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EFFECT OF FAST NEUTRON IRRADIATION ON THE RECOVERY AND RECRYSTALLIZATION OF NIOBIUM *

H.L. FOTEDAR ** and W.A. MONTEIRO
Instituto de Energia Atômica (CCTM), Cx. Postal 11.049, Pinheiros, São Paulo, SP, Brazil

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Effect of fast neutron irradiation ($E > 0.1$ MeV) on the recovery and recrystallization of high purity niobium has been studied, utilising transmission electron microscopy and isochronal microhardness measruements, in the temperature range 25–1200°C for 1 h. The sigmoidal recovery curves show an initial increase in microhardness in the temperature range 25–300°C, which is related to the migration of interstitial impurity atoms O, C and N to dislocations and defect agglomerates produced by cold work and irradiation. Recrystallization in cold worked niobium proceeds by subgrain growth (controlled by subgrain coalescence) and strain induced grain boundary migration. Fast neutron irradiation to a fluence of $\phi = 1.3 \times 10^{18}$ nvt facilitates the formation of recrystallization nuclei by subgrain coalescence and thus accelerates the initial nucleation process in cold worked and irradiated specimens by about 150°C.

L'effet de l'irradiation par les neutrons rapides ($E > 0,1$ MeV) sur la restauration et la recristallisation du niobium de haute pureté a été étudié en utilisant la microscopie électronique par transmission et des mesures isochrones de microdureté dans l'intervalle de températures de 25 à 1200°C pendant 1 h. Les courbes de restauration sigmoïdes montrent un accroissement initial de microdureté dans le domaine de températures 25–300°C, qui est à relier à la migration des atomes interstitiels d'impuretés O, C et N vers les dislocations et les agglomérats de défauts produits par écrouissage à froid et irradiation. La recristallisation dans le niobium écroui procède par croissance des sous-grains (contrôlée par la coalescence des sous-grains) et la migration des contours de grains induite par la déformation. L'irradiation par les neutrons rapides à une fluence de $\phi = 1,3 \times 10^{18}$ nvt facilite la formation de germes de recristallisation par coalescence des sous-grains et ainsi accélère le processus de germination initiale dans les échantillons écrouis et irradiés à environ 150°C.

Der Einfluss der Bestrahlung mit schnellen Neutronen ($E > 0,1$ MeV) auf die Erholung und Rekristallisation von hoch reinem Niob wurde transmissionselektronenmikroskopisch und durch isochrone Mikrohärtemessungen nach jeweils 1 h zwischen 25 und 1200°C untersucht. Die sigmoidalen Erholungskurven zeigen zu Beginn zwischen 25 und 300°C eine Mikrohärtezunahme, die in Beziehung steht mit der Wanderung der Zwischengitterverunreinigungsatome O, C und N zu Versetzungen und Defektagglomeraten, welche durch Kaltverformung und Bestrahlung gebildet werden. Die Rekristallisation in kaltverformtem Niob erfolgt durch Subkornwachstum (durch Subkornvereinigung kontrolliert) und durch dehnungsinduzierte Korngrenzenwanderung. Die Neutronenbestrahlung bis zu einer schnellen Dosis von $1,3 \cdot 10^{18}$ n/cm^2 ermöglicht die Bildung von Rekristallisationskeimen durch Subkornvereinigung und beschleunigt somit in kaltverformten und bestrahlten Proben bei 150°C den beginnenden Keimbildungsprozess.

1. Introduction

In order to obtain a better understanding of structure mechanical property relationship, many BCC metals [1], in recent years, have been extensively studied for their as-deformed and high temperature recovered structure as well as for structural changes produced by high flux neutron and heavy ion irradiations. For use in atomic power reactors, this type of material characterization becomes very important, since nuclear irradiation produces irradiation damage along with transmutation products which can significantly alter the microstructure thereby severely effecting high temperature mechanical properties of

* Research partially supported by FAPESP and Comissão Nacional de Energia Nuclear.
** LATF Fellow, Tufts University, Medford Mass. USA.

nuclear structural materials. Niobium has long been considered as an important high temperature nuclear structural metal for both fission as well as fusion reactor applications [2,3]. In Controlled Thermonuclear Reactor (CTR) applications, niobium as a first wall material can be subjected to high temperatures (up to 1000°C) and high neutron fluences (up to 10^{23} nvt) under complex stress conditions. Any combination of these will result in appreciable microstructural changes of the CTR first wall, effecting thereby its dimensional stability as well as its other mechanical and physical properties.

