

S. J. ZINKLE* AND J. S. HUANG**

*Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6376

**Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550

CONF-900466--8

ABSTRACT

DE90 009864

Polycrystalline niobium specimens were implanted with either 200 keV carbon ions or a combination of 50, 100, and 200 keV carbon ions to peak concentrations of 0.6 to 50 at. %. Microindentation techniques were used to measure the hardness and elastic modulus of the implanted layer. Both the hardness (H) and modulus (E) showed dramatic increases due to the carbon implantation. The measured peak hardness and modulus following uniform implantation with 16 at. % C were 15 \times and 3 \times that of niobium, respectively, which is comparable to the literature values for NbC. The peak hardness and modulus for the implanted specimens were observed at an indent depth of \sim 40 nm, which is about one-eighth of the depth of the implanted carbon layer. The decrease in the indentation mechanical properties at deeper indent depths is due to the interaction of long-ranging strain fields underneath the indenter with the niobium substrate.

INTRODUCTION

Ion implantation is a useful technique to modify the near-surface properties of metals. Previous studies have shown that implantation of ions such as C⁺ and N⁺ into metals such as Ni, Fe, Ti, and steel can increase the near-surface hardness by 100% or more under certain conditions [1-4]. In a recent microstructural study on carbon-implanted niobium [5], no evidence was found for the formation of a second phase for implanted carbon concentrations up to 16 at. % despite the fact that the equilibrium solubility of carbon in niobium is \ll 1% at room temperature. It was concluded that the carbon implantation created a metastable solid solution of Nb and C, with the implanted carbon atoms residing in interstices. A further study on a niobium specimen implanted with 50 at. % C revealed the presence of a subsurface fcc NbC layer [6]. The present study uses indentation techniques to measure the hardness and elastic modulus of these carbon-implanted specimens.

EXPERIMENTAL DETAILS

Polycrystalline niobium (99.9 wt % purity) with a carbon content $<$ 30 ppm was annealed at 1473 K for 1 h and mechanically polished to a finish of 0.1 μ m prior to carbon implantation. The mean grain size of the as-annealed material was 40 μ m. The specimens were implanted with sequential beams of 200, 100, and 50 keV C⁺ ions at a fluence ratio 4.5:2:1 at ambient temperature ($<$ 150°C) in order to produce a uniform carbon distribution over the depth range of 0.05 to 0.30 μ m from the surface. Samples with 0.6, 1.9, 5.8, and 16 at. % C were prepared [5]. In addition, one sample was implanted with 200 keV C⁺ ions alone to produce a peak carbon concentration of 50 at. % at a depth of 0.26 μ m [6]. Cross-sectional transmission electron microscope (TEM) observations found evidence of the carbon implantation extended to a depth of 375 nm in all cases [5,6]. The Nb-50 at. % C specimen contained a layer of fcc NbC at depths of 0.19 to 0.32 μ m.

JMH

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

The submitted manuscript has been
 authored by a contractor of the U.S.
 Government under contract No. DE-
 AC06-84OR21400. Accordingly, the U.S.
 Government retains a nonexclusive,
 royalty-free license to publish or reproduce
 the published form of this contribution, or
 allow others to do so, for U.S. Government
 purposes.

MASTER

Indentation techniques have been used for a number of years to investigate the hardness and elastic modulus of thin films [7-11]. In these experiments, the elastic modulus is typically obtained from an analysis of the unloading segment of a continuously monitored load vs. displacement curve [8-11]. The present study utilized the differential mode [11] of a Nanoindenter hardness tester, where a small 60 Hz ac current was superimposed on the dc indenter loading current, thereby allowing both the hardness and the modulus to be continuously determined. The indenter speed was 10 nm/s and the maximum depth of indentation was 1 μm . A minimum of 12 indentations were performed on each specimen with the results averaged over 2 nm- or 10-nm increments in depth. The indentation data for the Nb samples containing 1.9 and 5.8 at. % C showed a large amount of scatter at indenter depths <100 nm and the data are therefore not considered to be reliable.

