Tuning surface porosity on vanadium surface by low energy He⁺ ion irradiation

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Abstract

In the present study, we report on tuning the surface porosity on vanadium surfaces using high-flux, low-energy He⁺ ion irradiation as function of sample temperature. Polished, mirror-finished vanadium samples were irradiated with 100 eV He⁺ ions at a constant ion-flux of 7.2×10^{20} ions m⁻² s⁻¹ for 1 hour duration at constant sample temperatures in the wide range of 823-1173 K. Our results show that the surface porosity of V₂O₅ (naturally oxidized vanadium porous structure, after taking out from UHV) is strongly correlated to the sample temperature and is highly tunable. In fact, the surface porosity significantly increases with reducing sample temperature and reaches up to ~87%. Optical reflectivity on these highly porous V₂O₅ surfaces show ~0% optical reflectivity at 670 nm wavelength, which is very similar to that of “black metal”. Combined with the naturally high melting point of V₂O₅, this very low optical reflectivity suggests potential application in solar power concentration technology. Additionally, this top-down approach guarantees relatively good contact between the different crystallites and avoids electrical conductivity limitations (if required). Since V₂O₅ is naturally a potential photocatalytic material, the resulting sub-micron-sized cube-shaped porous structures could be used in solar water splitting for hydrogen production in energy applications.

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1. Introduction:

Recently, numerous investigations have been made on the effects of helium (He)-induced defects and impurities in metals and intermetallics since this is an important issue for metals considered as structural materials in reactors [1-3]. V and its alloys are regarded among the most promising candidates for structural materials because of their excellent mechanical properties, high thermal conductivity, good resistance to irradiation-induced swelling and damage, and low activation properties [4, 5]. High energy neutron irradiation of V causes the production of He from (n, α) transmutation reactions, which can be easily trapped by defects such as vacancies [2]. The usefulness of V as a structural material for future DEMO fusion reactors will depend, in part, on the influence of He on mechanical and structural properties. Even at relatively low concentrations, He may potentially cause material embrittlement [6]; at higher concentrations, He can lead to the formation of He bubbles [6-9] and void swelling [10, 11]. Consequently, the influence of He content in V is an important issue and requires more investigations [3]. V-oxygen systems are also very interesting and, in a certain sense, unique [12]. V forms more than ten distinct oxide phases with different electronic properties, ranging from metallic to insulating: VO, V₂O₃, VO₂, Magneli (V_nO_{2n-1}) and Wadsley (V_{2n}O_{5n-2}) homologous series, and V₂O₅ [12]. A number of V-oxides undergo metal–insulator transitions at different temperatures, viz., vanadium dioxide (VO₂) is a semiconductor for $T < 340$ K; at $T = T_t = 340$ K, the conductivity increases enormously by four to five orders of magnitude; and above this transition temperature VO₂ exhibits metallic properties [13]. Note that among all V-oxides, V₂O₅ is the most stable and therefore most common form of V-oxide [12]. Until now, V₂O₅ structures have been studied and

tested for a wide range of applications including solar energy conversion [14-16], chemical catalysts [17, 18], supercapacitors [19, 20], and bio-applications [21, 22]. Though it has enormous range of applications, every study placed a common emphasis on enhancing V_2O_5 surface area in a controlled manner. Particularly for bio- and energy-storage applications, tuning both the surface porosity and aspect ratio of such metal-oxide nanostructures [23-25] are very important. Recently, huge efforts have been made by several research groups to develop highly porous V_2O_5 surfaces using several techniques, viz., electrosynthesis and anodization [26, 27], phase transformation [28], thermal oxidation [28], and sol-gel processes [29, 30].

In this work, we focus on tuning the surface porosity of V_2O_5 by 100 eV He^+ ion irradiation (with constant ion fluence 2.6×10^{24} ions m^{-2}) at constant sample temperature (here after “target temperature”) in a wide range of 823-1173 K. Using these specific conditions, we performed He^+ ion irradiations for tuning the surface porosity of V_2O_5 . Note that this technique has been applied for the first time by de Respinis *et al.* to form m- WO_3 surface nanostructures and study their photocatalytic properties [31] and later studied by others too [32, 33]. Our study shows that surface pore diameter, depth, and number density are all highly tunable with target temperature during the 100 eV He^+ ion irradiation. This top-down approach guarantees relatively good contact between the different crystallites and avoids electrical conductivity limitations (if required). Although the solubility of He in metals (including V) is extremely low, significant concentrations of implanted He can lead to dramatic changes in microstructure and mechanical properties [34, 35]. Consequently, understanding the role of He in V systems is a critical issue in the development of structural materials for nuclear energy applications. This study is also significant in the understanding of microstructure evolution and fuzz formation on high-Z refractory metals for fusion applications. As with W [8, 9, 36-39], Mo [40-42], Ta [43], and Nb