Although to date many studies have been performed on the recovery of various types of fast particle irradiation damage on the physical, electrical and mechanical properties of FCC and BCC metals and alloys [4–20], yet at present few investigations are available that study in detail fast neutron irradiation effects on the microstructural related properties such as recovery and recrystallization in BCC metals in general and in niobium in particular.

In this paper we will present results detailing the recovery and recrystallization processes in pure niobium (VP grade) and the effect of fast neutron irradiation ($E > 0.1$ MeV) on these, utilising isochronal microhardness measurements and Transmission Electron Microscopy.

2. Experimental

High purity niobium rods (VP grade) were acquired from Materials Research Corporation. These had the following interstitial impurity content as detected by emission spectrografic analysis: C = 25 ppm; O = 50 ppm; N = 15 ppm.

The 1/4″ niobium rods were cold rolled to 95% in area, to a thickness of 250 μm. From these, specimens, with cross-sectional area 0.015 × 0.015 m^2 were cut and divided into two batches, selecting two samples for each treatment, one for electron microscopy work and the other for microhardness measurements: Batch (a) was isochronally annealed in the temperature range 100–1200°C for one hour in a dynamic vacuum of better than 10^{-7} torr, using direct resistance heating. Batch (b) was irradiated at a fast neutron flux of 7.7 × 10^{12} n/cm^2/s utilising position 35a, shelf 5 to a total fluence of 1.3 × 10^{18} nvt in the IEAR-1 swimming pool reactor at energies higher than 0.1 MeV. Specimens for irradiation were first thoroughly cleaned in boiling acetone, dried and then wrapped in 50 μm thick aluminium foil and finally enclosed in a 500 μm cadmium capsule to block thermal neutrons. For irradiation these capsules were placed within a special irradiation device [21] consisting of two concentric aluminium tubes hermetically sealed at the top with entry for a chromel-alumel thermocouple to monitor any increase in the specimen temperature due to gamma heating. This was found to be around 140°C in the present case.

The onset of recovery and recrystallization was monitored by the measurement of microhardness using a 100 g weight in a Vicker microhardness tester. Prior to hardness testing specimen were first mechanically polished to ensure a planar surface, followed by electrolytic polishing using the following conditions:

Electrolyte: solution of 9 : 1 H_2SO_4 (95%) and 1 HF (48%) by volume
Cathode: platinum
Temperature: 0°C
Voltage: 14 volt

The microstructural changes were monitored with a Hitachi HU-12 transmission electron microscope, equipped with a goniometer, at an operating voltage 125 KeV. Thin foils in the form of 3 mm discs for microscopy work were largely prepared by chemical thinning and polishing, utilising a solution of 70% HNO_3 and 30% HF. Extensive specimen rotation and tilting was employed to reveal deformed and recovered substructure. The low magnification micrographs were enlarged 4 times and average cell or subgrain intercept determined by using a line intercept method.

3. Results

3.1. Microhardness tests

Fig. 1 shows the isochronal microhardness recovery of cold worked and cold worked neutron irradiated Nb as a function of annealing temperature for an annealing period of 1 h. To obtain data points in the curve, 15 identations were made for each sample.

