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A COMPARATIVE STUDY OF BLISTERING IN Nb, V and V-20% Ti[†]

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ABSTRACT

A comparative study of the radiation blistering of the surfaces of polycrystalline niobium, vanadium, and vanadium-20 wt% titanium alloy has been made for different doses of helium ions implanted at 0.5 MeV for target temperatures ranging from room temperature to 900°C. The degree of blistering appears to decrease with increasing irradiation temperature for all the three materials studied. Both at room temperature and at 900°C, the degree of blistering appears to decrease slightly in the order Nb, V, and V-20% Ti alloy. Estimates of the surface erosion of annealed polycrystalline Nb and V implanted at room temperature with 0.5-MeV helium ions indicate that the erosion by this blistering process is approximately two orders of magnitude faster than the erosion by physical sputtering under the same conditions. The results suggest that, in most of the structural materials considered for fusion reactors, helium blistering will be an important erosion process.

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1. INTRODUCTION

During the operation of a large steady-state D-T fusion reactor, energetic deuterons and tritons from the unburned fuel and energetic helium ions from the nuclear reaction may leak out of the confining field either as charged particles (escaping by such processes as classical diffusion, magnetic instabilities, or magnetohydrodynamically unstable skin currents) or as neutrals (formed, for example, by charge exchange near the plasma boundary or at a beam limiter). These energetic projectiles striking the surfaces of major components (such as vacuum walls, beam limiters, diverter walls, etc.) can cause a variety of surface phenomena as reported in Refs. 1–6. One of the most important of these is radiation blistering. The formation of blisters in the surface region of irradiated solids has been observed by several workers.^{7–12} The bursts of gas released by rupturing blisters was first observed mass-spectrometrically by Kaminsky⁷ and has also been reported by others.¹⁰ These bursts of gas will contaminate the plasma and the peeling of the blister skins will result in wall erosion. The formation of blisters on niobium—a material prominently considered for the vacuum walls of fusion reactors—was recently reported by the present authors,^{13–16} who irradiated the surfaces with 0.5- or 1.5-MeV He^+ and with 0.125–0.5-MeV D^+ ions for different doses and target temperatures. These results showed that vacuum walls made of niobium could be seriously eroded by helium irradiation but that irradiation with deuterons had a distinctly smaller effect. Measuring

the degree of blistering by the ratio of blistered area to total irradiated area, for example, one finds that 6.5% of the area irradiated by 0.25-MeV D^+ (total dose = 2.0 C/cm^2 , target temperature = 700°C) was occupied by blisters whereas $\sim 32\%$ of the area irradiated by 0.5-MeV He^+ ions (total dose = 1.0 C/cm^2 , target temperature = 900°C) was blistered. In this comparison, note that the projectile energies, total doses, and target temperatures are different for the two projectiles.

The present paper reports a comprehensive study of the helium blistering in Nb, V, and the alloy V-20% Ti. The new results on the latter two materials are compared with some of the earlier results^{13, 16} on Nb. For a variety of reasons, Nb, V, Mo, and their alloys have been favored over other materials for the first wall of fusion reactors. In the present study the particular alloy V-20 % Ti was chosen because the swelling studies made by Wiffen¹⁷ after neutron irradiation in EBR-II have shown that this alloy does not swell at all under conditions that produce up to 2% swelling in unalloyed V. Thus it appeared to be of interest to see if the blistering effects in this alloy would be considerably less than in Nb and V.

2. EXPERIMENTAL TECHNIQUES

High-purity Nb and V (Marz grade) were obtained as polycrystalline foils from the Materials Research Corporation. The major impurities in Nb were 30 ppm C, 75 ppm , and 200 ppm Ta; and those in V were 57 ppm C and 100 ppm O. The V-20% Ti alloy was

