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[8]B. Huberman (to be published) has recently suggested that it is the effective attraction between an interstitial cation and the vacancy it has left behind that is the basic interaction responsible for the phase transition. It is difficult to find physical justification for Huberman's argument.

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[12]Note that if the vibrational contribution to $S(\rho)$ is of the form $S(\rho)_{vib} = k_B \rho \ln g_{vib}$, where g_{vib} denotes a characteristic constant, it follows from Eq. (3) that the effective degeneracy factor appearing in our model will be just $g_{eff} = g_{vib} g$.

Particle Release from Niobium Irradiated with 14-MeV Neutrons*

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The particle release from cold-rolled niobium surfaces under 14-MeV–neutron impact to a total dose of 4.6×10^{15} neutrons/cm^2 was investigated under ultrahigh-vacuum conditions and at ambient temperature. The type and amount of material released and deposited on a substrate surface was determined independently by four analytical techniques. Surprisingly, there were two types of deposits—one in the form of large chunks, the other a more even layer covering the surface. The chunk emission cannot be explained by existing neutron-sputtering theories.

It has been suggested[1-3] that the bombardment of the first wall of fusion reactors by MeV neutrons may lead to both serious wall erosion and plasma contamination. Unfortunately, the experimental information available on particle release by MeV-neutron impact on solids is very scarce and contradictory (for reviews, see Refs. 1–3). For example, for monocrystalline gold irradiated with 14-MeV neutrons, the particle release yield $S = 3\times10^{-3}$ atom/neutron was reported.[4] However, for iron irradiated with neutrons of a softer energy spectrum (from a fission reactor), $S = (5.7\pm0.8)\times10^{-3}$ atom/neutron was reported.[5] A theoretical estimate of S for niobium irradiated with 14-MeV neutrons by one of us (M.K.) yielded $S \approx 6\times10^{-5}$ atom/neutron—a value which was approximately 2 orders of magnitude smaller than the above-mentioned experimental value for gold. More recently Behrisch[6] and Behrisch and Vernickel[7] estimated a yield value for 14-MeV–neutron–bombarded niobium that was only about a quarter of that of Kaminsky. On the basis of such an estimated value, these authors concluded that neutron sputtering would have a negligible effect on wall erosion and plasma contamination during the operation of a fusion reactor. In view of the great discrepancy between the theoretical estimates and the available experimental results, it seemed imperative to conduct new experiments under controlled conditions.

The present experiments were undertaken to provide information on the erosion of surfaces of cold-rolled polycrystalline niobium under 14-MeV–neutron impact in an ultrahigh-vacuum environment. The Lawrence Livermore Laboratory's rotating-target neutron source[8-10] was used in conjunction with an insulated-core–transformer accelerator. The total neutron emission rate over the entire 4π solid angle of a fresh neutron-source target was about 3×10^{12} neutrons/sec. The irradiation run was monitored with two proton-recoil detectors.[9,10] The drift in counting efficiency of each recoil detector is thought to be less than 5%.[11] The total dose was calibrated independently by activation analyses,[10] for example, by use of the reaction ^{93}Nb$(n, 2n)^{92}$Nb. The

absolute accuracy in the determination of the average dose the sample received was estimated to be ±7.5%. The targets were mounted in a train assembly containing 17 targets and were placed inside a vacuum chamber. The distance between the neutron-source disk and the front face of the first target, a monocrystalline Si(111) disk approximately 2.5 cm in diameter and 0.5 cm thick, was ~1.75 cm. A space of 0.28 cm separated this disk from the second target—a circular cold-rolled polycrystalline niobium foil with a diameter of approximately 2.5 cm and a thickness of 0.013 cm. The third target, again a monocrystalline Si(111) disk with dimensions similar to those of target No. 1, was spaced ~0.28 cm from the second target. The center of the neutron-source disk and the center of each of the three target disks were on the same axis.