[44], the He^+ ion-irradiated V surface could also have a weakness against plasma and/or ion heat flux. Therefore, such V nano- and submicron-structures may not be favorable for protecting the V surface from possible melting and erosion. Nevertheless, this study could have a significant impact on ongoing fusion research, particularly in the basic understanding of fuzz formation. Optical reflectivity studies on nano- and submicron-structured V_2O_5 show sharp decreases in reflectivity, a behavior very similar to that of “black metal” [45]. In addition, the studies indicate naturally higher melting point. Therefore, another plausible application of such nano- and submicron-structures lies in solar power concentration technology [46]. *Ex situ* X-ray photoelectron spectroscopy (XPS) studies confirm the formation of a V_2O_5 phase that is a promising photocatalytic activity material [47]. In addition, optical reflectivity measurements on these V_2O_5 nano- and submicron- structures show ~0 % optical reflectivity. Thus the study opens another plausible application for solar water splitting for hydrogen production. The excellent control over nano- and sub -microscopic V porous structures and the good contact between the crystallites obtained with ion irradiation techniques may open a new pathway for such applications [31].

2. Experimental Conditions

Experiments have been performed at the Center for Materials under Extreme Environment (CMUXE) at Purdue University in the surface characterization laboratories UHFI (Ultra-High Flux Irradiation) and IMPACT (Interaction of Materials with Particles and Components Testing) [48]. Annealed and rolled V sheets of 99.95% purity and 0.25 mm thickness were used for these experiments; 10×10 mm samples were cut from one V sheet and then mechanically polished to a mirror-finished surface. For He^+ ion irradiation experiments, a Kaufman & Robinson, Inc. End Hall (EH) 400 ion source was used. All irradiations were performed in ultra-high vacuum (UHV)

chamber with a base pressure of 5.0×10^{-8} Torr; however, the working pressure during ion irradiation was 1.0×10^{-4} Torr. The selected ion energy (100 eV), ion-flux (7.2×10^{20} ions $\text{m}^{-2} \text{s}^{-1}$), ion-fluence (2.6×10^{24} ions m^{-2}), and range of target temperature (823-1173 K) were based on our previous studies involving He^+ -induced surface modifications in refractory metals [40, 41, 43, 44]. For precise temperature measurement, we used thermocouples rather than radiation thermometers; a thermal-feedback mechanism in the sample heater were corrected for the ion-induced heating of V samples during the experiment by altering the current supplied to the heating element based on the difference between actual and desired sample temperatures. After ion irradiation experiments, the samples were taken out from the UHV chamber and field emission (FE) scanning electron microscopy (SEM) was performed using a Hitachi S-4800 Field Emission SEM to monitor the He^+ ion-induced surface modifications. Atomic force microscopy (AFM) studies using Bruker Innova atomic force microscope were also conducted on selected samples for monitoring the ion-induced nanoscopic changes. XPS was performed on pristine and all post-irradiated V targets. For the XPS measurements, photoelectrons were excited by an Mg-K α (energy = 1253.6 eV) X-ray radiation source (SPECS XRC-1000), and the emitted photoelectrons were analyzed with Omicron Argus hemispherical electron analyzer using a round aperture of 0.63 mm (for imaging-XPS) and a second aperture at 6.3 mm (for conventional XPS). No sample charging was observed. All XPS spectra were analyzed with commercial CasaXPS software [49]. Optical reflectivity measurements were performed over a spectrum of incident light wavelength (λ) ranging from 200-1100 nm (using a combination of halogen and deuterium light source and a beam diameter of ~ 1 mm). Maya 2000 Pro Spectrometer from Ocean Optics was used for signal detection. Before the reflectivity measurements began, the spectrometer was calibrated with a Spectralon white reference plate having 100% reflectivity.

