02-04-76
02 07 07

Correlation between Blister Skin Thickness, the Maximum in the
Damage-Energy Distribution, and Projected Ranges of
Helium Ions in Nb for the Energy Range 10 - 1500 keV

By

R. G. St-Jacques, J. G. Martel, B. Terreault and G. Veilleux

S. K. Das, M. Kaminsky and G. Fenske

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Prepared for Presentation

2nd International Conference
on Surface Effects in Controlled Fusion Devices
San Francisco, Ca.
February 16-20, 1976

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

operated under contract W-31-109-Eng-38 for the
U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Energy Research and Development Administration, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona	Kansas State University	The Ohio State University
Carnegie-Mellon University	The University of Kansas	Ohio University
Case Western Reserve University	Loyola University	The Pennsylvania State University
The University of Chicago	Marquette University	Purdue University
University of Cincinnati	Michigan State University	Saint Louis University
Illinois Institute of Technology	The University of Michigan	Southern Illinois University
University of Illinois	University of Minnesota	The University of Texas at Austin
Indiana University	University of Missouri	Washington University
Iowa State University	Northwestern University	Wayne State University
The University of Iowa	University of Notre Dame	The University of Wisconsin

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the U. S. Energy Research and Development Administration.

CONF-760209--10

**Correlation between Blister Skin Thickness, the Maximum in the
Damage-Energy Distribution, and Projected Ranges of
Helium Ions in Nb for the Energy Range 10 - 1500 keV**

**R. G. St-Jacques, J. G. Martel, B. Terreault and G. Veilleux
I. N. R. S. -Energie, Université du Québec, C. P. 1020
Varenes, Québec, Canada**

**S. K. Das, M. Kaminsky, and G. Fenske[†]
Argonne National Laboratory
Argonne, Illinois 60439**

Abstract

The skin thickness of blisters formed on polycrystalline niobium by $^4\text{He}^+$ irradiation at room temperature for energies from 15 to 80 keV have been measured. Similar measurements were conducted for 10 keV $^4\text{He}^+$ irradiation at 500°C to increase blister exfoliation, and thereby allow examination of a larger number of blister skins. For energies smaller than 100 keV the skin thicknesses are compared with the projected range and the damage-energy distributions constructed from moments interpolated from Winterbon's tabulated values. For energies of 10 and 15 keV the projected ranges and damage-energy distributions have also been computed with a Monte Carlo program. For energies larger than 100 keV the projected ranges of $^4\text{He}^+$ in Nb were calculated using either Brice's formalism or the one given by Schiott. The thicknesses for 60 and 80 keV, and those reported earlier for 100 to 1500 keV correlate well with calculated projected ranges. For energies lower than 60 keV the measured thicknesses are larger than the calculated ranges.

RECEIVED BY TIC MAR 4 1976

Introduction

It has been pointed out [1, 2] that during the operation of thermonuclear reactors the surfaces of components exposed to bombardment by energetic helium ions from the plasma region can be seriously eroded by radiation blistering. The bursts of gas released by blister rupture from the surfaces of irradiated components can lead to plasma contamination. A determination of the surface erosion yields (number of atoms lost per incident ion) requires measurements of the blister skin thickness and of the area from which the skin has peeled off. Recent experimental results on the dependence of blister skin thickness in polycrystalline Nb [3] and V [4] on the helium ion energy indicated a good correlation with the calculated projected ranges of the helium ions for the energy range 100 keV - 1500 keV. In contrast, recent experimental results on helium blistering of monocrystalline niobium for a lower helium ion energy range of 1.5 - 15 keV indicated that the skin thickness determined by Rutherford backscattering was about a factor of two to three larger than the calculated value for the mean range [5] and also 2-3 times higher than the experimentally determined depth of maximum ^3He concentration [6]. For the $^4\text{He}^+$ energy range 15 keV - 100 keV no skin thickness values for Nb are known. In the present experiments a systematic study of the correlation of the skin thickness measured directly by scanning electron microscopy with both the calculated projected-range values and the maximum in the damage-energy distribution has been conducted for the helium-ion energy range 10 - 80 keV in polycrystalline niobium.

