THE EFFECT OF RADIATION ON THE PROPERTIES OF SUPERCONDUCTING MATERIALS*

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It has been clearly demonstrated that the physical perfection of superconducting materials has a large influence on the superconducting properties. In general, it has been found that the current carrying capacity is proportional to the defect density, and also to the degree of difference between the defect and the matrix. Physical heterogeneities have been introduced into the materials by mechanical deformation, inclusion of second phases, voids, and impurities, and, finally, by irradiation. The inhomogeneities are viewed as pinning centers which restrict the motion of magnetic flux through the material. On the basis of a Lorentz force model, as the flux motion is pinned, higher transport currents may be supported by the material. An analysis of the kinds of pinning centers which are effective in the various superconducting materials, and the energetics involved, have been given in some detail in the first two presentations of this session of the Summer Study by J. Livingston[1] and W. Webb.[2] The flux pinning model was originally developed in a series of papers over about a two-year period by Anderson,[3] Friedel, de Gennes and Matricon,[4] Silcox and Rollins,[5] Kim, Hempstead and Strnad,[6] and Anderson and Kim.[7]

Introduction of defects by irradiation offers several advantages over the other methods of creating physical heterogeneities, particularly for the brittle beta-tungsten intermetallic compounds. The radiation damage may be introduced quantitatively, and, for certain types of radiation, the defects are introduced uniformly throughout the sample. Although the fine structure within an individual damaged "spot" is complicated and difficult to examine, the size and distribution of the damage spots is uncomplicated as compared to other types of structural heterogeneities. The size and density of the induced damage may be detected quantitatively by transmission electron microscopy, and thus the possibility is offered to relate these factors directly with the electrical properties. To date relatively little direct examination of radiation damage in the superconducting materials has been done. The radiation effects in the soft superconductors anneal out at room temperature, and thus direct observation of the defect structure in these materials is impractical. In the refractory type II superconductors the radiation effects do not anneal out at room temperature, but direct observation of the defect structure has been delayed by the difficulties involved in preparing well-defined single phase material, and in thinning the material for observation by transmission microscopy.

A number of investigations have been carried out since 1960 on the effect of irradiation on the properties of the superconducting materials. General trends may be defined:

- In Pb and Sn, the superconducting properties have been altered by deformation, alloying and irradiation, but the largest effects have been realized by deformation. The irradiation effects generally anneal out below room temperature.

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— In the NbZr and NbTi alloys, large changes in the superconducting properties have been introduced by deformation and introduction of second phases, but with the exception of a "peak" effect observed in NbZr, irradiation has very little influence on the superconducting properties of both annealed and worked material.

— In Nb, both deformation and irradiation alters the superconducting behavior, but the largest change has been realized by neutron irradiation. The samples were exposed to irradiation at room temperature, and thus the effects observed are stable at room temperature.

— In the beta-tungsten compounds, the superconducting properties have been shifted by introduction of second phases and irradiation. The largest changes in the current density have been realized by irradiation. The irradiation induced properties (at least J_c) are stable to temperatures well above room temperature.

It is clear that the most fruitful area for investigations of irradiation effects on superconducting properties lies with the type II superconductors. These materials are of practical importance, the effects observed are large, and are stable at temperatures used for observation of the defects. Single crystal Nb has been available for several years, and single crystal Nb_3Sn has recently been prepared.

A review of investigations of the effect of irradiation on the properties of superconducting materials is presented in the following sections. The soft superconductors are included for background information, but for the reasons stated above, the emphasis is placed on the beta-tungsten materials.