The undoped, optical-grade monocrystalline Si(111) disks (obtained from the Materials Research Corporation) had a purity of 99.999%. They were first mechanically and then chemically polished and had a surface microfinish of ~0.03 μm. The cold-rolled polycrystalline niobium sample was obtained from Materials Research Corporation (Marz grade). It was mechanically polished and lightly electropolished[12] and had an average surface microfinish of ~5 μm (a coarse mirror finish with some scratch traces still present). The average grain size of the cold-rolled niobium was 3–10 μm. The target chamber was evacuated with sorption pumps and subsequently with a combination titanium-sublimation–ion pump. At the beginning of the neutron irradiation run, the pressure in the chamber was $\sim 1.5\times10^{-9}$ Torr, and it dropped to $\sim 4\times10^{-10}$ Torr towards the end of the ~54-h irradiation run. The total 14-MeV–neutron dose on the niobium foil was estimated from the total number of counts of the proton-recoil counters (with the appropriate corrections for the relative positions of source, counter, and target, for the effective neutron absorption length, and for the neutron flux peaking in the forward direction). The estimated dose was $\sim 4.6\times10^{15}$ neutrons/cm^2, and the average dose rate was $\sim 2.4\times10^{10}$ neutrons cm^{-2} sec^{-1}. During the irradiation the targets were at ambient temperature (estimated to be near room temperature). The irradiated targets were transported under ultrahigh-vacuum conditions ($\sim 1\times10^{-9}$ Torr) from Lawrence Livermore Laboratory to Argonne National Laboratory for analysis.

To determine the type and amount of the materials released from the surface of one sample (e.g., niobium target No. 2) and deposited on the surface of the one facing it [e.g., Si(111) target No. 1] the analytical techniques used were Rutherford backscattering (using a 750-keV $^4He^+$ ion beam from a 2-MeV Van de Graaff accelerator), Auger spectroscopy, ion-microprobe microanalysis (an Applied Research Laboratories ion microprobe), and scanning electron microscopy (a Cambridge Stereoscan Mark IIA) in conjunction with an energy-dispersive x-ray spectrometer. The amount of deposited material could be estimated quantitatively by using calibration standards prepared by vapor deposition. For the niobium deposits, the detection sensitivities [expressed as fractions of a monolayer (ML) of niobium deposited on silicon substrate] of three of the analytical techniques (in order of decreasing values) were, for Rutherford backscattering, ~0.0005 ML; for ion microprobe, ~0.001 ML; and for Auger spectroscopy, ~0.01 ML. The scanning electron microscope together with an energy-dispersive x-ray spectrometer was also used to identify the deposits. A metallograph was used for visual inspection of the irradiated targets. To test contamination buildup during the period of storage, unirradiated targets were kept in the ultrahigh-vacuum storage chamber. No significant contamination buildup could be detected.

An examination of the surface of Si(111) target No. 1 which faced the cold-rolled polycrystalline niobium target revealed the surprising result that the niobium deposits appeared in two forms. One form covered the substrate surface as a fractional atomic layer with an estimated "average" coverage degree of ~0.026 ML. The other form appeared as chunks of various irregular shapes as illustrated in Fig. 1. The optical micrograph in Fig. 1(a) shows some of the chunks. The secondary-ion ($^{93}Nb^+$) micrograph shown in Fig. 1(b) was obtained for the same area as in Fig. 1(a); it confirmed that the chunks were niobium. The larger fraction of the chunks (approximately $\frac{4}{5}$ of the total deposits) appears to be roughly spherical in shape [e.g., chunk No. 1 in Figs. 1(c) and 1(d)], while the smaller fraction (approximately $\frac{1}{5}$ of the total deposits) appears to be more cylindrical in shape [e.g., chunk No. 3 in Fig. 1(c)]. Some of the more cylindrically shaped chunks have their long axes nearly normal to the surface of the Si(111) substrate. Many of the chunks show microprotrusions in certain regions.