RECEIVED BY TIC MAR 4 1970

Experimental Procedures

The polycrystalline niobium foils used were obtained from Materials Research Corporation (Marz grade). The foils used for the 15 keV to 80 keV irradiations at Argonne National Laboratory (ANL) were prepared at ANL by mechanical polishing and lapping and degreased in ultrasonic baths of trichloroethylene, acetone, distilled water and 2 rinses in methanol. Then the foils were annealed at 1200°C for 2 hours in a vacuum of $3 - 5 \times 10^{-7}$ Torr. Subsequently the targets were electro polished in an electrolyte containing 92.5% methanol, 5% H_2SO_4 , and 2.5% HF at -70°C at a current density of $\sim 0.05 \text{ A cm}^{-2}$. Finally, the samples were rinsed in ultrasonic baths of methanol. After this treatment the surfaces had an average surface roughness of less than 0.02 μm over 90% of the polished area as determined by scanning electron microscopy. The foils used for the 10 keV to 15 keV irradiations at I.N.R.S. -Energie (University of Québec) were mechanically polished with a Vibromet to an average surface roughness of $\sim 0.05 \mu\text{m}$ and rinsed, but were not annealed. For the helium implantation for the energy range from 10 keV to 15 keV $^4\text{He}^+$ ions from a duoplasmatron source (at I.N.R.S) were accelerated and magnetically mass analyzed before being focused on the target [7]. These implantations were conducted at both room temperature and 500°C. During the run the ion flux was $\sim 3.1 \times 10^{16} \text{ ions sec}^{-1} \text{ cm}^{-2}$ and the vacuum was held at 2×10^{-8} Torr. For the irradiations at 20 keV to 80 keV a low-energy ion accelerator with magnetic analyzer and with a duoplasmatron ion source (at ANL) was used. In these irradiation runs the $^4\text{He}^+$ ion flux was held in the range from 1×10^{14} to $1 \times 10^{15} \text{ ions sec}^{-1} \text{ cm}^{-2}$ and the vacuum was held at 8×10^{-9} Torr. For another 15 keV $^4\text{He}^+$ ion implantation a mass analyzed $^4\text{He}^+$ ion beam from a duoplasmatron ion source (at ANL) was used. The current densities were held at $4 \times 10^{14} \text{ ions cm}^{-2} \text{ sec}^{-1}$ and the vacuum was maintained at 2×10^{-6} Torr. The total

dose in each irradiation was chosen high enough for blisters to rupture, and varied from 0.2 to 0.5 C cm² for different energies. The ruptured edges of blister skins were examined in a Cambridge Stereoscan S4-10 scanning electron microscope. For each helium-ion energy at least eight measurements of blister skin thickness were made on two different irradiated spots. The magnifications were calibrated with replicas of ruled diffraction gratings for various working distances.

Results

Figure 1 (a) shows a scanning electron micrograph of a cold worked niobium surface after irradiation at 500°C with 10 keV ⁴He ions to a dose of 0.2 C cm⁻². Several ruptured blisters can readily be recognized. Figure 1 (b) shows an enlarged view of a portion of a ruptured skin, and Figure 1 (c) shows the depth of a crater formed by blister exfoliation. Measurements of the blister skins (with the appropriate tilt angle corrections) yield a value of $0.08 \pm 0.01 \mu\text{m}$, a value which agrees within the error limits with the measured crater depth. The error limits quoted represent the total error due to the scatter in individual measurements and the errors in the calibration of the microscope magnification and resolution. Figures 1 (d-f) and 1 (g-i) show scanning electron micrographs of surfaces of annealed polycrystalline niobium after irradiation at room temperature with ⁴He⁺ ions to the dose of 0.5 C cm⁻² at 15 keV and 20 keV, respectively. From the enlarged views of the blister skins [see for example Figures 1 (e) and 1 (h)] the measured skin thickness values are $0.11 \pm 0.01 \mu\text{m}$ and $0.13 \pm 0.01 \mu\text{m}$, for the 15 keV and 20 keV ⁴He⁺ ion irradiations, respectively. These skin thickness values agree within the error limits quoted with the measured crater depth values.

