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ABSTRACT

The swelling of several samples of Type 304 stainless steel bombarded with 1.25 MeV protons or 3.5-4.0 MeV Ni^+ ions has been studied using quantitative stereo electron microscopy. The swelling of proton bombarded samples is significantly greater than the Ni^+ bombarded samples and there was no indication of any saturation with dosage. Void formation occurred by sequential nucleation and growth.

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INTRODUCTION

As a means of expediting the study of swelling of cladding materials for fast-breeder reactor applications, an ion simulation capability has been developed at Argonne National Laboratory (ANL) using the 4 MV Dynamitron accelerator. Several samples of annealed Type 304 stainless steel have been irradiated with either 1.25 MeV protons or 3.5–4.0 MeV nickel ions to compare the influence of different bombarding ions on the swelling behavior. The structure of the damaged zone at various depths below the irradiated surface was examined using stereoelectron microscopy. Some preliminary data for samples preinjected with helium ions are also presented.

EXPERIMENTAL

The essential features of the beam transport system and the target assembly used for the irradiations are illustrated in Fig. 1. The system was maintained at a vacuum of $< 2 \times 10^{-6}$ Torr using oil-diffusion pumps equipped with liquid nitrogen cooled baffles. The ion beam, which was of low divergence, was magnetically analyzed and rastered at a frequency of 10kHz over the surface of the target using electrostatic deflector plates. Typical beam-on-sample conditions were either 100 μA of H_2^+ at 2.5 MeV, or 0.5 μA of $^{58}Ni^+$ at 3.5 - 4.0 MeV. The slit aperture was 0.5 cm^2 or greater to provide at least four specimens at each irradiation. The target current was measured by periodically inserting the shutter into the beam. The current was checked calorimetrically and, in the case of the nickel bombardments only, is subject to a maximum correction of 12% due to particle neutralization. The average particle flux, obtained from the quotient of the shutter current and the aperture area, differs by less than 10% from the flux on each specimen. The spatial uniformity of the beam was continuously monitored by a wire-loop beam-profile scanner during the irradiation, and by sweeping the beam across a narrow slit before commencing a run. The particle fluence quoted was obtained from the average of the calorimetric and beam currents measurements multiplied by the irradiation time.

Samples measuring 0.5-1 in. in diameter were cut from 0.015-in.-thick Type 304 stainless steel sheet stock used in the ANL reactor irradiation experiments. The samples were either diffusion bonded to copper mounts 0.3 in. thick or brazed on with nickel-silver alloy that had a melting temperature of 790°C. The sample mount and furnace block were clamped to the sample mount as illustrated. The temperature of the sample mount was controlled and measured by two chromel K thermocouples that were clad in stainless steel sheaths 0.025 in. in diameter and were inserted to a depth of 0.5 in. into 0.026-in.- diameter holes drilled in the side of the mount. The uniformity of the surface temperature of the sample was measured with an infrared pyrometer with the emissivity set to equalize the surface and sample mount temperatures with the beam off.

In the proton irradiations, spatial variation of the temperature across the surface was ± 10°C of the mean surface temperature, the temperature gradient through the sample was ≈ 6°C per mil, and the accuracy of the nominal irradiation temperature was ± 10°C. In the nickel irradiations, the accuracy of the irradiation temperature was ± 2°C.

SECTIONING PROCEDURE

Electron microscope specimens were sectioned at various depths below the irradiated surface by vibratory polishing.[1] The thickness of the layer removed in all samples, except the first proton irradiation, was established by measuring the depth of small hemispherical indentations in the surface using multiple-beam interference microscopy. Surface damage introduced by the mechanical polishing was removed by electropolishing the surface for ∿ 1 sec. The accuracy of the depth determination was estimated at ± 1000 A. The accuracy of the depth of the foil in the initial proton experiments was ± 5000 A. Specimens were separated from the copper mount with nitric acid, the irradiated surface was stopped off with lacquer, and the specimen was dimpled and penetrated with a jet of electropolishing solution.