RESULTS

The depth-dependent hardness of some of the carbon-implanted niobium specimens is shown in Fig. 1. In all cases, the maximum hardness ratio was observed at an indent depth of ~40 nm. As discussed later, the shallow indent depth for the peak hardness (40 nm) relative to the depth of the ion-implanted layer (~300 nm) is due to the interaction of the long-ranging stress fields underneath the indenter with the substrate. It is clear from Fig. 1 that the hardness of niobium is dramatically increased following carbon implantation. The hardness data for Nb-1.9 at. % C is shown as a dashed line for indent depths below 100 nm to reflect the uncertainty in the shallow-depth data for this specimen.

The results in Fig. 1 are plotted as the ratio of the C-implanted specimen hardness to that of pure Nb in order to minimize any possible systematic error in the measured hardness due to uncertainties in the details of the shape of the indenter, strain rate effects, etc. The hardness of the Nb specimen measured at a depth of 1 μm was 1.1 GPa, which agrees with the tabulated Vickers hardness number of annealed Nb [12]. The measured hardness of the Nb specimen increased with decreasing indent depth (as is typical in annealed metals), reaching a value of 3.3 GPa at an indent depth of 50 nm.

Figure 2 compares the depth-dependent hardness ratios of niobium implanted with 16 and 50 at. % C. Both curves show a dramatic hardness increase (~12 to 15 times that of Nb) at shallow indent depths due to the carbon implantation. Three subtle differences between the curves are apparent. The peak hardness is higher and occurs at a shallower indent depth (35 to 40 nm vs 45 nm) for Nb-16% C, whereas the rate of hardness

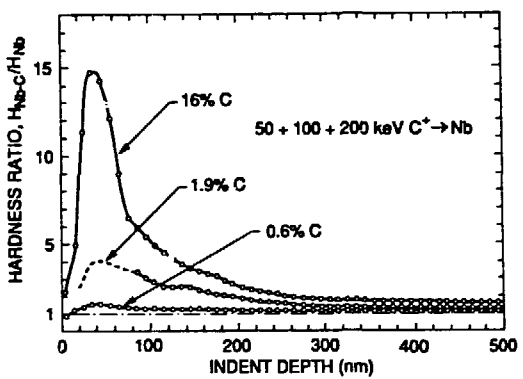


Fig. 1. Depth dependent indentation hardness of C-implanted niobium.

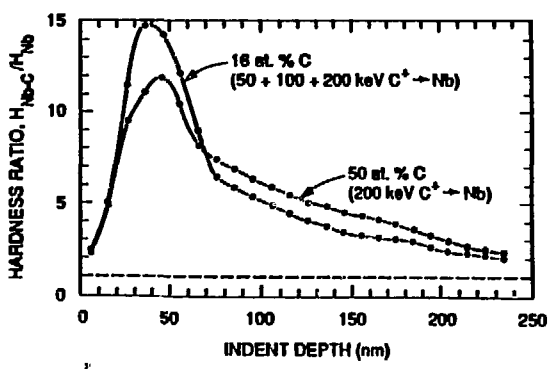


Fig. 2. Comparison of hardness profiles for Nb implanted with 16 and 50 at. % C.

decrease from the peak value is less rapid for Nb-50% C. This leads to higher hardness values for Nb-50% C relative to Nb-16% C at indent depths >70 nm. As discussed later, these small differences in the shape of the indentation hardness curves may be attributed to differences in the implanted ion profiles (200 keV C^+ vs 50 + 100 + 200 keV C^+). Note that even for a uniform implanted C layer width of 250 nm (Nb-16% C), the measured hardness is not constant over any 10-nm increment in indent depth.

The depth-dependent elastic modulus of the Nb-50% C specimen is shown in Fig. 3. The peak modulus occurred at an indent depth of ~ 35 nm. The modulus decreased rapidly with increasing indent depth between 40 and ~ 170 nm, whereupon the modulus became constant with a value comparable to that of the pure niobium specimen. The measured elastic modulus of unimplanted niobium was independent of indent depth, with a value of ~ 92 GPa. This result is in reasonable agreement with the literature value for niobium of $E = 105$ GPa [12].

Figure 4 compares the depth-dependent elastic modulus ratios for the carbon-implanted niobium specimens. The peak modulus for all of the specimens occurred at an indent depth of ~ 35 nm, which is consistent with the observed hardness peaks (Figs. 1 and 2). The highest measured peak modulus was obtained with Nb-16% C. For indent depths >40 nm, the measured modulus for the Nb-50% C specimen decreased more slowly than Nb-16% C. This produced a higher modulus for Nb-50% C at deeper indent depths (>50 nm) compared to Nb-16% C, in general agreement with the observed hardness behavior (Fig. 2). The elastic modulus of all implanted specimens became comparable with that of Nb for indent depths >170 nm.

