, the gamma induced wettability decrease was clearly visible on unoxidized surfaces, suggesting a marked difference in the underlying mechanism responsible for the change in surface energy/surface wettability.

Surface Morphology and Chemistry studies

As the difference in the mechanism behind the RISA effect is noted for unoxidized samples, microscopic and spectroscopic analysis were performed on the irradiated samples to explore the possibility of surface oxidation or a permanent surface change as a result of ionizing irradiation. Surfaces were observed before and after irradiation with the SEM and are shown in Fig. 2. Significant surface change can be observed in all the samples. The SEM images of Zircaloy in Fig. 2 shows localized pits/cracks after irradiation which had high local oxygen concentrations when examined with EDS. The observations is similar to the localized corrosion observed in Zircaloy in the presence of corrosive fluids reported earlier by several authors [9-11]. However, in the present work, this was observed even in the absence of a corrosive liquid and is believed that the moisture in the ambient environment resulted in radiolysis and liberation of free oxygen and hydroxyl ions leading to the accelerated localized corrosion, even at room temperature.

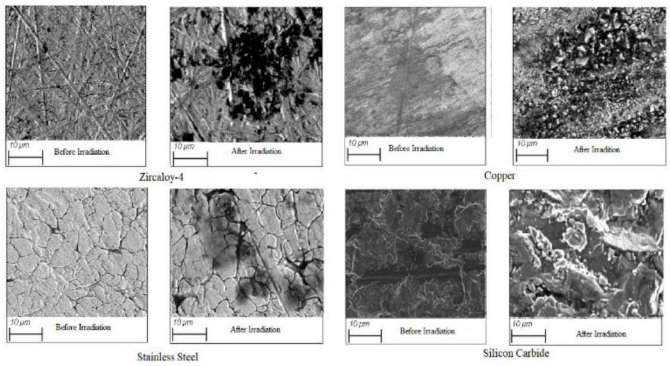

Fig. 2. SEM Images of different surfaces before and after irradiation.

Localized corrosion was also evident in stainless steel but was observed as intergranular corrosion. It was observed from the examination of surfaces at different total dose that oxidation started at the grain boundaries and propagated with the increase in total dose. At high total dose, the intergranular corrosion propagates inside the grains as can be seen from

Fig. 2. Irradiated copper surfaces also showed pitting corrosion similar to that in Zircaloy. However, the extent of damage was much higher in copper, which, resulted in the superhydrophilicity reported earlier. The oxidation observed in SiC was slightly different where the oxide was observed quite uniformly over the surface. It is likely that the smaller grain size in SiC was responsible for more uniform corrosion. The authors carried out further XPS survey scans on the samples before and after oxidation and an increased oxygen peak was clearly observed for all the samples, further confirming surface oxidation [8]. The authors also performed water absorption (capillary wicking) measurements and all the irradiation samples were found to act as wicking surfaces after irradiation as result of the morphological changes due to localized corrosion [8]. Further, the authors performed ECP measurement at different total dose levels and the measured ECP followed very closely with the observed trend in contact angle measurements as shown in Fig. 3. Interestingly, the physical understanding of the ECP values related the trend to the different nature of oxide that formed during irradiation of surfaces and is discussed in detail in [8].

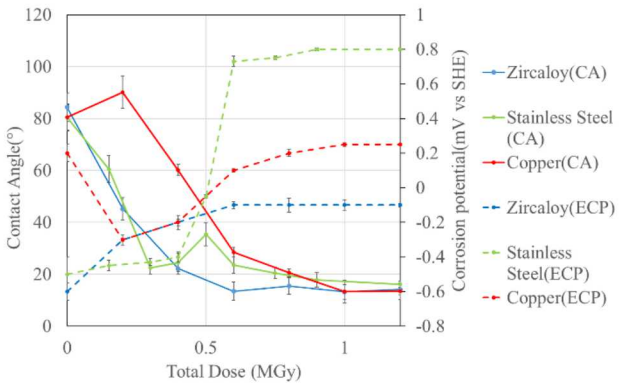

Fig. 3. ECP vs Contact angle Variation with Irradiation.