So far the size distribution of the chucks has

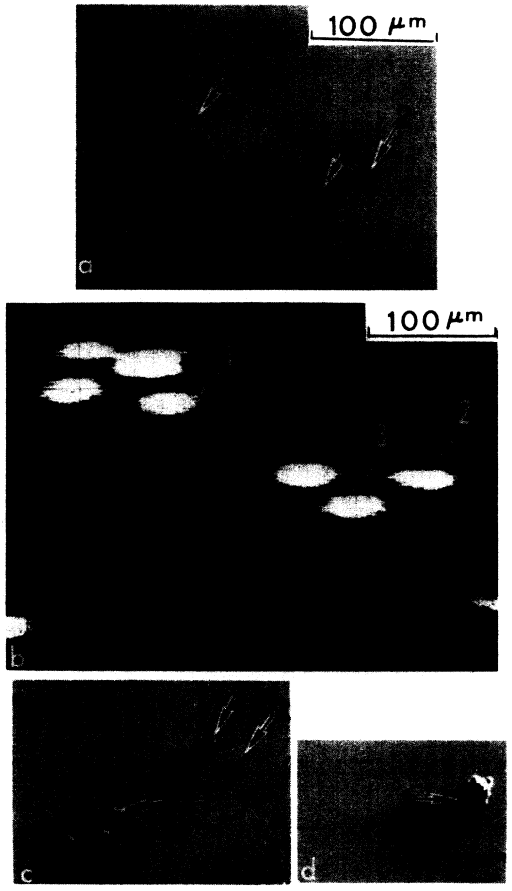

FIG. 1. Niobium deposited on a silicon (111) substrate when a niobium target at ambient temperature (estimated to be near room temperature) was irradiated with 14-MeV neutrons to a total dose of 4.6×10^{15} neutrons/cm^2. (a) Optical micrograph of niobium chunks deposited on a Si(111) surface. (b) Secondary-ion ($^{93}Nb^+$) micrograph of the same area as in (a). (c) Scanning electron micrograph (backscattered electron image) of the same area as in (a), showing the size and shape of the deposited chunks of Nb. (d) An enlarged view of a roughly spherical chunk, No. 1, shown in (c).

been only crudely estimated from the enlarged scanning electron micrographs. Since the chunks were irregular in shape, the "average" diameter of either a roughly spherical or a cylindrically shaped chunk was defined as the diameter of a circle whose area is equal to that of the projection of the chunk onto the surface plane. For the cylindrically shaped chunks, the "average" diameter ranged from about 0.5 to 5 μm, while the lengths of the cylinders ranged from about 3 to 15 μm. A majority of these chunks have a volume of $\sim4\times10^{-11}$ cm^3, which corresponds to $\sim2\times10^{12}$ atoms/chunk. The spherically shaped chunks had "average" diameters ranging from approximately 1 to 5 μm. A majority of these chunks have a volume of about 1×10^{-11} cm^3, which corresponds to about 5×10^{11} atoms/chunk. For both types of chunks, the distribution over the irradiated substrate surface area is nonuniform. The estimates given above are very crude and work is in progress to improve the accuracy of these estimates.

An investigation of the Si(111) surface of target No. 3 which faced the backside of the polycrystalline niobium target No. 2 revealed niobium chunk deposits similar to those reported above for target No. 1. The surface of Si(111) target No. 1 which faced the stainless steel flange revealed chunk deposits of stainless steel. The surface of cold-rolled polycrystalline niobium which faced the Si(111) target No. 1 revealed chunk deposits of silicon.

By ion milling the chunks to about $\frac{1}{10}$ of the original size by using the ion microprobe with 20-keV O^- ions, it was determined that the chunks consisted of niobium and that they did not contain contaminants to any significant degree. The binding of the niobium chunks to the Si(111) substrate appeared to be rather strong since the chunks could not be readily scrapped off mechanically, or burned off by the high flux (~3 mA/cm^2) of 20-keV oxygen ions. In a second irradiation run the cold-rolled niobium foil was replaced by an annealed one. A preliminary examination of the deposits revealed again niobium chunks but their number was smaller than observed for the cold-rolled foil.