Note that the observed reflection in our system is mainly specular. A specular reflection, which is a reflection of a mirror like surface (keeping in mind that different surfaces to different wavelengths may or may not be mirror like). Specular reflection will result when the surface roughness is smaller than the applied wavelength of light (and diffuse reflection will result when the surface roughness is larger than the wavelength). A specular reflectance of 100% would correspond to an ideal mirror, typical specular reflectance are less than the maximum value (*i.e.*, 100%). For collecting the reflected light a “*reflection probe*” from Ocean Optics has been used which can collect light at the same angle as it illuminates, and can be used for either specular or diffuse reflection measurements. In fact it is made of 6 illumination fibers around a single read fiber (in the center), which results in a 25° full angle field of view. Each illumination fiber project a cone of light from the source and all of them overlap at the sample in the center, exactly where the central read fiber is situated. Thus, in principle the reflectivity for an ideal mirror will be ~100%. During our measurements the “*reflection probe*” was placed at 90° to the sample surface (along the sample surface normal). The distance between sample and “*reflection probe*” was ~1 mm.

3. Results and Discussion

3.1. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies

Figure 1 depicts FE-SEM images of polished (mirror-finished) pristine and 100 eV He⁺ ion-irradiated (having an ion-flux of 7.2×10^{20} ions m⁻² s⁻¹ for 1 hour duration, giving a total ion-fluence of 2.6×10^{24} ions m⁻²) V samples as function of target temperature in the range of 823 - 1173K. As evidenced in Fig. 1(a) SEM results of the pristine sample show a reasonably clean and flat surface morphology, up to several micrometer scales, along with a few mechanical polishing-induced scratches. As substantiated in Fig. 1(b), He⁺ ion irradiation even at 823 K

target temperature deteriorates the V surface significantly, leading to the formation of homogeneously populated, irregularly shaped porous structures on the entire V surface. Similar porous structures were also observed at 873 K (Fig. 1 (c)); however, these structures are relatively more pronounced in size (sub-micron size). Note that these structures are very different than those of our previous studies on Mo [40, 41] where we observed the formation of fiber-form nanostructures (nano-tendrils or “fuzz”) under similar irradiation conditions. The nano-tendrils and fuzz structures in Mo are ultimately the result of sub-surface He clusters formed from the trapping of penetrating He^+ ion irradiation. The sub-surface He then forms pressurized bubbles that erupt through the surface, leaving behind dense nano-tendrils or fuzz structures. Mo fuzz was observed under similar irradiation conditions when the target temperature was kept between 873 and 1073 K. There was no Mo fuzz formation beyond this temperature window, instead the appearance of pillar-like nanostructures were observed. However, below this temperature window homogeneous Mo nanograins (773 K) and a combination of nanopores and nano-tendrils with relatively very low number density and thickness (823K) were observed. While the discrepancy in behavior between these two materials is not yet clear, future work will look at combined experimental and modeling approaches to determine the material characteristics responsible for these various surface structures. Another 100K enhancement in V target temperature causes unique homogeneously populated cube-shaped porous structures on the entire V surface (Fig. 1 (d)). The calculated average edge size for these cubic pores was ~300 nm. At 1073K, the edge size of the cubic pores increased and reached up to ~400 nm (Fig. 1(e)). Finally, at 1173K the pore edge size reached up to ~500 nm (majority) and even ~875nm (minority) (Fig. 1(f)). At this target temperature, the shape and facets of the cubic pores are clearly evidenced. This sequential enhancement in pore size, along with a corresponding reduction in surface pore number density,