With all the surface characterization details discussed above, it can be reasonably concluded that gamma irradiation, even at room temperature, causes localized corrosion which increased with net dose, which, was also responsible for the increase in wettability and surface energy. Increased wettability is well known to improve two phase heat transfer and hence it can be reasonably concluded that considering this effect of ionizing irradiation may become critical in determining CHF and thermal operation limits (a margin that might have been missed in calculations so far), considering the fact that gamma rays are emitted continuously in a nuclear reactor [4]. On the other hand, while the increased corrosion due to gamma irradiation is well-documented for Zircaloy and Steel based alloys in the nuclear community, its impact on advanced cladding materials such as SiC is of significant interest [12].

Application to engineer superhydrophobic surfaces

An interesting and important observation from the fundamental study explained so far, is the change in surface morphology as a result of localized corrosion on the surfaces. Such morphological changes have been artificially introduced through several methods such as chemical etching, photolithography, ion-milling, etc., to increase the wettability of the surfaces. Such microscopic changes could be accompanied by chemical treatment, particularly those containing hydrophobic agents/radicals (for example: fluorosilane) to generate superhydrophobic surfaces (CA > 150°). Superhydrophobic surface generation is of commercial interest in several applications [7].

Since such microscopic changes were inherently observed on the irradiated samples in the present case, the authors tried to leverage the observation by vapor-depositing fluorosilane on the post-irradiated surface to create a superhydrophobic surface. To accomplish this, we took samples irradiated at different total dose and placed them in a polytetra-fluoroethylene (PTFE) container with an open vial of 1H,1H,2H,2H-perfluorodecyltriethoxysilane (fluorosilane, Alfa-Aesar). The sealed PTFE container was then placed at 140 °C in the oven for 30 minutes. The sample was taken out and cooled for 24 hours in a room temperature environment. Contact angle was measured after 24 hours. The measured contact angle on different surfaces after chemical treatment at different irradiation dose is shown in Fig. 4.

It can be seen from Fig. 4 that nearly all the samples (both metallic and ceramic) showed increased contact angle. The rate of increase was observed to be the highest for copper which turned superhydrophobic faster which is expected to be a result of the highly non-uniform surface damage of the irradiated samples reported earlier. The lowest was observed in silicon carbide where there was minimal non-uniformity on the surface compared to other surfaces. This leads to the conclusion that the process is likely to be impacted by the degree of non-uniformity of the irradiated surface which in turn depends on the nature of substrate and possibly the grain size. A comprehensive study is in progress to clearly quantify the role of grain size and other surface properties on the efficiency of the presented technique.

CONCLUSION

The present work describes the experiments conducted at the NSUF GIF facility at SNL to understand the fundamental mechanism of ionizing irradiation induced surface energy and surface wettability change. With the help of comprehensive surface examination and ECP studies, localized oxidation was confirmed on all the surfaces after irradiation which was concluded as the responsible mechanism for the enhanced surface wettability. The surface

energy change was observed to be a function of total dose but was independent of dose rate. The fundamental study could help develop more informed decisions on determining the thermal margin in nuclear reactors. Further, as a follow-on study, the mechanism was used to develop a technique which was effective in creating superhydrophobic surfaces.

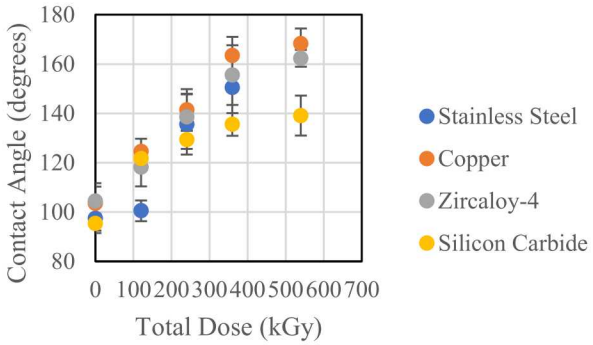

Fig. 4. Contact angle after chemical treatment on irradiated samples with different total dose.

ACKNOWLEDGEMENT

Maryla Wasiolek and Don Hanson (Sandia) are gratefully acknowledged for supporting the irradiation campaigns at the GIF.

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy under DOE Idaho Operations Office Contract DE-AC07- 051D14517 as part of a Nuclear Science User Facilities experiment.

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