a laboratory melt obtained from Dr. S. Harkness of Argonne National Laboratory. All the foils were first given a fine metallographic polish and then annealed at 1200°C for 2 hours in a vacuum of $3-5 \times 10^{-7}$ Torr and finally electropolished. In this process more than $35\text{ }\mu\text{m}$ were removed from the surface and left the samples micropolished; as determined with the aid of a scanning electron microscope, the average surface roughness over more than 90% of the polished area on the Nb and V samples was less than $0.02\text{ }\mu\text{m}$ (the resolution limit) but micropits $\sim 0.3\text{ }\mu\text{m}$ in diameter were observed on the V-20% Ti samples. The samples were irradiated with $0.5\text{-MeV } ^4\text{He}^+$ ions from a 2-MeV Van de Graaff. During the irradiation, the vacuum in the target chamber was maintained at $1-2 \times 10^{-8}$ Torr by ion pumping and the ion flux density was held constant at $1 \times 10^{13}\text{ ions cm}^{-2}\text{ sec}^{-1}$. A more detailed description of the experimental arrangement has been given previously.¹⁸

The irradiated surfaces were examined with a scanning electron microscope (Cambridge Stereoscan, Mark II). A Zeiss particle-size analyzer was used to measure the size distribution of the blisters from the enlarged micrographs.

3. RESULTS

Irradiation of Nb

Some typical examples of the blisters observed in annealed polycrystalline Nb irradiated at normal incidence with 0.5-MeV

He^+ to a total dose of 1.0 C/cm^2 at various temperatures are shown in Fig. 1. After irradiation at room temperature, very large interconnecting blisters (diameters up to $1000 \mu\text{m}$) are observed (Fig. 1a). The blisters have ruptured at many different places and in the area to the left a large portion of the skin has fallen off, exposing the inner surface. In the region marked by the arrow, secondary blisters have already formed on the exposed inner surface after the skin from the first blister had fallen off. As the irradiation temperature is increased to 600°C , the average blister size decreases (Fig. 1b), the diameter of the largest blister being about $400 \mu\text{m}$. At this dose and this irradiation temperature, the blisters have a wide range of sizes and most of them have ruptured. On further increasing the irradiation temperature to 900°C , the blister size is further decreased (Fig. 1c) to an average diameter of only about $15 \mu\text{m}$. In parallel with this decrease in blister size, the ratio of blister area to total irradiated area decreases from 62% at room temperature to $\sim 47.2\%$ at 600°C and to 12.5% at 900°C . As in the earlier results¹⁶ on cold-worked niobium, higher magnification reveals the presence of a class of much smaller blisters (diameter $\leq 1 \mu\text{m}$) on samples irradiated at 900°C . The areas occupied by these small blisters (diameters $< 2 \mu\text{m}$) were not included in calculating the ratios of blister area to total area (Table 1).

It was found that quite often the small blisters described above formed preferentially along the grain boundaries, particularly at lower doses. Figure 2 shows examples in a sample irradiated at

900°C with 0.5-MeV helium ions to a total dose of 0.1 C/cm². In Fig. 2(a), the small blisters along the grain boundaries produce a decorating effect. The larger dome-shaped blisters are also present. A magnified view of one of the grains is shown in Fig. 2(b), where the small blisters are present exclusively along the grain boundaries. These results show direct evidence for preferential accumulation of helium bubbles along the grain boundaries. Although blister formation is a surface phenomenon, the helium generated in the bulk material as a transmutation product will behave similarly and the helium bubbles along the grain boundaries will cause severe loss of ductility as a result of intergranular failure, as has been observed in stainless steel¹⁹ for example.

Irradiation of V

Irradiation of annealed polycrystalline V samples with normally-incident 0.5-MeV helium ions to a total dose of 1.0 C/cm² results in blisters that are very similar to those on Nb. Figures 3a and 3b show examples of the blisters formed after irradiation at room temperature and at 900°C, respectively. After room-temperature irradiation, irregularly shaped blisters with average diameters up to 350 μm were formed (Fig. 3a). The average diameter of an irregular blister is here defined as the diameter of a circle having the same area as that of the blister. The blister skin has ruptured and has fallen off at many places. The average blister size was smaller if the

irradiation was done at 900°C (Fig. 3b). Much as in the earlier observations on Nb,¹⁶ the average size of the dome-shaped blisters at this higher temperature is only $10\text{--}20\text{ }\mu\text{m}$, and in addition many small blisters (diameters = $0.5\text{--}1.5\text{ }\mu\text{m}$) were observed and can be seen as small dots in Fig. 3b. Comparison of the blisters formed on V and on Nb under identical irradiation conditions both at room temperature (Figs. 1a and 3a) and at 900°C (Figs. 1c and 3b) suggest that the degree of blistering (expressed in Table 1 as the ratio of blister area to total irradiated area) may be slightly lower in V than in Nb.