RECEIVED BY TIC MAR 4 1976

Figures 2 (a-c), (d-f), (g-h) and (i-k) show scanning electron micrographs of surfaces of annealed polycrystalline niobium after irradiation at room temperature with $^4\text{He}^+$ ions at 30 keV, 40 keV, 60 keV and 80 keV, respectively for the same total dose of 0.5 C cm^{-2} . Again, each micrograph shows blister exfoliation. Figures 2 (b), (e), (h), and (k) show enlarged views of portions of ruptured skins for the energies listed above, and Figures 2 (c) and (f) show depths of craters formed by blister exfoliation. Measurements of the blister skins (with the appropriate tilt angle corrections) yield values of $0.17 \pm 0.03 \mu\text{m}$, $0.24 \pm 0.02 \mu\text{m}$, $0.29 \pm 0.03 \mu\text{m}$, and $0.34 \pm 0.04 \mu\text{m}$ for 30 keV, 40 keV, 60 keV, and 80 keV irradiations, respectively. The skin thickness values at 30 keV and 40 keV agree within the error limits with the measured crater depth values. For the 60 keV and 80 keV irradiations the large number of exfoliated blisters allowed the measurement of many skin thicknesses with sufficient accuracy that additional measurements of crater depths were considered unnecessary.

Figure 3 (a) illustrates the correlation between the measured skin thicknesses (the data points are marked by the ion energies 10 - 80 keV), the projected range distributions (dashed curves), and the damage-energy distributions (solid curves). These curves were obtained using an Edgeworth series. The moments (up to the fourth) used in the series were interpolated from Winterbon's [8] tabulated values. These tabulated values are based on a Thomas-Fermi nuclear stopping cross-section, together with Lindhard et al.'s velocity-proportional electronic stopping cross section ($S_e(E) = k E^{1/2}$). The variable k used in figure 3 (a) equals the theoretical value k_{LSS} given by Lindhard et al. [9] (i.e. $k/k_{\text{LSS}} = 1$). Figure 3 (b) shows projected range, and damage-energy distributions which were calculated using a Monte-Carlo code [10]. One notices readily in Figure 3 (a) that the average blister

skin thickness correlates closely with the projected range at 80 keV, but for energies decreasing from 60 keV to 10 keV the thickness values become increasingly larger than the corresponding depth at which the maxima in the projected range and the damage-energy distributions appear. In the case of the Monte-Carlo calculations [Figure 3 (b)], the average skin thickness correlates reasonably well to the maxima in the projected range distribution down to 30 keV. Below that energy the thickness values become increasingly larger than the maxima of the range distributions.

Figure 4 shows a plot of projected ranges of helium ions in niobium for different energies calculated according to the method formulated by Schiott [11]. The dotted curve represents calculations using Thomas-Fermi nuclear stopping cross sections together with Lindhard et. al.'s [9] electronic stopping cross sections, which are proportional to projectile velocities. This latter assumption of velocity proportional electronic stopping is strictly true for velocity values v smaller than $v_0 Z_p^{2/3}$ (here $v_0 = e^2/h$, Z_p = atomic number of projectile), which corresponds to helium-ion energies less than 250 keV. The solid curve was calculated using Thomas-Fermi nuclear stopping cross sections together with Brice's [12] expression for electronic stopping which uses the semiempirical values of stopping power from Ziegler and Chu [13]. It should be noted that for ion energies lower than 200 keV the electronic stopping power values given by Brice [12] and by Lindhard et al. [9] have nearly similar slopes, but Brice's values are approximately 70% larger. Figure 4 also shows blister skin thickness values for He^+ ion irradiated niobium obtained in the present investigation (for 10 - 80 keV He^+), those obtained earlier by Kaminsk et al. [3] (for 100 - 1500 keV He^+), those reported by Roth et al. [5] (for 1 - 9 keV He^+) and by Behrisch et al. [6] (for 15 keV He^+). It may be noted that for the energy range from 250 keV to