3.1.1. Cold worked specimen

As is shown in fig. 1, the microhardness first in-

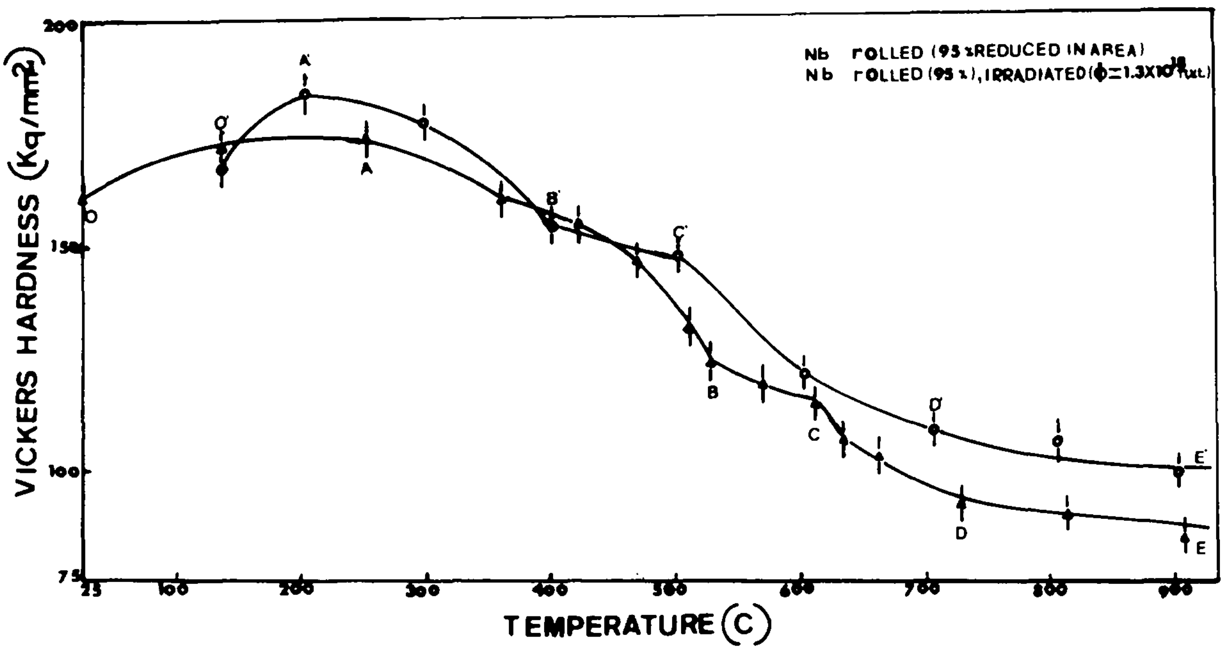


Fig. 1. Isochronal microhardness recovery of cold worked and cold worked neutron irradiated niobium as a function of annealing temperature. Annealing time 1 h.

creases slowly with temperature reaching a maximum at 252°C, then decreases slightly up to 462°C. Thereafter the decrease in microhardness is rapid as recovery proceeds around 600°C, after which the decrease continues until after about 700°C there is relatively little change in the microhardness. The micohardness versus temperature curve (OABCDE) can be divided into 3 regions:

Region: OAB ($T < 462$°C), related to hardening and recovery processes.

Region: BCD (462–722°C) related to recrystallization processes.

Region: DE (>722°C), involving grain growth processes.

3.1.2. Cold worked and irradiated specimens

Initially the microhardness increases rapidly with temperature with hardness reaching a maximum around 210°C, decreasing thereafter only slightly up to about 300°C. After this there is a rapid decrease in hardness as the temperature is further increased. There is, however, a slight delay in the overall recovery spectrum around 500°C, then the hardness decreases gradually, and after about 800°C, the microhardness remains practically unchanged.

Comparing the two curves it can be argued that fast neutron irradiation in general tends to shift the microhardness versus temperature curve (O′A′B′C′D′E′) to lower temperature. Furthermore the microhardness is higher for irradiated samples and remains so even up to very high temperatures (900°C). A surprising exception to the general increase in microhardness in the irradiated samples occurs at point O′ which is the as irradiated hardness value at 140°C and is lower than the hardness for cold worked specimens.

3.2 Transmission electron microscopy

3.2.1. Cold worked specimens

Fig. 2 shows tangled dislocations in the early stage of cell formation in niobium cold worked and annealed at 420°C for 1 h. Dislocation free cells appear to nucleate in regions of high dislocations density. Fig. 3 (a) is an electron microscopy image for a specimen cold worked and then annealed at 500°C for 1 h, showing subgrains bounded by high dislocation densities. The boundary on the top left corner is preferentially disappearing such that the two subgrains are coalescing into a similar orientation. Note the high dislocation density within the larger subgrain. Fig. 3 (b)

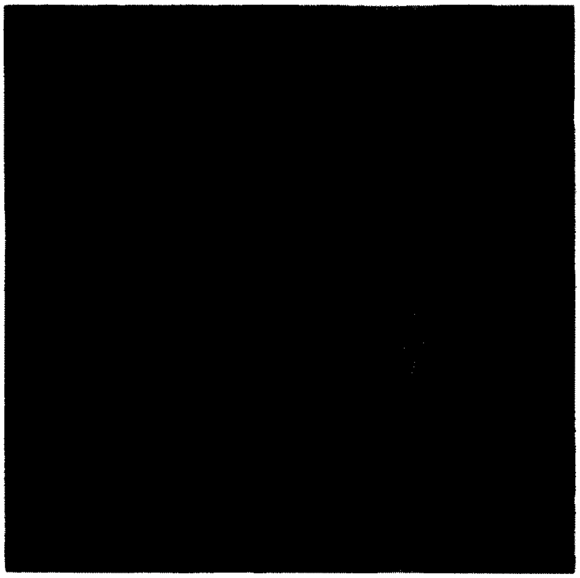


Fig. 2. Dislocation tangles and early formation of cell strucure in niobium, 95% cold worked in area, and annealed at 420°C for 1 h.