Irradiation of V-20% Ti

The blistering observed in V-20% Ti alloy after irradiation at room temperature with 0.5-MeV helium ions at normal incidence to a total dose of 1.0 C/cm^2 is shown in Fig. 4a. The blisters are very similar to those observed for V (Fig. 3a) under similar irradiation conditions. Most of the blisters have ruptured and the blister skin has fallen off at several places. The blister diameters, which range from 10 to $250\text{ }\mu\text{m}$, appear to be slightly smaller than those observed in irradiated V (Fig. 3a). Much as in the case of Nb and V, irradiation of V-20% Ti with 0.5-MeV helium ions to a total dose of 1.0 C/cm^2 produced a smaller degree of blistering at 900°C than at room temperature, as seen in Fig. 4b. At the higher irradiation temperature, the diameters of most of the dome-shaped blisters are in the range $8\text{--}20\text{ }\mu\text{m}$. In addition, many small blisters with an average diameter

of about 1 μm were also observed. After 900°C irradiation, the blister density on the V-20% Ti appears to be higher than that on the V.

However, in this comparison one should keep in mind that the average surface smoothness of the electropolished V-20 % Ti alloy was inferior to that of V and Nb. Thus it is not certain whether the blister density on the V-20% Ti is higher than that on the V because of the difference in surface finish. Experiments are in progress to check this on surfaces with similar surface smoothness.

4. DISCUSSION

From the quantitative estimates (Table 1) of the degree of blistering (defined, as noted above, as the ratio of the blistered area to the total irradiated area), it is apparent that under identical irradiation conditions the degree of blistering at room temperature decreases slightly as one successively changes from Nb to V and to V-20% Ti samples. The formation of extremely large blisters in polycrystalline Nb has been discussed earlier by the present authors,¹³ who pointed out that one of the most important factors responsible for this blistering is the extremely low solubility and diffusivity of helium in niobium. The reason that the degree of blistering observed in V is slightly less than that in Nb may be at least partly due to a slightly higher diffusivity of helium in V than in Nb—though no experimental data on the diffusivity of helium in V is known to the authors. It is likely that the mobility of helium will be higher at 900°C than at room temperature and that at the

high temperature some of the implanted helium may be lost through the surface by atomistic helium diffusion or by small bubbles migrating to the surface and subsequently rupturing. (The blisters considered here would be too small to be detected by the scanning electron microscope.) This loss can partially account for the observation that the degree of blistering by helium projectiles is less at 900°C than at room temperature. These observations agree qualitatively with the mass-spectrometric results of Bauer and Morse,²⁰ who studied helium re-emission from niobium surfaces during helium-ion implantation and found that the rate of release of helium when the dose exceeded 1.18×10^{18} ions/cm² was higher at $500\text{--}700^{\circ}\text{C}$ than at room temperature.

As mentioned in Section 2, the primary helium flux in our experiment was kept constant at 1×10^{13} ions cm⁻² sec⁻¹ and the maximum dose was 1.0 C/cm^2 . However, since the diffusivity of He in the metals studied is very low (for helium release studies from heated Nb surfaces, see Bauer and Morse²⁰) the implantation of energetic helium ions is a strongly cumulative process. This means that the degree of surface blistering depends primarily on the total dose. Thus, serious blistering still would be expected if the maximum dose (e.g., 1.0 C/cm^2 as in the present experiment) were accumulated with a lower flux continuing over a correspondingly longer time.