Figure 5 shows the dependence of the maximum hardness and elastic modulus ratio on implanted carbon concentration. It should be emphasized that since the implanted region for the 50 at. % C specimen was not uniform over an extended depth, the actual hardness and modulus of the implanted layer may be higher than the measured value due to interference effects from the Nb substrate and surface layers. Also the results for the 1.9% C and 5.8% C specimens have considerable uncertainty. All plotted values may be taken to be a lower bound of the actual mechanical properties of the implanted layer, since some contribution from nonimplanted regions may have occurred.

It is useful to compare the hardness and modulus of the implanted specimens with the corresponding values for NbC. Using the measured "bulk" hardness for Nb of 1.1 GPa and the peak hardness ratio for Nb-16% C of 15, the estimated hardness of the C-implanted layer is 16 GPa. This may be compared with the measured bulk Vickers hardness of NbC, $H = 24$ GPa [12,13]. The measured peak elastic modulus associated with the C-implanted layer in Nb-16% C was 300 GPa. The elastic modulus of NbC is

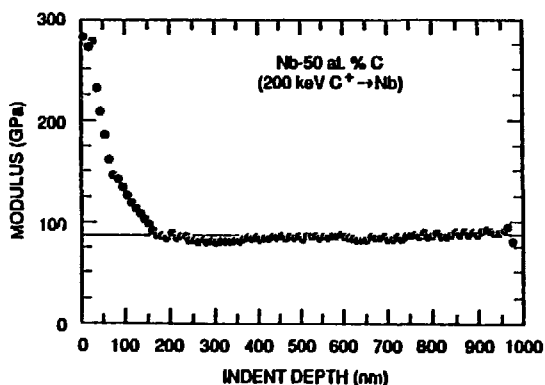


Fig. 3. Depth-dependent elastic modulus for Nb-50 at. % C.

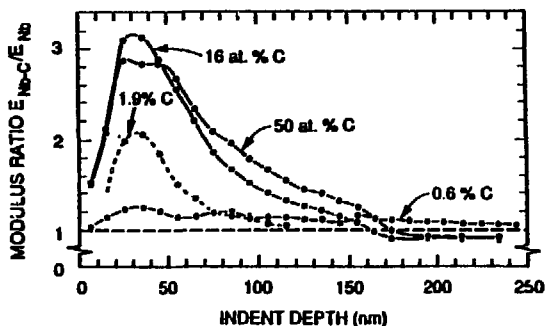


Fig. 4. Depth dependent elastic modulus for C-implanted Nb.

340 GPa [12,13]. Since second-phase formation was not found in a microstructural examination of the specimens implanted with up to 16 at. % C, it appears that the strain associated with nonequilibrium accommodation of excess carbon is responsible for increasing the hardness and modulus of the implanted layer to values approaching that of NbC. The hardness and modulus results for Nb-50% C, where a subsurface NbC layer was identified, were less than the values for bulk NbC. This may be attributed to contributions from the neighboring Nb regions. Alternatively, it is possible that the metastable Nb-16 at. % C phase has a higher hardness and modulus than NbC.

DISCUSSION

Implantation of carbon into niobium caused a dramatic increase in both the hardness and elastic modulus. The magnitudes of the changes are among the largest reported for ion implanted materials, and clearly shows that implanted carbon is very effective in modifying the near-surface mechanical properties of niobium. For comparison, a hardness increase of ~250% was observed following 83 keV C⁺ implantation into Ti to a peak concentration of 36 at. % C [14]. This may be contrasted with the present finding of a hardness increase for Nb of ~1400% following uniform implantation of 16 at. % C with 50 to 200 keV C⁺ ions.