Quantitative metallographic analyses were performed to determine the distribution of the void and dislocation loop densities using stereo pairs of micrographs taken 5° apart with a Jem 200 electron microscope. The swelling is defined by $S = \Delta V/V-\Delta V$, where ΔV is the void volume.

DISTRIBUTION OF IONS AND ION DAMAGE

The rate of atomic displacement as a function of proton energy in the sample was calculated from the Rutherford scattering cross section using the Kinchin and Pease[2] model for defect formation. The mean proton energy at the measured depth of the electron microscope foil was obtained from tabulations by Janni.[3] The variation of the damage rate with depth in Type 304 stainless steel irradiated with 1.25 MeV protons is illustrated in Figure 2.

The corresponding result for 3.5 $^{58}Ni^{+}$ and 3.25 MeV $^{12}C^{+}$ calculated by Brice[4] using the Lindhard theory is given in Fig. 3 together with the spatial distribution of the stopped ions normalized to 1. The magnitude of the Thomas-Fermi electronic stopping constant, used in these calculations (1.554) was taken from experimental determinations by Bowman et al.[5] The result of a similar calculation by Brager et al[6] at 5 MeV is also illustrated. An upper limit for the displacements per atom may be obtained by dividing the energy deposition expressed in eV cm^{-3} by $0.82/2E_d$ where E_d - 32 eV.[7] Such calculations show that in the present energy range the intense damage zone is limited to about 1 micrometer from the surface and varies by about a factor of three between the surface and the peak. From the range straggling it is found that the concentration of Ni^{+} ions injected into the sample at the mean range is 1.85×10^{-2} atomic fraction/mC-cm^{-2}; however, at the depth of 0.5 μm the concentration is reduced by an order of magnitude.

RESULTS

H_2^{+} Irradiations: Data obtained from the quantitative microscopy of proton-irradiated samples at 450, 525, and 600°C are listed in Table I. A plot showing the void number density, void diameter, and swelling versus depth below the irradiated surface for the 525°C irradiation is given in Fig. 4 and micrographs of the voids at depths of 3.5, 6.2, and 8.2 μm are shown in Fig. 5. Void formation is confined to depths within the proton trajectory. With increasing depth, there is, in general, a progressive increase in the void number density, mean void diameters, and swelling corresponding to the four-to fivefold increase in displacement rate and total number of displacements in the extracted foils. The unexpected small value of the swelling observed in some samples between one-half and two-thirds of the range originates in a reduction of void growth that is uncompensated by an increase in number density in this region. Similar effects have been observed in proton irradiated Type 316 stainless steel.[8] The evolution of the microstructures with dosage that is apparent from the samples analyzed is as follows. At dosages $\approx$ 5 displacements per atom, the structure consists of isolated Frank loops lying on (111) planes interspersed with a random array of small voids. A narrow depletion zone along a grain boundary was observed in one specimen irradiated at 450°C. The majority to the voids were not associated with any visible nucleation sites. The larger voids formed at 525, and 450°C were polyhedral-shaped with (111) faces truncated by (100) planes. With increase in dosage (increasing foil depth), the mean void diameter increases as does the minimum void size. Fewer faulted dislocation loops are visible, and a complex tangle of dislocations develops. The stereo-micrographs indicate that above 30 displacements/atom at 525°C the dislocation lines thread through the voids. The data for 450°C irradiation show a similar trend.

Comparison of the above data with that obtained in the irradiation at $\sim$ 600°C sheds some light on the temperature dependence of the swelling behavior. At 600°C a very rapid increase in swelling with depth was observed. At the 8.0-μm level, a swelling of 73% corresponding to a dosage of 35 displacement per atom was measured. Other trends in the structure varied more slowly: dislocation structure was coarser, voids tended to be more rounded, and the mean void size increased. A rapid increase in void number density with temperature was noted in the number densities normalized to a constant dose rate. The normalization is justifiable on the basis of the linear relationship between void number density and displacement rate observedin these samples and proton irradiated Type 316 stainless steel pre-injected with helium.(9)