1500 keV the skin thickness values agree within $\sim 15\%$ with the calculated projected-range values according to Brice, but for the energy range 60 - 80 keV the agreement is better with the calculated projected-range values according to Schiott. For He^+ ion energies below 40 keV the blister skin thickness values are higher than the projected range values, the difference increasing with decreasing ion energy. For 15 keV He^+ ion the value obtained by Behrisch et al. agrees closely with the one obtained in the present investigation. It must be pointed out that the skin thickness values reported by Roth et al. [5] were for monocrystalline Nb (100) surfaces and were estimated from the Rutherford backscattering measurements, whereas those by Kaminsky et al. and those in the present investigation were obtained by direct measurements of blister skin thicknesses in the scanning electron microscope.

Discussion

The results presented in this paper for helium ion irradiated niobium reveal that the average blister skin thickness values for ion energies above 60 keV correlate closely with the projected ranges calculated either according to Brice (for 100 - 1500 keV) or according to LSS (for 60 - 80 keV). For helium ion energies below 40 keV the blister skin thicknesses are larger than the calculated projected ranges either according due to Brice or due to LSS. The results for the energy range 80 keV - 1500 keV imply that the blister skin separation from the bulk occurs near the region of maximum helium concentration. This finding is consistent with the model for blister formation and rupture formulated earlier by some of the authors [2]. According to this model near the end of the projected range of the helium ions, where the helium concentration is at a maximum, the implanted helium atoms combine with vacancies to form gas filled bubbles. These helium bubbles formed in niobium at 400°C appear to be nearly spherical and have been observed by transmission electron

microscopy to be typically $30 - 40 \text{ \AA}$ in diameter [14]. When the density of these bubbles increases with increasing dose, the bubbles interconnect and grow to larger diameters. When the gas pressure within the bubble is high enough, the stresses can be partially released by plastic deformation of the surface skin to form visible blisters. When the stresses exceed the rupture strength for a damaged region, the blisters exfoliate [2]. The observation that for energies below 40 keV the blister skin thicknesses are larger than the projected range values can be attributed in part to the more uniform distribution of implanted helium for a large portion of the implant depth leading to volumetric changes (swelling) of that region for sufficiently high doses. For example, the helium concentration, in niobium bombarded at room temperature by 10 keV He^+ to a dose of $.16 \text{ C/cm}^2$ is about 30 at.%, hence swelling is very likely to occur. It has been suggested by Behrisch et al. [6] that the blister skin separates at the end of the range of the ions where according to the authors the maximum in the stress distribution should lie. However, more careful calculations of the stress distributions in the implant region are needed to assess if indeed the maximum of this distribution lies at the end of the range of the ions and is sufficient to cause exfoliation of blister skins. The topic of stress distributions in helium implanted solids is discussed by Hall and Wiedersich [15] in this conference.

Acknowledgements

The authors would like to thank Mr. P. Dusza for his help in the experiments and to Dr. R. Varma for the one of the 15 keV He^+ irradiation.

References

[†]Work performed under the auspices of the Energy Research and Development Administration.

- [1] M. Kaminsky, IEEE Trans. Nucl. Sc. NS18, (1971) 208.
- [2] S. K. Das and M. Kaminsky, J. Appl. Phys. 44, (1973) 25.
- [3] M. Kaminsky, S. K. Das, and G. Fenske, Appl. Phys. Lett. 27, (1975) 521.
- [4] M. Kaminsky, S. K. Das and G. Fenske, J. Nucl. Mat. 59, (1976) 86.
- [5] J. Roth, R. Behrisch and B. M. U. Scherzer, J. Nucl. Mat. 53, (1974) 147.
- [6] R. Behrisch, J. Bottiger, W. Eckstein, U. Littmark, J. Roth and B. M. U. Scherzer, Appl. Phys. Lett. 27, (1975) 199.
- [7] J. G. Martel, R. St.-Jacques, B. Terreault and G. Veilleux, J. Nucl. Mat. 53, (1974) 142.
- [8] K. B. Winterbon, Ion Implantation Range and Energy Deposition Distribution, Vol. II (Plenum Data Company, New York, New York 1975).
- [9] J. Lindhard, M. Scharff and H. E. Schiott, Mat. Fys. Medd. Dan. Vid. Selsk. 33, (1963) no. 14.
- [10] B. Terreault, J. G. Martel and R. St.-Jacques, (to be published).
- [11] H. E. Schiott, Mat. Fys. Medd. Dan. Vid. Selsk. 35, (1966) no. 9.
- [12] D. K. Brice, Phys. Rev. A6, (1972) 1791.
- [13] J. F. Ziegler and W. K. Chu, Thin Solid Films 19, (1973) 281.
- [14] W. Bauer and G. J. Thomas, Defects and Defect Clusters in B.C.C. Metals and their Alloys, Nuclear Metallurgy Vol. 18, edited by R. J. Arsenault (National Bureau of Standards, Gaithersburg, Maryland, 1973) p. 255.
- [15] B. O. Hall and H. Wiedersich, these proceedings p.