as function of target temperature can be understood in the realm of a surface pore percolation mechanism [48, 50]. In general, He is characterized by its closed-shell electronic structure, and so prefers to keep such structure whenever it interacts with different environments. Any interaction with other elements that break such a structure can elevate the system energy. Therefore, He prefers to occupy sites in metals with a large effective volume [5]. Under normal conditions, He is impermeable to V surfaces. Therefore, when He^+ ions are implanted and/or bombarded into V, they do not stay uniformly distributed throughout the V lattice. The helium agglomerates to form bubbles; when the bubbles form just below the surface, it can cause blistering. Blister formation commonly occurs in metals under helium implantation at elevated temperatures [51]. However, at higher temperatures the helium bubbles move through the sample (due to enhanced diffusion) and may migrate to the surface, resulting in the formation of surface pores [51, 52] like in our present case. Another possibility of such pore formation may be due to a surface-rupturing phenomenon. Recently, Lasa *et al.* have shown, using their molecular dynamic (MD) calculations, that pores on the metallic surface may form by surface rupturing caused by the growth of sub-surface bubbles [53]. Additionally, the role of grain boundaries (GBs) is also very crucial for such unique surface morphology changes, *i.e.*, formation of cube-shaped sub-micron-sized surface pores. In general, defects in V, such as GBs, dislocations, and vacancies, are considered to be the main regions for helium dissolution and accumulation. In such mechanisms, GBs play a pivotal role; in fact, they are acting as a transition region between two adjacent crystal lattices, so the chemical composition and crystallographic structure of GBs are distinct from those of the bulk crystal [5, 54]. Further, some elements may also segregate GBs due to the different chemical composition between GBs and the surrounding bulk [55]. The fact that GBs are one of the most propitious sites for helium accumulations in V has already been

demonstrated by Ryazanov and his group [56-59] and Satou *et al.* [60]. Additionally, the sliding of GBs may be considered to be one of the principal mechanisms of plastic deformation for polycrystalline V at high temperatures (above $0.4T_m$, where T_m is the melting point; in the present case T_m is 1910°C and so all the target temperatures considered here lie in this range) [5, 61], which can be described as the relative displacement of the two constituent grains in the direction parallel to the boundary interface. Another plausible factor that may also be considered is the role of sputtering. Our calculations, using ITMC simulation [62, 63] for 100eV He⁺ ion irradiation on Mo, shows that the role of sputtering is trivial (below the lower threshold). However, for the case of V, calculated sputtering yield using ITMC simulation [62, 63] is ~ 0.01 atoms/ion (above the lower threshold) and may also play a significant role in such specific irradiation conditions (high ion-flux and above $0.4T_m$ target temperatures). Additionally, since the target temperature is rather high, the role of recrystallization cannot be discarded. In summary, it is hard to precisely predict which mechanism is governing the formation of such unique cube-shaped structures contributing to high surface porosity in V. This study opens the opportunity to perform future modeling work combined with new experiments to determine the governing mechanism responsible for such unique sub-micron cubical surface pores.

Figures 2-4 show 100 eV He⁺ ion irradiation (2.6×10^{24} ions m⁻² constant ion fluence) -induced V surface morphology changes at 823, 873, 973, 1073, and 1173 K target temperatures in more detail. In Fig. 2, the left and right columns correspond to ion-induced surface modifications at 823 and 873K, respectively. The 823 K target temperature induces fine, irregularly-shaped porous structures on the entire surface. Though the observed surface pore structures at 873 K are somewhat similar to those at 823 K, the pore number density is significantly lower than that of the 823 K case. Another notable observation is the appearance of a very fine nanostructure inside

the individual pores, as evidenced by the [high-resolution images](#) in Fig. 2(b) and (d) (from the [regions in Fig. 2 \(a\) and \(c\), respectively](#)). Note that the observed surface pore structures are significantly different than those of our recently reported Nb results, [which were irradiated under similar conditions \[44\]](#). While the discrepancy in the behavior between these two materials (Nb and V) is not yet clear, it seems [sputtering could also be an important factor](#). The ITMC simulations [\[62, 63\]](#) on Nb and V show that (for 100eV helium ion irradiation) Nb sputtering yield is below the threshold level and so its role is trivial; however, for V it is slightly higher than the lower threshold [sputtering yield](#) (~ 0.01 atoms/ion), so sputtering may also play a role in such surface modifications. Future work will look at joint experimental and modeling approaches to determine the materials' characteristics responsible for such different surface structures.