The effect of nucleation on the void number density and growth can be seen in the two samples irradiated at 500 and 600°C subsequent to a helium injection followed by an anneal at 800°C. At this timperature, helium is mobile and can form small bubbles that subsequently grow into voids. Both samples, when compared with uninjected samples, showed reduced number densities and increased void diameter. This result is opposite to the refinement effect observed in samples preinjected with helium at room temperature prior to irradiation.(10) Similar results were observed recently in EBR II irradiations of preinjected and subsequently annealed Type 304 stainless steels by Harkness and Kestel.(11)

Ni^+ IRRADIATIONS

Table II lists the results of the metallography of samples irradiated with Ni^+ ions taken at depths of 0.2-0.4 μm. A detailed study of the damage versus depth is still incomplete. Voids were observed in foils that received dosages of 25 displacements per atom or more at 500 to 600°C. Compared with the proton irradiated samples on the basis of calculated dosage, the microstructure of th Ni^+ bombarded foils was significantly finer in scale. At 25 displacements per atom at 500°C, black-spot damage was observed, and dislocation loops which were mostly unfaulted, were small as were the void diameters. The voids were randomly dispersed in the dislocation structure, many were intersected by dislocations, as previously observed, but the number density was significantly lower. With increase in temperature, coarsening of the structure, decrease in the void number density, and increase in mean void diameter were observed. The maximum swelling observed was 4.6% in a foil receiving a calculated dosage of 120 displacements/atom at 600°C.

DISCUSSION

The similarity in the flux, fluence, and temperature dependences of void formation in Type 304 stainless steel under neutron irradiation[13] to the ion-irradiation results observed in these experiments strengthens the basis of the ion simulation technique as a tool for screening radiation damage effects in reactor materials. However, from a comparison of the ionbombardment-swelling results published to date, it is clear that considerable effort will be required to establish reliable quantitative simulation of reactor irradiations.

The present results on Type 304 stainless steel are in reasonable agreement with published ion-bombardment studies carried out on Type 316 stainless steel by Keefer et al using H_2^+ bombardments,[14] and by Kulcinski et al using Cu^+ ions.[12] There is an order of magnitude larger swelling in H_2^+ irradiations on the basis of the calculated number of displacements, compared with Ni^+ irradiations. Results of a comprehensive study of swelling in Type 316 stainless steel by Hudson and co-workers[15] indicate swelling magnitudes intermediate between the light and heavy ion irradiations up to intermediate dosages. The apparent reduction of swelling with increase in projectile mass might be due to recombination effects within the larger collision cascades. At higher dosages the data of Hudson et al shows clear evidence of a reduction in swelling rate above 40 displacements/atom. Saturation effects have also been observed in nickel irradiated 316 stainless steel.(16) Thus the absence of the decreased swelling rate in the H_2^+ irradiations is the most serious discrepancy in the ion swelling data obtained to date.

Our results of swelling, void size, and number density for the H_2 irradiations at 525°C taken from foils at depths greater than one-half the proton range agree very closely with the data of Keefer et al, whereas the 72% swelling observed at 600°C is consistent with the absence of saturation behavior. Significantly, foils taken closer to the bombarded surface showed fivefold less swelling, which suggest that the injected hydrogen affects the void growth. Further H_2^+ bombardments using a transmitted beam are required to determine the effect of hydrogen on swelling.

Although the energy of the ANL ion-bombardment system limits the range of self ions to ∿ 1 μm, simulation of bulk behavior appears to be satisfactory. Within the errors of depth determination in the irradiations at 517°C, no loss of defects at the 0.2 ∿ μm depth (1.6×10^{-3} displ/atom 1 sec) is apparent. Further the magnitude of the swelling is comparable to that obtained with 5 MeV Cu^{++} irradiation of Type 316 stainless steel, where the maximum damage occurs at a 50% greater depth than in the Ni^+ irradiation. We conclude that at high displacement rates where the recombination of Frenkel pairs is predominant, the average diffusion distance [on a similar basis to that estimated by Li et al(17)] is about 100 A, so that vacancy loss to the surface has a minor influence on the void formation kinetics. The unique advantage of the microampere Ni^+ beam capability is that it permits adequate sampling of the material in a single irradiation under condition where the displacement cascades are similar to a fast-neutron irradiation and where chemical contamination of the steel is avoided.