It is well known that hardness measurements are sensitive to the properties of layers underneath the indenter lying within 10 times the indent depth. Samuels and Mulhearn [15] experimentally verified that the boundary between plastic and elastic deformation associated with a Vickers or Brinell standard indentation of brass is roughly hemispherical with a radius equal to ~12 to 15 times the indent depth. It immediately follows that it is difficult to measure the true mechanical properties of an implanted surface layer by indentation methods unless the layer is uniform over an extended range on the order of 10 to 15 times the indent depth. Figure 6 shows in schematic form the indentation of niobium containing a uniform implanted carbon layer near the surface. The 1% plastic deformation and elastic-plastic ($\leq 0.05\%$) boundaries as determined by Samuels and Mulhearn [15] are shown for an indent depth of 50 nm. It can be seen that both the 1% and the elastic-plastic boundaries for this indent depth exceed the uniform implanted

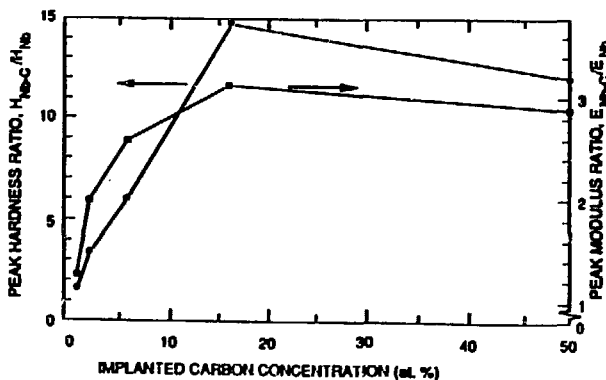


Fig. 5. Mechanical properties of C-implanted niobium at an indent depth of ~40 nm.

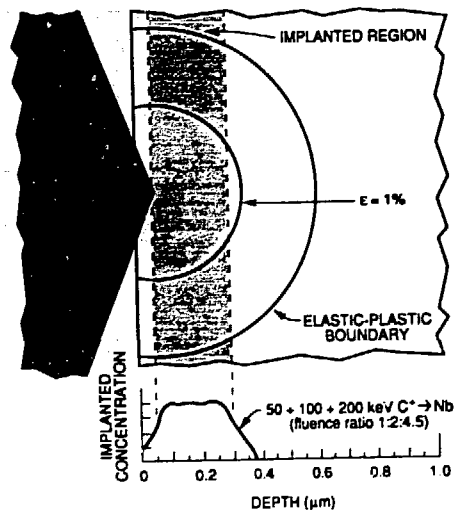


Fig. 6. Schematic of strain fields present during indentation of an ion-implanted surface layer.

carbon depth of $\sim 0.3 \mu\text{m}$. From this simple picture, it is apparent that an indent depth $< 50 \text{ nm}$ is required to obtain a reasonable measurement of the hardness of a uniform implanted layer $0.3 \mu\text{m}$ wide.

Based on the preceding discussion, we are now in a position to understand the slight differences between the indentation results for Nb-16% C and Nb-50% C (Figs. 2 and 4). Due to the absence in the Nb-50% C specimen of carbon atoms implanted at 50 and 100 keV, the concentration of implanted carbon is less than that of Nb-16% C within 100 nm of the surface. Since the measured hardness is most sensitive to the material properties closest to the indenter, this produces a softer near-surface region for the Nb-50% C specimen and hence lower hardness and elastic modulus. The opposite is true at deeper indent depths: The Nb-50% C specimen had 3 times higher fluence of 200 keV C^+ ions than Nb-16% C, which produced a higher (although nonuniform) carbon concentration in Nb-50% C at depths $> 100 \text{ nm}$ from the surface. As the indent depth approaches and exceeds 100 nm, these layers have a larger contribution to the measured hardness and modulus and cause the measured properties of Nb-50% C to be larger than those for Nb-16% C. The peak in the measured hardness and modulus occurs at deeper indent depths for Nb-50% C since the center of its carbon-implanted zone ($0.26 \mu\text{m}$ depth) is deeper than that for Nb-16% C ($0.17 \mu\text{m}$ depth).

In the present study, the hardness and elastic modulus of the uniformly implanted specimens decreased from the maximum values for indent depths $> 35 \text{ nm}$. In other words, the indentation results began to be affected by the substrate properties when the ratio of the carbon-implanted layer thickness to indent depth became less than $300/35 = 8.5$. In an earlier study on ion-irradiated copper [16], the corresponding critical ratio of layer thickness to indent depth was determined to be ~ 5 . In the copper study, the hardness increase in the irradiated layer was only $\sim 70\%$ higher than that of the unimplanted substrate. Theoretical stress-strain considerations suggest that the relative indent depth (normalized to implanted layer thickness), where substrate effects become noticeable, should depend on the hardness and elastic modulus of the two layers. This relationship between film hardness and the ratio of film thickness to indentation depth has been previously noted [17] and may be summarized as follows: Hard surface films become sensitive to substrate effects at shallower indent depths compared to films of moderate hardness.