Figure 3 details ion irradiation-induced surface modifications at 973 K [\(\(a\)-\(c\)\)](#) and 1073 K [\(\(d\) - \(f\)\)](#). Notably at 973K, observed surface pore structures are more pronounced in shape and populated homogeneously on the entire V surface. Almost all the surface pores are a cubic shape having an average edge size of [~300 nm](#). A closer observation in Fig. 3(a) shows a significant reduction in the population of very fine nanostructures inside the individual pores (marked by a black circle in Fig. 3(a) and high-resolution SEM image in Fig. 3(b)) and relatively clearer facets of the individual pore edge as compared to that of the 873 K (Fig. 2 [\(a\)-\(d\)](#)). Another notable observation is the evidence of partially broken surface pore edges (Fig. 3(b)-(c)) which indicate the occurrence of a pore-percolation phenomena [\[48, 50\]](#) due to combined high flux ion irradiation and simultaneous target heating. [SEM imaging has been performed on entire sample \(figures not shown\) and similar structures were observed everywhere](#), showing a [superior](#) degree of surface pore homogeneity. Further, at 1073 K the average pore edge size increases significantly and reaches up to [~400 nm](#) (with a corresponding reduction in surface pore number

density). Like the previous target temperature case, a reduction in the population of very fine nanostructures inside the individual pores (marked by a blue circle in Fig. 3(d), and high-resolution images in Figs. 3(e) (taken from the region marked a blue in Fig. 3(d)) and 3(f). Note the unique freely-hanging nanostructures (integral part of the corresponding surface pore edge), evidencing the intermediate stages of a pore-percolation phenomena [48, 50] during the growth of such surface pores. Figure 4 depicts the surface morphology at 1173K. Here, the surface pore size increases notably and reaches up to ~500 nm (majority) and even ~ 875nm (minority); correspondingly, the surface pore number density decreases. The resulting surface pores are more geometrically defined in cubical shapes and have clear, faceted edges. The other most notable feature is evidence of surface-like cracking (marked by green arrows in Fig. 4 (a) - (c)). Early-stage of surface-like crack formation is also seen at 1073 K (figure not shown); though less pronounced, these cracks were clearly visible. These surface-like cracks are shallow and mainly due to interconnection of surface pores along grain boundaries. Figure 4 ((d)-(f)) depicts high-resolution images from different regions showing relatively larger pores and a few freely hanging fine nanostructures inside the individual pores. The observed surface cracks at 1173K are populated and inter-connected with each other homogeneously on the entire V surface. The observed surface-like cracking in V under these irradiation conditions is unique since cracking under low-energy He⁺ ion irradiation has not been observed on other BCC refractory metals viz. W, Mo, Nb, Ta etc. Note, several factors may play roles in cracks formation and growth including: grain boundary, temperature, microstructure, chemistry, morphology, etc. The main observation on the surface-like crack formation patterns seen in our case does clearly indicate intergranular pore formation and propagation along the grain boundaries. Similar observation has been reported by Stratulat *et al.* recently [64]. Surface cracks in some applications, including

plasma-facing materials for nuclear fusion, are not preferred and could deteriorate the material's performance and lifetime. Recently, Xu *et al.* [65] (using high-flux deuterium plasma) and Dutta *et al.* [66] (using helium ion pulse) have shown evidence of similar surface cracking in W. While the surface cracking in W studied by Dutta *et al.* [66] is relatively close to cracks observed in V, the ion irradiation conditions are different. The formation mechanism of such surface cracks may be understood as follows: growth-induced interstitials and/or defects such as GBs, dislocations, and vacancies are almost always present in the cast refractory V as a second phase and may contribute to the appearance of cracks at GBs since they are considered to be the main regions for He dissolution and accumulation [67]. The pores in the V act like crack nuclei or stress concentrators [67]. Note that during plastic deformation of V at elevated temperatures, the diffusion and the collection of He in surface pores can be accelerated significantly [67]. As more He^+ ions are implanted and/or bombarded into the V surface, the cavities expand [67, 68]. The resulting He bubbles are highly over-pressurized. Up to a certain bubble size, the excess pressure is relieved by loop punching [68]. The formation of such surface cracks can be interpreted from the inter-bubble fracture model which was first suggested by Greenwood *et al.* [69] and later on discussed by Evans [70]. According to which, the bubbles grow due to an increase in internal pressure, effectively decreasing their spacing. Eventually, several adjacent bubbles will create a local stress that is sufficient to form subsurface cracks and these may lead to the formation of such surface cracks shown in Fig. 4.