Some evidence may now be cited in support of the sequential nucleation and growth model for voids in H_2^+ bombarded stainless steel. In Types 304 and 316 stainless steel, both the minimum void size and the mean size increase with dosage at constant temperature and ion flux. Secondly, the coarse structure observed at 6 displacements/atom in the annealed helium preinjected samples again suggests the observed void number density is determined in the very early stages of the bombardment. Thirdly, since the number density can be normalized to a fixed dose rate after a finite dose where voids are resolvable in the microscope, the void number density corrected to a constant ion flux may be plotted versus dosage. Such a correlation shows a weak dependence of number density on dosage over the range 1 - 50 displacements per atom for both Types 304 and 316 stainless steel.

The average number density computed above was 3×10^{15} cm^{-3} for proton irradiated 304 stainless steel and corresponds to 10^{-3} displacements/atom/sec. This value is comparable to the void number density observed in selenium irradiated nickel,[15][18] but contrasts strongly with the results of C^{++} irradiated Type 316 stainless steels which shows a rapid increase in the number density with dosage to a maximum of 3×10^{16} cm^{-3} for 25 displacements/atom at 525°C. Number densities of this magnitude were observed only in our H_2^+ irradiation at 450°C. The number density observed at 500°C in Ni^+ irradiated of Type 304 stainless steel without helium was also approximately the same magnitude as the cited H_2^+ irradiation results. These comparisons lead us to believe that in the carbon ion irradiation experiments the high number density of voids may be associated with carbide precipitation.

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TABLE II

Results of Quantitative Metallography of Ni^+ Bombarded Type 304 Stainless Steel and a Cu^+ Bombarded Type 316 Stainless Steel[12]

Temp., °C	Displ. Rate, sec^{-1} 10^{-3}	Dosage, displ/atom	Void Diam, A	Void Density, $cm^{-3} \times 10^{-15}$	Swelling, %	Disl. Density, cm^{-2}
500	4	20	121 ± 44	2.0	0.2	6.9×10^{10}
517	1.6	33	270 ± 89	2.1	2.1	
	3.0	60	278 ± 78	2.	2.3	
600	9	120	342 ± 133	2.1	4.6	3.3×10^{10}
600	4.2	18	145 ± 82	0.55	0.1	5.6×10^{10}
500[a]	2.7×10^{-2}	40	180	6.0	7.8	

[a] Cu^+ bombardment.

TABLE I

Results of Quantitative Microscopy of Proton-Irradiated Type 304 Stainless Steel

Temp., °C	Displ. Rate, $sec^{-1} \times 10^4$	Dosage, displ/atom	Void Diam, A	Void Density, $cm^{-3} \times 10^{-15}$	Swelling, %	Disl. Density, cm^{-2}	Helium, ppm
450	3.2	16.6	102 ± 37	16	0.9		0
	4.7	24.5	127 ± 37	26	3.3		
525	1.4	6.6	174 ± 43	0.87	0.3	$2.8 \times 10^{15} cm^2$ 416A	0
	1.8	8	237 ± 65	2.4	1.8		
	2.2	10	185 ± 55	1.5	0.6		
	3.7	20	325 ± 111	2.5	4.8		
	5.0	30	230 ± 70	7.0	4.4	1.1×10^{15} 169A	
600	4	14	480 ± 180	0.22	1.3		0
	4.7	16	428 ± 168	0.34	1.4		
	10	35	671 ± 238	2.7	73		
620	2.1	6	471 ± 192	0.16	0.9		0
500	3.1	5.1	263 ± 85	0.3	0.3		10
600	3.5	6	939 ± 322	0.056	2.4		10