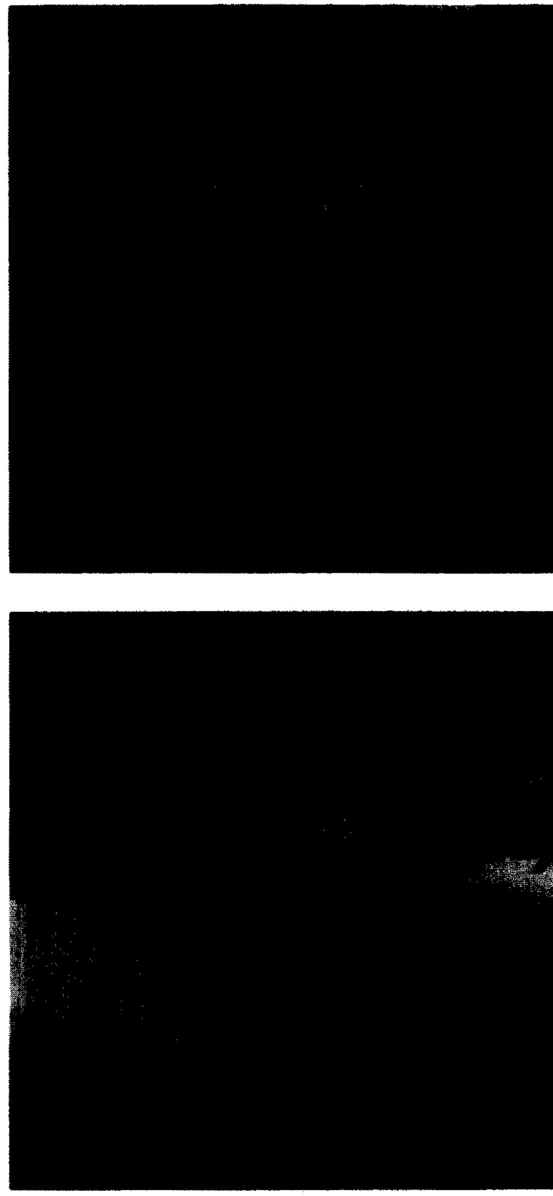


Fig. 3. (a) Subgrains bounded by high dislocation density walls in a specimen of niobium 95% cold worked in area annealed at 500°C for 1 h. (b) Subgrains coalescing in a specimen cold worked 95% and annealed at 722°C for 2 h.

shows another example of subgrain coalescence for a cold worked specimen annealed at 722°C for 2 h. Fig. 4 shows a completely recrystallized subgrain, growing preferentially into heavily deformed regions of a specimen cold rolled 95%, annealed at 520°C for 1 h. Fig. 5 is an electron micrograph showing a high angle grain boundary bulging into a region of high dislocation density (specimen annealed at 500°C). The growing boundary leaves in its wake subgrains of the same orientation as the growing grain. As the grain boundary moves it acquires dislocations lying in its path and thus attains a greater degree of misorientation relative to its neighbours. Fig. 6 is an electron-micrograph showing cellular substructure along with microtwins in a Niobium sample cold worked 95% and annealed at 520°C for 1 h. Fig. 7 is a composite micrograph showing completely recrystallized region of the specimen annealed at 722°C for 1 h. The subgrains are bounded by extensive tilt and twist dislocation networks. Fig. 8 shows a growing high angle boundary scavenging dislocations in it path and leaving a dislocation-free region behind it (annealing temperature 1150°C, 1 h). Fig. 9 shows a variation of average cell or subgrain size vs. annealing temperature for cold worked samples. Annealing time 1 h. There is relatively little change in the average cell size in the temperature interval 25–400°C, showing that dislocations undergo rearrangement to form energetically more favourable configurations, along with the annhilation of point defects and point defect agglomerates produced