Figure 5 depicts surface porosity (η) vs target temperature (T) plots. Surface porosity calculations (using commercial ImageJ software [71]) have been performed for 873-1173 K. The target temperatures 823 and 873K were excluded from this analysis simply because the resulting surface pore structures at these temperatures are very irregular in shape, making it difficult to

perform such calculations. Note that for surface porosity calculations (and for “surface-pore” edge length histograms; described below) several highest-fidelity SEM images were used and then averaged for better statistical analysis. Surface-porosity (η) can be defined as: $\eta = (\text{total surface pore area}) / \text{area considered for counting the total number of surface pores (i.e., total SEM image area)}$. By this definition, $\eta=1$ corresponds to a surface entirely populated by surface pores; $\eta=0$ corresponds to a flat, pore-free surface. The value η will give quantitative information about the degree of “surface porosity” of V at a corresponding target temperature. For example, a surface-porosity (η) of 40% will indicate that 40% of the total area in an SEM image is populated by surface pores. This concept of “surface porosity” is not unlike a two-dimensional (2D) void formation. The surface porosity (η) was plotted as a function of temperature and fitted with an exponential decay function defined as $\eta = A_0 \exp(-T/t) + \eta_0$, where A_0 and t correspond to the amplitude and decay constants; merely to guide the eye. The best fits were obtained with η_0 coefficient = 0.55, $A_0 = 2482.19$, and $t = 109.13$. Perhaps the physical meaning of η_0 may be understood as the lowest (saturated) value of surface porosity at the highest target temperature in the system. Further, Fig. 6 depicts average surface pore edge length histograms as a function of target temperature. The histograms clearly show a sequential enhancement in the surface pore edge length from ~311 nm (973K) to ~392 nm (1073 K) to ~510 nm (1173K). The histograms also indicate the formation of a few surface pores having edge length of ~875 nm. Furthermore, to more finely resolve surface features and quantify pore depth, high-resolution AFM studies were also performed on selected samples. Figure 7 shows 2D and 3D AFM images and a line profile of one of the typical surface pores observed on He^+ ion-irradiated V samples at 1173K. Similar to SEM studies, 2D AFM surface topography (in tapping mode) also shows homogeneously populated surface pores with ~ 800 nm edge length

(Fig. 7(a)). Figure 7(b) shows the 3D AFM topography of the same region. Sectional analysis on the AFM images show that the average typical depth of the resulting surface pores are ~550 nm. Because of the very high surface roughness, the AFM tip may not follow down to the bottom of the surface pore and the corresponding pore depth may be underestimated. Nevertheless, the study gives an idea about the surface pore depth roughly within the experimental limitation. One of the typical surface pores is shown in Fig. 7(c) and its line profile is shown in Fig. 7(d) (along the marked green line in Fig. 7(c)).

3.2. X-ray Photoelectron Spectroscopy (XPS) Studies

To study surface composition changes due to He^+ ion irradiation-induced surface modifications at various temperatures, *ex situ* core-level XPS was also conducted. Figure 8 shows survey core-level XPS spectra of 1 keV Ar^+ ion sputter-cleaned pristine, pristine, and 100 eV He^+ ion-irradiated (at 973 and 1173 K) polished (mirror finished) V samples. Data for the irradiated V surfaces are vertically shifted for clarity. XPS (*in situ*) on a 1 keV Ar^+ ion sputter-cleaned pristine sample was performed to determine chemical compositions of the V sample without exposing it to the open air (non-oxidized). The *in situ* XPS spectrum of the sputter-cleaned pristine sample shows only pure V XPS peaks. No impurity, C, or O peaks were observed. However, the *ex situ* core-level XPS spectrum from the pristine V sample shows the presence of pure V and O peaks but no other impurities [72, 73]. A similar trend has also been seen for elevated-temperature V samples. To determine the oxidation characteristics of the ion-irradiated V samples compared to the pristine samples, high-resolution XPS spectra were also performed on all the above four samples (Fig. 9). All spectra were resolved into their respective components by a mixed Gaussian-Lorentzian (GL, $m = 30$) line shape (where $m = 0$ is pure Gaussian and $m = 100$ is pure Lorentzian) using commercial CasaXPS peak-fitting software [49]. For all high-

resolution XPS spectra, the major fitting parameters, binding energy (BE), and full width at half maxima (FWHM) are summarized in Table 1. Irradiated and pristine (not sputter-cleaned) V samples demonstrate only V-oxide XPS peaks; V_2O_5 2p doublets in majority. Note that peak fitting shows the existence of V_2O_3 2p doublets as well; however, their concentration (at. %) is much lower (Table 2).