TABLE I

Results of Quantitative Microscopy of Proton-Irradiated Type 304 Stainless Steel

Rate, 10^4	Dosage, displ/atom	Void Diam, A	Void Density, $cm^{-3} \times 10^{-15}$	Swelling, %	Disl. Density, cm^{-2}	Helium, ppm
	16.6	102 ± 37	16	0.9		0
	24.5	127 ± 37	26	3.3		
	6.6	174 ± 43	0.87	0.3	$2.8 \times 10^{15} cm^2$ 416A	0
	8	237 ± 65	2.4	1.8		
	10	185 ± 55	1.5	0.6		
	20	325 ± 111	2.5	4.8		
	30	230 ± 70	7.0	4.4	1.1×10^{15} 169A	
	14	480 ± 180	0.22	1.3		0
	16	428 ± 168	0.34	1.4		
	35	671 ± 238	2.7	73		
	6	471 ± 192	0.16	0.9		0
	5.1	263 ± 85	0.3	0.3		10
	6	939 ± 322	0.056	2.4		10

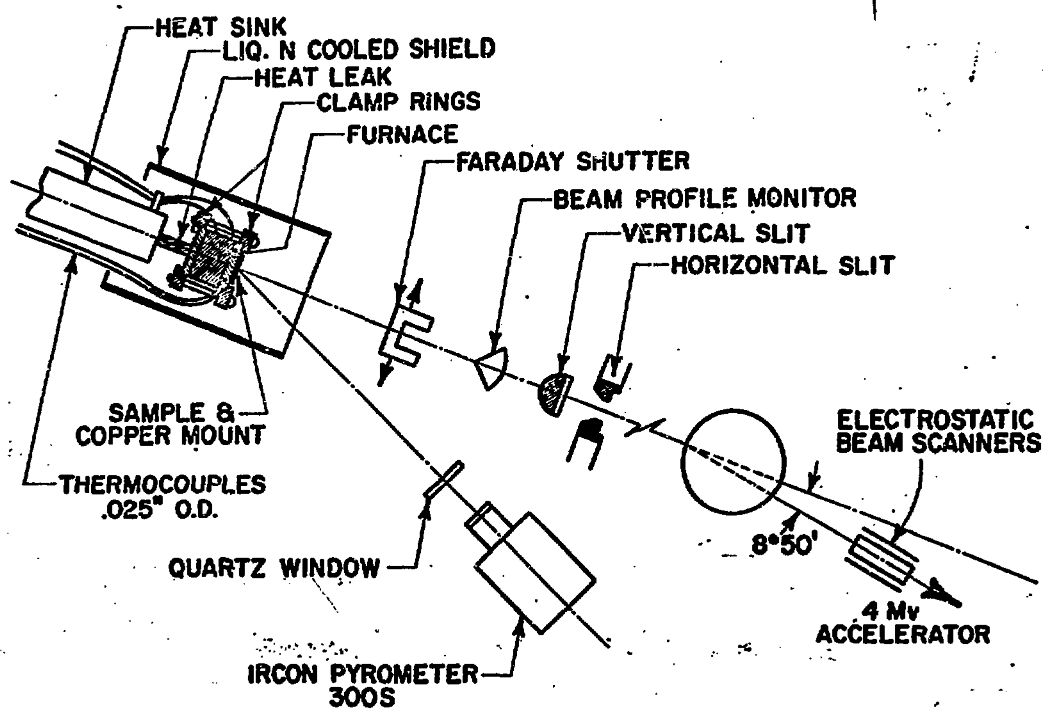

Fig. 1. Sample holder and beam-transport system used for ion bombardments.