Figure Captions

Figure 1: Scanning electron micrographs of polycrystalline niobium irradiated with $^4\text{He}^+$ ions for different energies and doses: (a) 10 keV and $.2 \text{ C/cm}^2$ at 500°C , (d) 15 keV and $.5 \text{ C/cm}^2$ at room temperature, (g) 20 keV and $.5 \text{ C/cm}^2$ at room temperature. Blister skin thickness and crater depth are shown for 10 keV bombardment in (b) and (c), for 15 keV bombardment in (e) and (f), and for 20 keV bombardment in (h) and (i).

Figure 2: Scanning electron micrographs of annealed polycrystalline niobium irradiated at room temperature to a dose of $.5 \text{ C/cm}^2$ with $^4\text{He}^+$ ions at energies of (a) 30 keV, (d) 40 keV, (g) 60 keV, and (i) 80 keV. Blister skin thickness and crater depth are shown for 30 keV bombardment in (b) and (c), for 40 keV bombardment (e) and (f). Skin thickness are shown for 60 keV bombardment in (h) and for 80 keV bombardment in (k).

Figure 3: A. Plots of projected range probability distributions (dashed curves) and of damage-energy distributions (solid curves) as a function of depth into Nb target for different incident $^4\text{He}^+$ ion energies. These curves were obtained using an Edgeworth Series. The data points with error bars are measured blister-skin thickness for polycrystalline niobium irradiated at room temperature (except 10 keV which was at 500°C) with $^4\text{He}^+$ ions to total doses ranging from $.2$ to $.5 \text{ C/cm}^2$.

B. Plots of projected range probability distributions (dashed curves) and of number of displaced atoms (solid curves) as a function of depth into Nb target for different $^4\text{He}^+$ ion energies. These curves were obtained using a Monte-Carlo code.

Figure 4: Projected ranges of $^4\text{He}^+$ ions in niobium as a function of projectile energy. The dotted curve marked LSS was calculated using Thomas-Fermi nuclear stopping and Lindhard et al. is velocity proportional electronic stopping cross sections. The solid curve marked Brice was calculated using Thomas-Fermi nuclear stopping and Brice's semiempirical expression for electronic stopping. The data points with error bars are measured skin thickness values for He^+ ion irradiated niobium obtained in the present irradiation (X), by Kaminsky et al. [3] ($\cdot$), by Roth et al. [5] (I) and by Behrisch et al. [6] for 15 keV He^+ .

POLYCRYSTALLINE NIOBIUM IRRADIATED WITH $^4\text{He}^+$ IONS

0keV (500°C, 0.2 C/cm²)

15keV (ROOM TEMP, 0.5 C/cm²)

20keV (ROOM TEMP, 0.5 C/cm²)

ANNEALED POLYCRYSTALLINE NIOBIUM IRRADIATED AT ROOM TEMPERATURE TO A DOSE OF $0.5\text{C}/\text{cm}^2$
WITH $^4\text{He}^+$ IONS

30 keV

40 keV

60 keV

80 keV

Fig. 2
St. Jacques et al.

NUMBER OF DISPLACED ATOMS (10²²)

PROJECT

PROJECTED RANGE PROBABILITY (per Å)

Fig. 3
St. Jacques et al.

Fig. 4
St. Jacques et al.