3.3 Optical Reflectivity Studies

To monitor He^+ ion-induced surface modifications (particularly the surface porosity), optical reflectivity measurements were also performed. Figure 10 shows optical reflectivity spectra in the wavelength range 200-1100 nm for irradiated and pristine mirror-polished samples. The observed total reflectivity for the pristine V sample was ~47% (for $\lambda = 670\text{nm}$). The value of reflectivity gradually decreases with decreasing target temperature and reaches nearly zero for 873K, i.e., ~47% (pristine) to ~9% (1173K) to ~5% (1073K) to ~2% (973K) and to ~1% (873K) at $\lambda = 670\text{nm}$. The significant reduction in reflectivity, as compared to that of a pristine sample, may be understood in the realm of enhanced surface porosity due to microstructure evolution as a result of He^+ ion irradiation at elevated temperatures. The sequential reduction of reflectivity with decreasing target temperature corroborates well with the trend of sequential enhancement of surface porosity with decreasing target temperature.

4. Conclusions

Annealed and rolled V sheets of 99.95% purity and 0.25 mm thickness provided 10×10 mm samples that were mechanically polished to a mirror-like finish. Tuning the surface porosity of V surfaces has been achieved by temperature-dependent high-flux 100 eV He^+ ion irradiation (using constant ion-fluence of 2.6×10^{24} ions m^{-2}). Resulting surface morphologies were

intensively studied by scanning electron (SEM) and atomic force (AFM) microscopy, which revealed a sequential dependence of surface porosity with target temperature (exponential reduction of surface porosity with increasing target temperature). The presented method of tuning surface porosity on V surface is unique and able to generate homogeneously populated surface pores from nanometer to sub-micrometer dimensions in well-defined cube-shaped surface pores (up to $\sim 800 \times \sim 800 \times \sim 500$ nm in size). A significant reduction in optical reflectivity (down to almost 0%) of 100 eV He⁺ ion-irradiated V samples at 873 K, as compared to that of the pristine V sample (with optical reflectivity of $\sim 47\%$), may be attributed to the formation of sub-micron size surface pores. Similar to W and Mo, He⁺ ion-irradiated V surfaces could have some weakness against plasma and/or ion heat flux. As a plasma-facing component, such structures would not be favorable for protecting the V surface from possible melting in future DEMO fusion reactors. Nevertheless, the present study is significant in ongoing fusion research, particularly for the understanding of fuzz formation on high-Z refractory metals. Nearly 0% optical reflectivity for 670 nm wavelength, which is very similar to that of “black metal,” and naturally higher melting points of V₂O₅ suggest its potential application in solar power concentration technology. Since this top-down approach guarantees relatively good contact between the different crystallites and avoids electrical conductivity limitations (if required), and V₂O₅ is naturally a potential photocatalytic material, the observed enhanced sub-micron size cube-shaped porous structures have promising application toward solar water splitting for hydrogen production and renewable, environmentally-friendly clean energy applications.

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Table 1: Summary of the binding energy (BE) and full-width half-maximum (FWHM) values for each fitted peak in the high-resolution XPS spectra.

Sample	V 2p _{3/2}		V 2p _{1/2}		V ₂ O ₅ 2p _{3/2}		V ₂ O ₅ 2p _{1/2}		V ₂ O ₃ 2p _{3/2}		V ₂ O ₃ 2p _{1/2}	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
pristine, Sputter-cleaned	512.7	1.9	520.2	2.0	-	-	-	-	-	-	-	-
pristine	-	-	-	-	517.5	2.5	524.0	2.8	514.3	1.3	521.3	2.7
973K	-	-	-	-	516.8	2.0	523.7	2.7	515.3	2.5	520.9	2.0
1173K	-	-	-	-	516.9	2.4	523.6	1.9	515.5	2.0	521.9	2.5

Table 2: Summary of calculated atomic concentrations for each peak in the high-resolution XPS spectra.