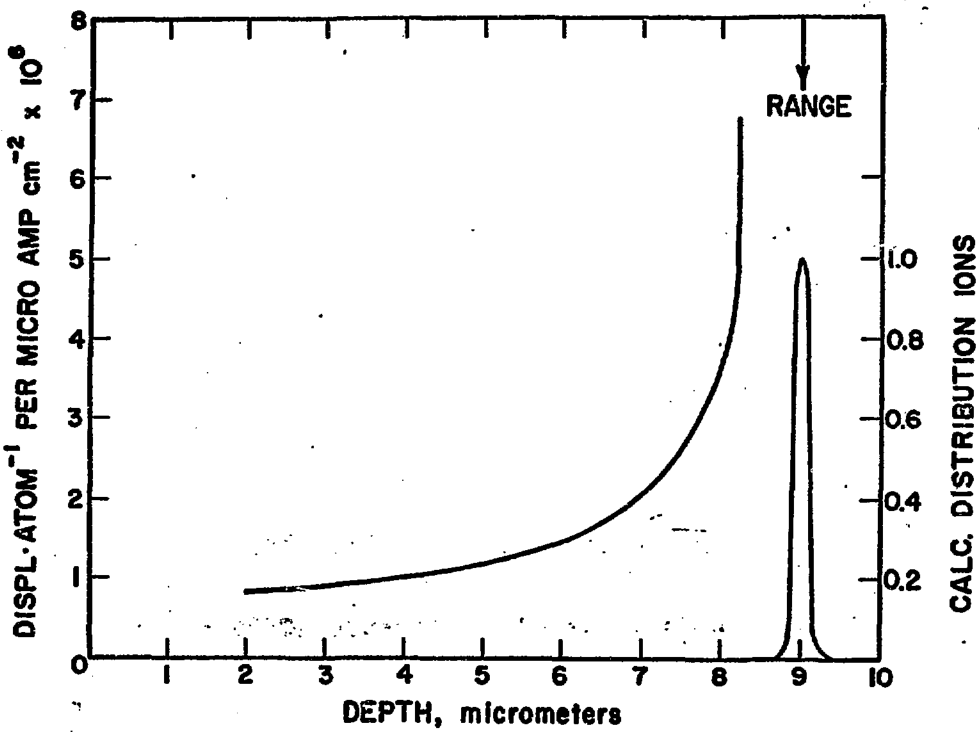

Fig. 2. Atomic displacement rate per unit current density versus depth from the bombarded surface for 1.25 MeV protons on a stainless steel target.