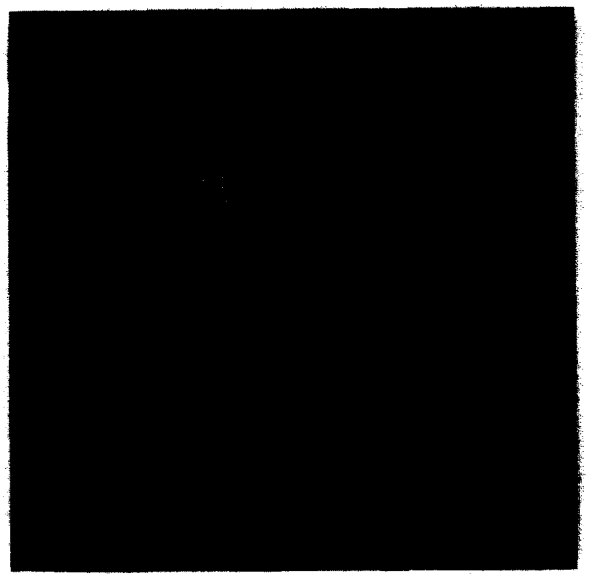
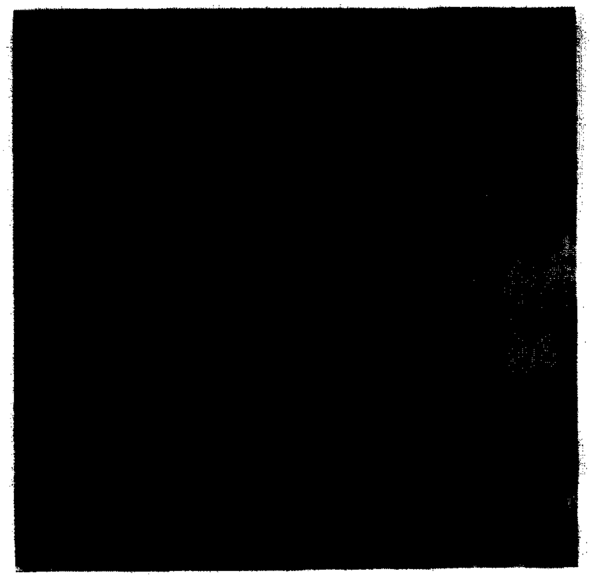


Fig. 4. A completely recrystallized subgrain, growing into a heavily deformed region in a Nb specimen 95% cold worked and annealed at 520°C for 1 h.



. Cell structure and microtwins in 95% cold worked specimen annealed at 520°C for 1 h.

by plastic deformation. After 400°C recrystallization begins such that subgrain size continues to increase linearly up to 680°C after which the subgrain size tends to saturation.

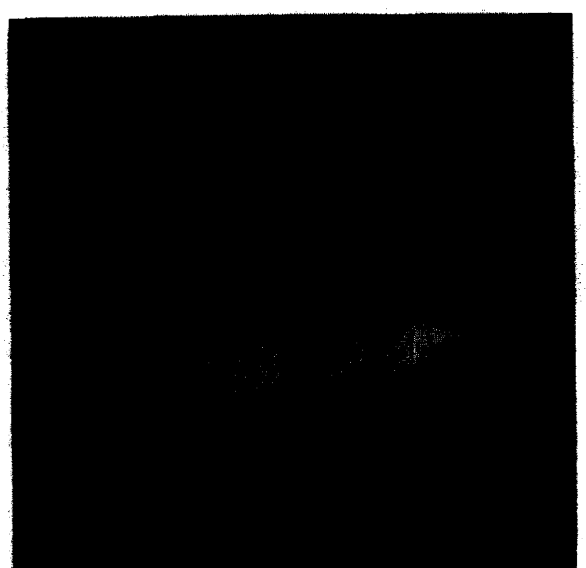


Fig. 5. High angle grain boundary bulging into a region of high dislocation density, 95% cold worked specimen annealed at 500°C for 1 h.

3.2.2. Cold worked and irradiated specimens

Fig. 10 is an electron micrograph of a specimen that was cold worked and irradiated to a fast neutron dose of 1.3×10^{18} nvt and annealed at 300°C for 1 h. An extensively tangled and cellular dislocation structure is observed. A high density of point defect aggregates in the form of black dots are also observed with a minimum size of these dots observed to be 42 Å. Previous studies [27] have shown that these black dots are dislocation loops of predominantly interstitial type. As is clear from the micrograph, these loops tend to pin the dislocations and act as obstacles to fresh dislocations. The tangled and wavy nature of the dislocations indicate that dislocations have cross slipped and climbed.

4. Discussion

4.1. Unirradiated specimens

The initial increase in the microhardness vs temperature curve (OA) in fig. 1 in the temperature range 27–267°C can be attributed to the migration of interstitial impurity atoms [22,23], such as O, N and C, to the defects (dislocations, vacancies) produced by cold