A crude estimate based on the assumption that the niobium deposits were smeared out evenly over the Si(111) substrate No. 1 yielded an equivalent surface-coverage degree of 0.86 ML for all types of niobium deposits. For Si(111) target No. 3 the average surface-coverage degree of the niobium deposit was found to be $\sim20\%$ higher than the value quoted above for target No. 1. For the cold-rolled polycrystalline niobium sample, the fractional "atomic" layer deposit alone gives a yield value of $S=(8.7\pm3.0)\times10^{-3}$ niobium atom per neutron. Considering both the chunk and the atomic layer deposits, a total yield $S=0.25\pm0.10$ niobium atom per neutron is obtained.

On the basis of the two types of deposits observed, the authors speculate that target particle emission via momentum transfer from collision cascades will contribute only partially to the fractional atomic layer deposit but will not con-

tribute significantly to the chunk deposits. The mechanism for the emission of chunks is not clearly understood. A possible mechanism for the ejection of chunks could be related to the energy deposited by a 14-MeV neutron interacting with niobium lattice atoms in the near-surface region via elastic and inelastic collisions. (The calculated mean and maximum energies for primary knock-on niobium atoms are 181 and 600 keV, respectively.[1]) This deposited energy can lead to localized thermal and ionization (electron) spikes which in turn may cause the generation of shock waves. The interference of such shock waves in a small volume in the near-surface region in which the stored energy is very high (as a result of cold working) may set up stresses large enough to release energy by initiating submicroscopic cracks or by propagating already existing microcracks and cause the emission of chunks. However, one cannot exclude the possibility that other mechanisms may contribute to or dominate the chunk-ejection process.

The yield $S = 0.25 \pm 0.1$ niobium atom/neutron obtained for cold-rolled polycrystalline niobium with a surface finish of only ~ 5 μm at near room temperature leads to an annual erosion rate of 0.6 ± 0.3 mm/yr for a neutron flux of 4×10^{14} neutrons cm^{-2} sec^{-1}. If the erosion rates for a fusion reactor wall at operating temperature are similar to those obtained here, then erosion by neutron impact cannot be neglected, contrary to the conclusion by others.[6,7]

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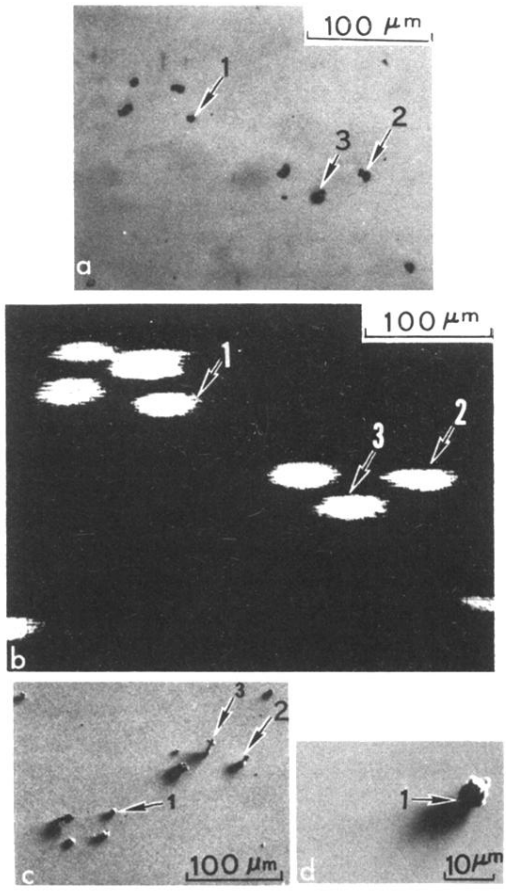

FIG. 1. Niobium deposited on a silicon (111) substrate when a niobium target at ambient temperature (estimated to be near room temperature) was irradiated with 14-MeV neutrons to a total dose of 4.6×10^{15} neutrons/cm^2. (a) Optical micrograph of niobium chunks deposited on a Si(111) surface. (b) Secondary-ion ($^{93}Nb^+$) micrograph of the same area as in (a). (c) Scanning electron micrograph (backscattered electron image) of the same area as in (a), showing the size and shape of the deposited chunks of Nb. (d) An enlarged view of a roughly spherical chunk, No. 1, shown in (c).