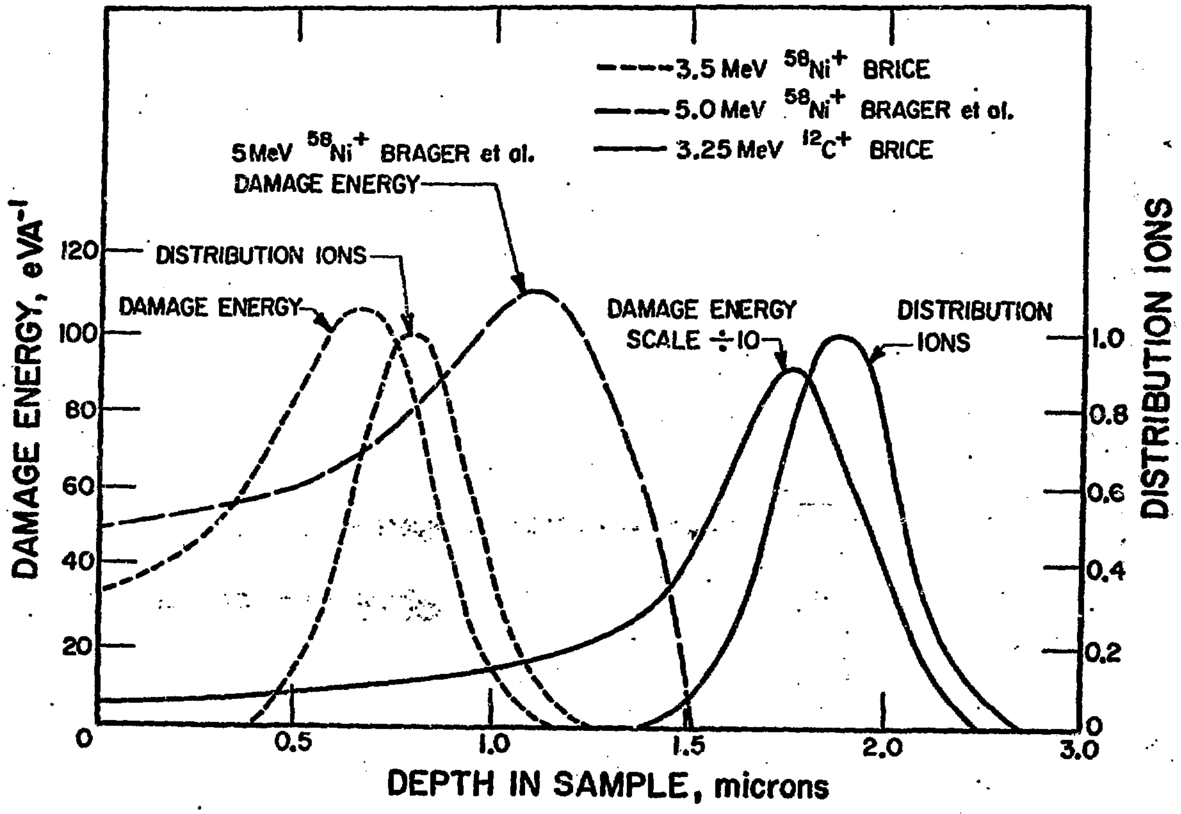

Fig. 3. Damage energy and distributions of stopped ions normalized to 1 for 3.5 and 5.0 MeV $^{58}Ni^+$ and 3.25 MeV $^{12}C^+$ on a stainless steel target.

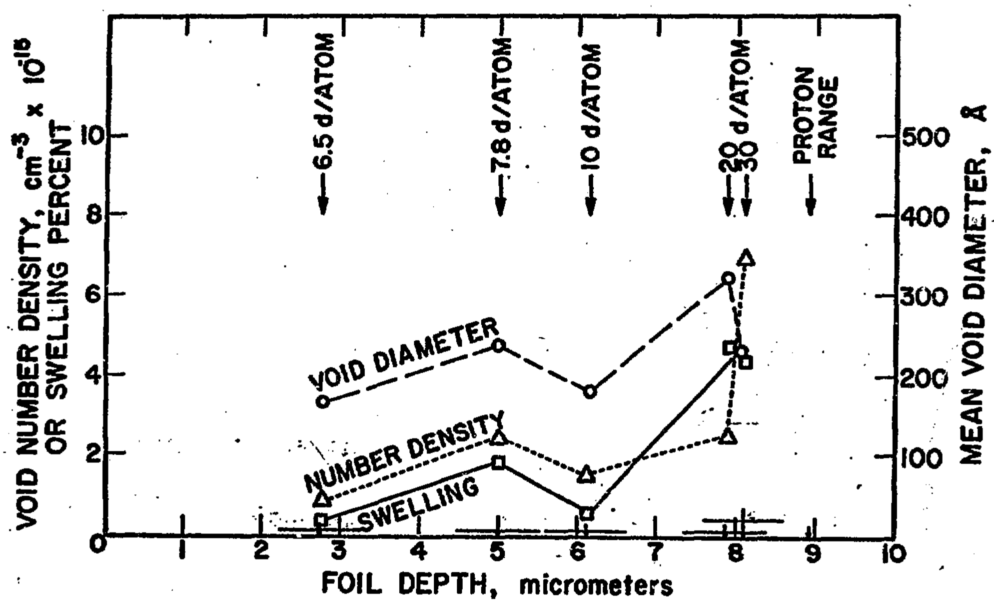

Fig. 4. Void number density, mean void diameter, and swelling for proton-irradiated Type 304 stainless steel.