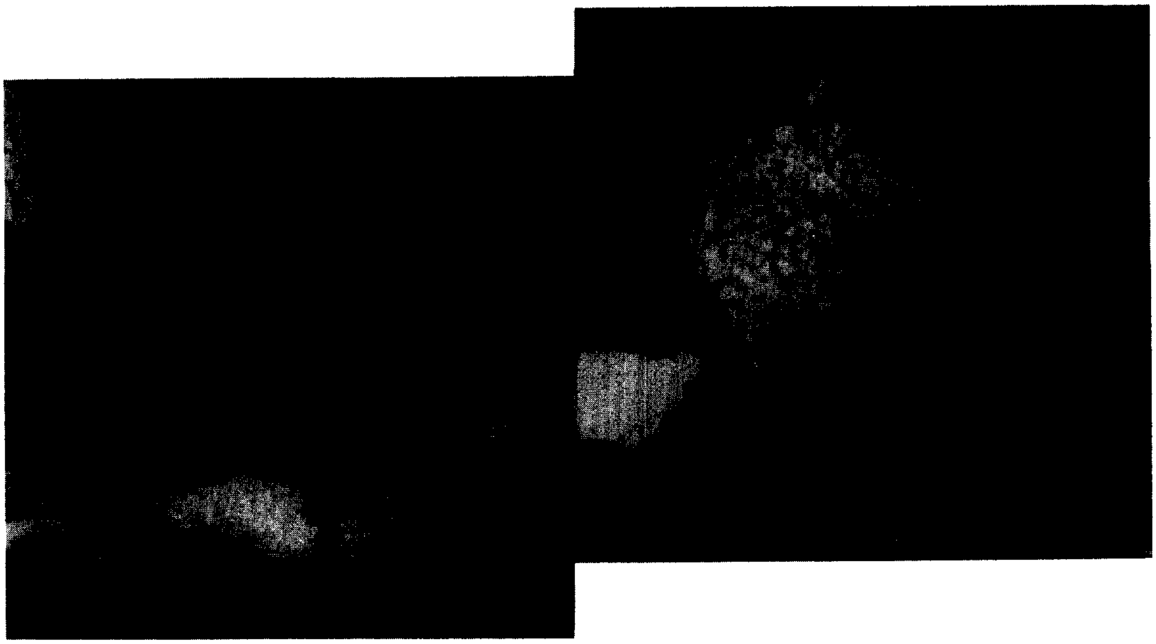


Fig. 7. Dislocation networks and recrystallized substructure in 95% cold worked Nb annealed at 722°C for 1 h.

work, thereby pinning them and increasing their effectiveness as barriers to dislocation slip produced during indentation testing. In the temperature interval 267–462°C a gradual decrease in hardness can be attributed to the recovery processes, during which vacancies anneal out and dislocations rearrange by thermal activation (glide and climb), thereby reducing the overall internal stresses. There is relatively little increase in the overall cell size in the temperature interval 27–420°C, as shown in fig. 9, indicating the preponderance of recovery processes in this temperature interval. The rapid decrease in the microhardness around 462°C is due to the commencement of recrystallization. TEM results in figs. 2 and 6 show that dislocation free cells form within regions of high dislocation density, producing a cellular substructure. Once one of these dislocation-free subgrains acquire high misorientation with respect to its neighbours the subgrains will grow, sweeping up isolated dislocations or constituents of low angle grain boundaries (figs. 4 and 5) such that the periphery of a growing subgrain acquires an even higher dislocation density.

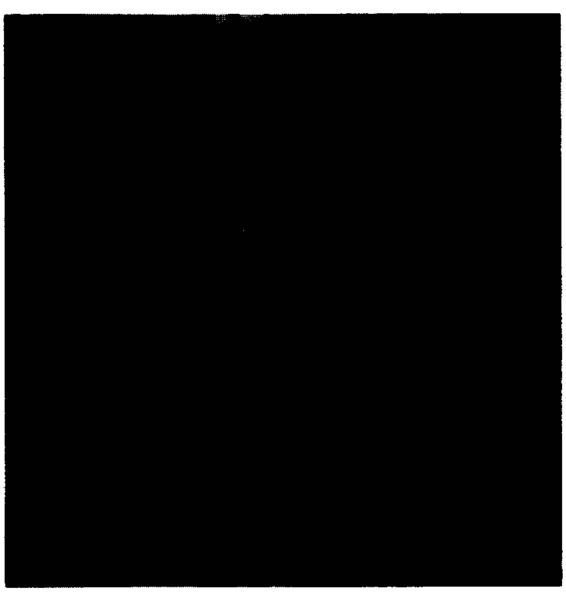


Fig. 8. 95% cold worked Nb, annealed at 1150°C for 1 h. A moving grain boundary absorbing dislocations in its path.