One important parameter for the design of the first wall of a fusion reactor is the rate at which the wall is eroded by

blistering. A preliminary value can be estimated directly from micrographs such as Figs. 1a, 3a, and 4a by measuring the skin thickness and the area from which the skin has dropped off. The skin thickness can be measured directly from the high magnification micrographs of the fractured edges of the blisters as shown earlier.^{13, 16} For room-temperature irradiation with 0.5-MeV He^+ ions to a total dose of 1.0 C/cm^2 , the erosion rates estimated in this way are ~ 0.2 atom per incident He ion for a Nb target and ~ 0.1 atom per incident He ion for V. These erosion rates are 50–100 times those due to physical sputtering. For the case of 0.5-MeV He^+ impact on Nb, for example, a sputtering yield of $S = 0.0023$ atom per incident He ion was calculated by Kaminsky³ on the basis of the theory of Goldman and Simon.²¹ The above rates of erosion by helium blistering are underestimates because the peeling is only well started at the rather small total dose of 1.0 C/cm^2 ; as seen in Fig. 1a, for example, the ruptured skin is barely adhering to the surface in many cases and may fall off after a small additional dose or by thermal shock. Furthermore, the estimates took no account of the blistering that had already begun on the areas exposed to irradiation after the first skin peeled off. (Such a region is marked by the arrow in Fig. 1a, and also can be seen in Fig. 7B of Ref. 13.) In addition, the vaporization of the blister skin as a result of heating by bremsstrahlung absorption can become important. For example, in the actual operation of a large steady-state D-T reactor, a power of about 25 W/cm^2 from bremsstrahlung may be

deposited on the first wall. Because of the presence of helium gas inside the blister, this heat deposited cannot be dissipated easily through the thin blister skin. A rough estimate indicates that the heat deposited by bremsstrahlung in a blister of 500 μm diameter will raise the temperature of the skin sufficiently that the entire skin ($\sim 10\,000\text{ \AA}$ thick) can vaporize in about 2 hours. While it is possible to determine the degree of blistering for irradiation at 900°C (as shown in Table 1), it is difficult at this time to evaluate the erosion rate. To obtain a reliable estimate of the erosion rate it appears necessary to increase the total dose and the resulting skin loss.

5. CONCLUSIONS

a. The degree of blistering by room-temperature irradiation appears to decrease slightly in changing the target material successively from Nb to V and to V-20% Ti.

b. Higher target temperatures during irradiation appear to reduce the degree of blistering. This suggests that higher operating temperatures ($\geq 900^{\circ}\text{C}$) for the first wall would tend to reduce surface erosion by blistering.

c. The erosion rates for helium blistering of Nb and V are about two orders of magnitude higher than the corresponding sputtering yields under the same irradiation conditions at room temperature.

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Table 1

RATIO OF BLISTER AREA* TO TOTAL IRRADIATED AREA

Irradiation	Nb	V	V-20% Ti
temperature			
Room temp.	87%	52.0%	47.2%
600°C	47.2%	. . .	. . .
900°C	12.5%	1.68%	7.4%

*The area occupied by blisters with diameters $< 2\mu\text{m}$ has not been included.

FIGURE CAPTIONS

Fig. 1. Scanning electron micrographs of annealed polycrystalline Nb surfaces after irradiation with 0.5-MeV $^4\text{He}^+$ ions to a total dose of 1.0 C/cm^2 . (a) Secondary-electron image after irradiation at room temperature. (b) Back-scattered electron image after irradiation at 600°C . (c) Secondary-electron image after irradiation at 900°C .

Fig. 2. Scanning electron micrographs (secondary-electron images) of annealed polycrystalline Nb surfaces after irradiation at 900°C with 0.5-MeV $^4\text{He}^+$ ions for a total dose of 0.1 C/cm^2 .

Fig. 3. Scanning electron micrographs of an annealed polycrystalline V surface after irradiation with 0.5-MeV $^4\text{He}^+$ ions for a total dose of 1.0 C/cm^2 . (a) Secondary-electron image after irradiation at room temperature. (b) Back-scattered-electron image after irradiation at 900°C .

Fig. 4. Scanning electron micrographs (back-scattered-electron images) of annealed polycrystalline V-20% Ti alloy after irradiation with 0.5-MeV $^4\text{He}^+$ ions for a total dose of 1.0 C/cm^2 : (a) at room temperature and (b) at 900°C .

Figure 1

Figure 2

Figure 3

Figure 4