	Number of Counts (%)						Total Atomic Concentration (%)		
Sample	V 2p _{3/2}	V 2p _{1/2}	V ₂ O ₅ 2p _{3/2}	V ₂ O ₅ 2p _{1/2}	V ₂ O ₃ 2p _{3/2}	V ₂ O ₃ 2p _{1/2}	V	V _x O _y	
								V ₂ O ₅	V ₂ O ₃
pristine, Sputter- cleaned	68.11	31.89	0	0	0	0	100	0	0
pristine	0	0	54.53	28.63	1.29	15.55	0	83.16	16.84
973 K	0	0	36.16	29.09	16.92	17.83	0	65.25	34.75
1173 K	0	0	58.56	14.91	9.77	16.76	0	73.47	26.53

Figure 1: FE-SEM Images of pristine (mirror-polished) and 100 eV energy He^+ ion (having a constant ion fluence of $2.6 \times 10^{24} \text{ ions m}^{-2}$) -irradiated V samples (as a function target temperature): pristine (a); 823 K (b), 873 K (c), 973 K (d), 1073 K (e), and 1173 (f).

Figure 2: FE-SEM Images of 100 eV energy He^+ ion (having ion fluence of 2.6×10^{24} ions m^{-2}) -irradiated V samples at 823 K (a) - (b), and 873 K (c) - (d). Figures (b) and (d) are high-resolution images from figures (a) and (c), respectively.

Figure 3: FE-SEM Images of 100 eV energy He^+ ion (having ion fluence of $2.6 \times 10^{24} \text{ ions m}^{-2}$) -irradiated V samples at 973 K ((a)- (c)) and 1073K ((d)- (f)) at low and high resolutions. Note that figure (b), (c) and (e) are the high-resolution images from the region marked by the black circle in figure (a), white circle in figure (a), and blue circle in figure (d). Figure (f) has been taken from a different region at 1073 K.

Figure 4: FE-SEM Images of 100 eV energy He^+ ion (having ion fluence of 2.6×10^{24} ions m^{-2}) -irradiated V samples at 1173 K at low and high resolutions. Note that figures (a) - (c) are in increasing order of higher magnification, showing surface cracking clearly. Note the marked green arrows on figures (a) - (c), indicating surface cracking as observed on the sample surface (in addition to relatively large surface pore formation). Figures (d)-(f) are high-resolution SEM images showing various large and unique surface pore structures on the V samples

Figure 5: Surface porosity (defined by the ratio of total surface pore area to the total V_{surface} area (total SEM image area); see more details in text) vs. sample temperature plot for V samples irradiated with 100 eV He^+ ions to a fluence of 2.6×10^{24} ions m^{-2} at temperatures of 973, 1073, and 1173 K.

Figure 6: Average cubic surface pore edge length histograms as a function of sample temperature for V samples irradiated with 100 eV He^+ ions to a fluence of 2.6×10^{24} ions m^{-2} at temperatures of 973, 1073 and 1173 K.

Figure 7: AFM surface topography (in tapping mode), of 100 eV He⁺ ion (having a fluence of 2.6×10^{24} ions m⁻²) -irradiated V sample at 1173 K: two dimensional (2D) AFM image (a), 3D AFM image (b), 3D AFM image ($5 \times 5 \mu\text{m}^2$ scan area) (c), and line profile of one of the surface pores (d)

Figure 8: *Ex situ* XPS survey spectra of selected V samples. The top spectrum corresponds to 100 eV He⁺ ion (having a fluence of 2.6×10^{24} ions m⁻²) -irradiated V sample at 1173 K. The bottom two spectra correspond to a pristine, mirror-polished V sample both before and after 1 keV Ar⁺ ion sputter-cleaning (to remove the native contaminants and resolve the pure V XPS peaks) (see text for more details).

Figure 9: *Ex situ* high-resolution core-level XPS spectra of 2p doublets for 1 keV Ar^+ ion sputter-cleaned pristine (a), pristine (b), and 100 eV He^+ ion (having a fluence of 2.6×10^{24} ions m^{-2}) -irradiated at 923 K (c) and 1173 K (d) mirror-polished V samples. All spectra were fitted using commercial CasaXPS peak fitting software (see text for details).

Figure 10: Optical reflectivity measurements of pristine and 100 eV He^+ ion-irradiated (having a fluence of 2.6×10^{24} ions m^{-2}) mirror-polished V samples at 873, 973, 1073, and 1173 K target temperatures. Note the almost zero reflectivity for 873 K, where the surface porosity was maximum (up to 87%).