The nucleation of a recrystallized grain proceeds by subgrain coalescence [24,25]. As shown in fig. 3, one of the subgrains is gradually disappearing such that subgrains sharing this boundary merge into the same orientation resulting in an increased subgrain size; this larger subgrain is surrounded by high angle grain boundaries which have higher mobility. Figs. 4 and 5 show that when these high angle grain bounda-

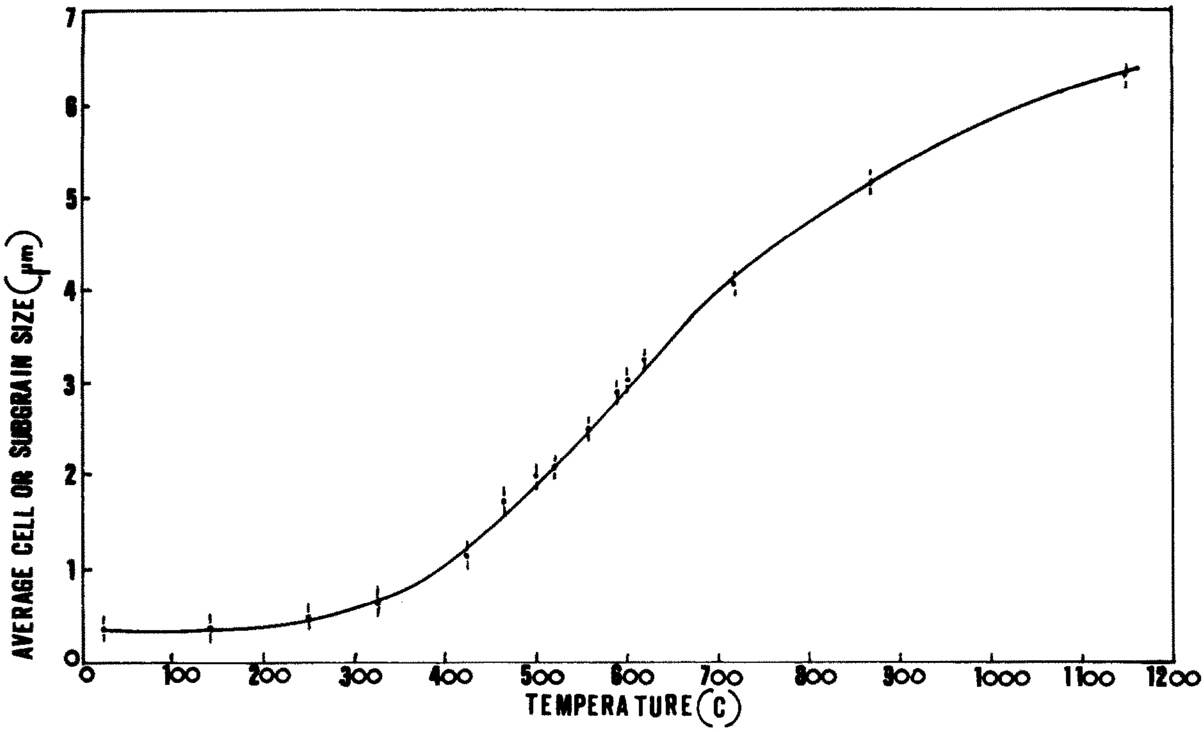


Fig. 9. Variation of average subgrain diameter vs. isochronal annealing temperature for 95% cold worked Nb. Annealing time 1 h.

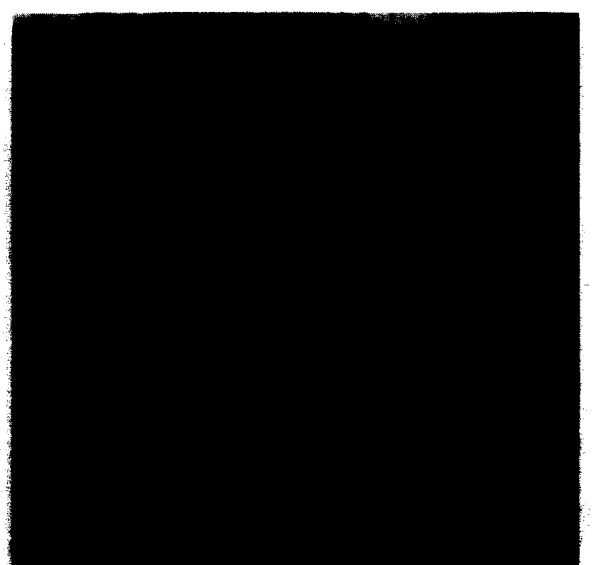


Fig. 10. Dislocation tangles and cells along with small defect clusters as revealed under kinematical diffraction contrast, 95% cold worked Nb, irradiated to a fast neutron fluence of 1.3×10^{18} nvt posteriorly annealed at 300°C for 1 h.

ries are at the periphery of a highly deformed region, the recrystallization can then proceed rapidly by strain-induced grain boundary migration [26]. There is a temporary delay, however, in the over all recrystallization process at C in the BCD region of the curve in fig. 1. This has been attributed to microtwinning, as shown in fig. 6. These microtwins form during recovery anneal as a result of the accomodation of local strains due to rapid formation of subgrains [1]. Above 722°C, the recrystallization is virtually complete and the grain growth begins such that microhardness remains virtually unchanged (figs. 7 and 8).