In summary, to obtain a true measure of the mechanical properties of a surface-modified layer, the extent of the uniformly implanted layer should be > 10 times the indentation depth. Accurate measurements of the film properties may be obtained for smaller ratios of layer thickness to indent depth only if the mechanical properties of the film and substrate are comparable.

CONCLUSIONS

Carbon ion implantation is very effective in increasing the hardness and elastic modulus of niobium. Implantation with 16% C increased the hardness and modulus by factors of ~ 15 and 3.2, respectively, relative to that of niobium. Since there was no microstructural evidence for the formation of a second phase in this specimen, the change in mechanical properties is probably due to interstitial hardening by the implanted carbon. The peak hardness and modulus values determined for Nb-50 at. % C, where NbC was formed over a limited depth range, were comparable to that of Nb-16 at. % C. Absolute measurement of the hardness and modulus of the implanted layers by indentation techniques was hampered by the shallow implant depth. In order to avoid contributions

from the substrate during mechanical property measurements, the indent depth should be less than one-tenth the thickness of the implanted layer.

ACKNOWLEDGMENTS

The ion implantations were performed by R. Patterson. Work performed under the auspices of the U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. and contract W-7405-eng-48 with Lawrence Livermore National Laboratory.

REFERENCES

1. H. Herman, *Nucl. Instr. Methods* **182/183**, 887 (1981).
2. J. B. Pethica, R. Hutchings, and W. C. Oliver, *Nucl. Instr. Methods* **209/210**, 995 (1983).
3. W. C. Oliver et al., *Mat. Res. Soc. Sym. Proc.*, vol. 27, Eds. G. K. Hubler et al. (Elsevier Science Pub. Co., 1984), p. 603.
4. M. Nastasi et al., *J. Mater. Res.* **3**, 226 (1988).
5. J. S. Huang, R. G. Musket, and M. A. Wall, *Mat. Res. Soc. Sym. Proc.*, Vol. 128, Eds. L. E. Rehn et al. (MRS, Pittsburgh, 1989), p. 327.
6. J. S. Huang, *Met. Res. Soc. Sym. Proc., Beam-Solid Interactions: Physical Phenomena* (MRS, Pittsburgh, 1990); also UCRL-102036 (Oct. 30, 1989).
7. E. Pitts, *J. Phys. D: Appl. Phys.* **3**, 1803 (1970).
8. M. Kh. Shorshorov, S. I. Bulychev, and V. P. Alekhin, *Sov. Phys. Doklady* **26**, 769 (1981).
9. M. F. Doerner and W. D. Nix, *J. Mater. Res.* **1**, 601 (1986).
10. W. C. Oliver, C. J. McHargue, and S. J. Zinkle, *Thin Solid Films* **153**, 185 (1987).
11. J. B. Pethica and W. C. Oliver, *Mat. Res. Soc. Sym. Proc.*, Vol. 130, Eds. J. C. Bravman et al. (MRS, Pittsburgh, 1989), p. 13.
12. *Metals Reference Book*, 5th ed., Ed. C. J. Smithells (Butterworths, Boston, 1976).
13. *Engineering Property Data of Selected Ceramics*, Vol. 2, Carbides, Battelle Columbus Lab. Metals and Ceramics Information Center Report MCIC-HB-07 (August 1979).
14. W. C. Oliver et al., *Mat. Res. Soc. Sym. Proc.*, Vol. 127, Eds. G. K. Hubler et al. (Elsevier Science Pub. Co., 1984), p. 705.
15. L. E. Samuels and T. O. Mulhearn, *J. Mech. Phys. Solids* **5**, 125 (1957).
16. S. J. Zinkle and W. C. Oliver, Oak Ridge National Laboratory Report ORNL/TM-10126 (1986).
17. J.-E. Sundgren and H.T.G. Hentzell, *Vac. Sci. Technol. A*, **4**, 2259 (1986).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.