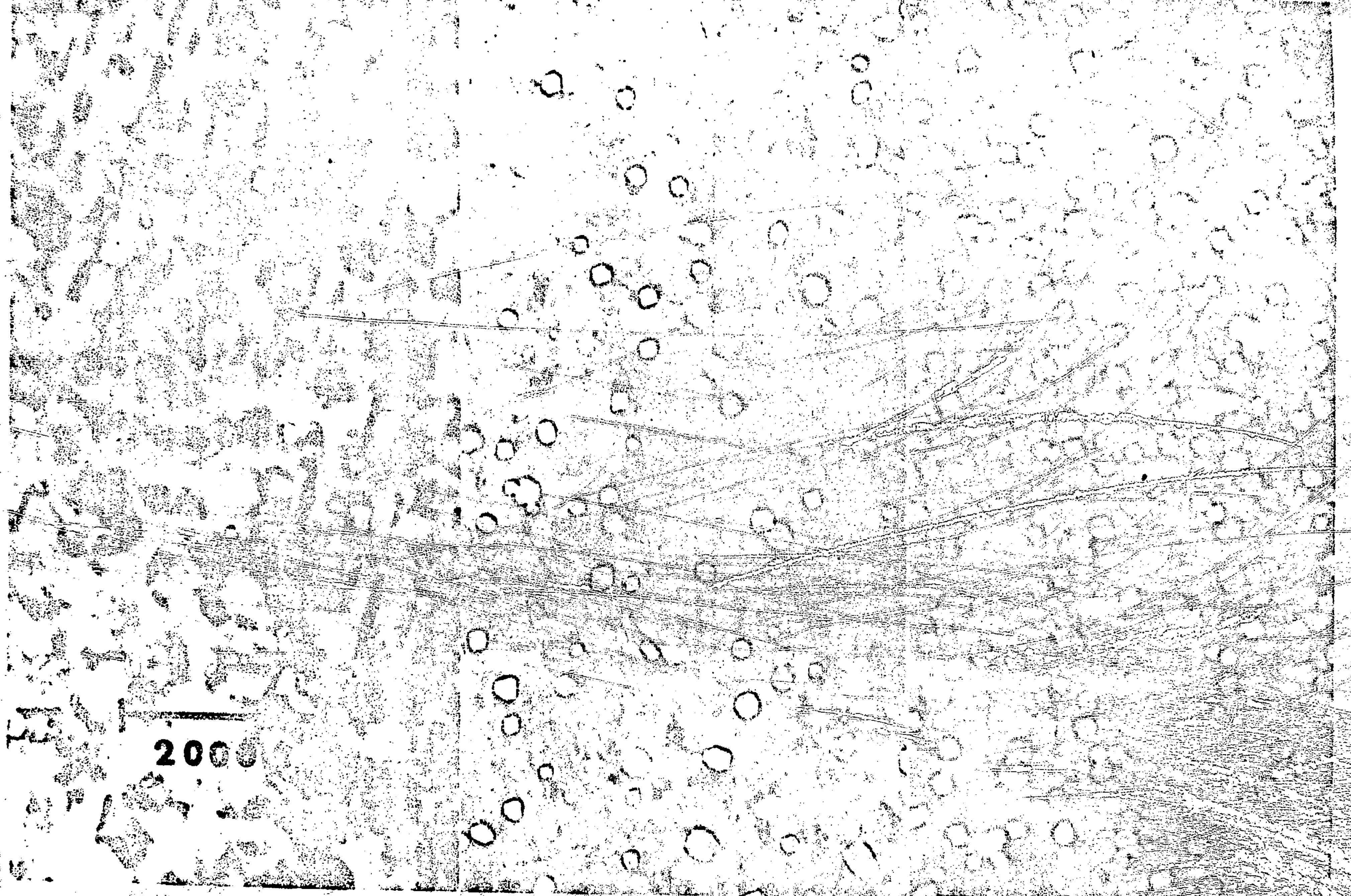

Fig. 5. Void Structures at 3.5, 5.2, and 8.2 μm corresponding to Fig. 4.

Fig. 1. Sample holder and beam-transport system used for ion bombardments.

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