4.2. Irradiated specimens

Post irradiation annealing of cold worked and irradiated samples results in an overall increase in microhardness as shown by the curve O′A′B′C′D′E′ in fig. 1. The hardness corresponding to point O′ refers to the as-irradiated value at 140°C, and is lower than the hardness for cold worked samples (unirradiated). The reason for this lower hardness at O′ may be due to thermal cycling which our samples underwent while in the reactor. The IEA-1 reactor during the period of this investigation, was in operation for only 8 h a day. The time employed for our irradiation was 48 h; this means that our samples were in place during reactor start up and shut down for 6 days and may have been subjected to temperature fluctuations. This thermal cycling in the presence of a large number of irradiation produced defects could result in the rearrangement of dislocations resulting in the lowering of internal stresses, such that microhardness decreases slightly at O′. Beyond O′ however, the curve O′A′B′ in fig. 1 behaves in a similar manner when compared to the curve OAB such that the initial microhardness increases up to around 300°C, and thereafter decreases gradually as the temperature is further increased. The irradiated specimens contain, in addition to deformation induced defects, radiation produced defect clusters or dislocation loops of predominantly interstitial type [27]. These are visible in the electron micrograph in fig. 10 as small black dots with a minimum diameter of 42 Å. The interstitial impurity atoms principally O and C migrate to these radiation produced defect clusters or loops in the temperature range 150–300°C thereby strengthening them as barriers to dislocation slip [22, 27]. The relative increase in the microhardness in irradiated specimen is therefore due to the strengthening of radiation produced defect clusters and the increase in the total number of effective obstacles to slip dislocation motion. The lowering of the irradiated curve below the unirradiated one at B′ may be due the ease in the formation of recrystallized nuclei [20] as also due to the precipitation of carbon atoms due to irradiation [28]. The recrystallization in the cold worked and irradiated samples commences earlier around 300°C, this is because the kinetics of subgrain coalescence are governed by either cooperative climb of edge dislocations or vacancy diffusion processes [24] which will be accelerated in the presence of defects produced by fast neutron irradiation. The hardening in the region around 500°C may be attributed to the appearance of small defect clusters of vacancy type in addition to large interstitial loops. Such defect clusters were observed by Ohr et al. [27] on post irradiation annealing of Nb at 600°C. They further observed that these small defect clusters of vacancy type showed no depletion near the grain boundaries. This suggests that at higher temperatures as recrystallization proceeds, it is possible that these vacancy type clusters could temporarily impede the subgrain growth, thus giving rise to a microhardness hump in the B′C′D′ region of the irradiated specimens in fig. 1. Beyond C′ the microhardness shows continuous recovery and the overall hardness remains higher than the unirradiated cold worked niobium, even at high annealing temperatures (900°C), presumably due to still high residual density of point defect agglomerates produced by irradiation. Comparing the two curves at high temperatures, around D, in fig. 1 it appears that recrystallization finish temperature (D and D′) is relatively unaffected by irradiation. It is possible that at these high temperatures subgrain boundaries are of higher angle, thus possess greater mobility (fig. 8) such that the radiation produced defect clusters are not effective in resisting grain growth.

5. Conclusions

1) Initial increase in the microhardness in the temperature range 25–300°C has been attributed to strengthening of obstacles to dislocation slip by interstitial impurity atoms O, N and C, for both irradiated and unirradiated niobium.

2) Recrystallization in 95% cold worked Nb proceeds by subgrain growth (controlled by subgrain coalescence) as also by strain induced grain boundary migration.

3) Post irradiation annealing after fast neutron bombardment to an estimated fluence of 1.3×10^{18} nvt for cold worked Nb results in an overall increase in microhardness by about 10 kg/mm^2 initially (207° C) and about 15 kg/mm^2 at high temperature (722°C).

4) Fast neutron irradiation facilitates the formation of recrystallization nuclei by subgrain coalescence and thus accelerates initial recrystallization processes by about 150°C, in cold worked and irradiation specimens.

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