THE EFFECT OF IRRADIATION ON THE PROPERTIES OF THE SOFT SUPERCONDUCTORS

In an effort to compare the effect of alloying and radiation damage on Sn, Rinderer and Schmid[8] irradiated pure tin strips with 5.3 MeV α particles at 4.2°K. The more massive α was used to produce a large number of defects. The sample thickness was chosen to be ~ 2 X the penetration depth of α particles in Sn (~ 0.2 mm) and the samples were exposed on both sides. Large increases in resistance were realized, and the T_c was decreased by a factor of 50 more than alloyed samples with equivalent resistance changes (Lynton et al.[9]). However, van Itterbeek and coworkers[10] later found the same T_c as a function of resistivity relationship for α-irradiated samples as had been observed in the alloyed samples. Thallium and indium samples were also α irradiated at 4.2°K. The irradiated Tl behaved similarly to Tl wires plastically deformed at 4.2°K, and the In compared, in T_c vs ρ behavior, to TeIn alloys. The radiation damage in these soft materials anneals out at low temperatures. More than half of the effect is lost at 16°K for the In (van Itterbeek et al.[10]), and all of the irradiation induced effect is annealed out of the Sn at room temperature in 24 hours (Rinderer and Schmid[8]).

Druyvesteyn and van Ooijen[11] measured the increase in the critical field of Pb after neutron irradiation at 78°K. As with the former two groups, these investigators found that the superconducting property measured, in this case H_c, may be related to the radiation induced change in resistivity. The $dH_c/d\rho$ obtained by irradiation and by cold rolling at 78°K are similar. Cold rolling, however, leads to changes in H_c which are a factor of ten larger than that induced by neutron damage for fluxes of $\sim 10^{18}$ n/cm^2.

In two of the three investigations of the influence of irradiation on superconducting properties of the soft metals, the relation between the change in the superconducting property measured with the change in resistivity was similar, independent of the means of introducing the lattice defects. Since the defects resulting from irradiation, alloying, and cold rolling introduce quite different types of crystallographic inhomogeneities, the superconducting properties appear to be more directly related to resistivity. Disagreement between the measured effects and those anticipated by theory is explained on the assumption that the sample is heterogeneous and contains microscopic regions with different resistivities.

Blank and coworkers,[12] from magnetization measurements, observed increases in the frozen-in magnetic moment for rhenium and tin which had been neutron irradiated at 77°K. The T_c of Rh increased, while that of Sn decreased, as has also been seen by the other investigators. The changes in T_c and the magnetization were not related to ρ, but it was noted that addition of tungsten also increases the T_c of Rh, while the introduction of impurities decreases the T_c of Sn. The comparative temperatures of annealing out of the introduced damage may be related to the comparative melting points of these two materials.

Coffey and coworkers[13] observed changes in the resistivity of pure annealed lead which had been deuteron irradiated at 30°K. A change in the normal resistivity of 0.5×10^{-8} Ω·cm was observed at the highest exposure of $\sim 10^{21}$ deuterons/cm^2. About 75% of the induced resistivity increase remained after a 77°K anneal, and 1% after a 300°K anneal.

THE EFFECT OF IRRADIATION ON THE PROPERTIES OF NbZr

Babcock and Riemersma[14] observed no change in the operation of a Nb75%Zr25% solenoid after exposure, in liquid helium, to a 400 MeV proton flux of 8×10^{10} p/cm^2.

McEvoy et al.[15] observed no change in the flux shielding properties of 25% cold worked Nb75%Zr25% after an exposure to a fast neutron flux of 1×10^{18} n/cm^2 (at $\sim$ 50°C), and proposed that the lack of change was due to the fact that the material had already been cold worked prior to irradiation. However, Keller et al.[16] observed no change in the current carrying characteristics, with the exception of a peak effect near H_{c2}, of annealed NbZr exposed to a deuteron flux of 10^{17} d/cm^2 at 30°K. Coffey et al.,[13] at the same laboratory, observed about a 20% decrease in the J_c of cold worked NbZr and NbTi, deuteron irradiated under the same conditions as stated above.

THE EFFECT OF IRRADIATION ON THE PROPERTIES OF Nb

Chaudhuri and coworkers[17] have measured the superconducting and normal state low temperature thermal conductivity of single crystal Nb and V samples irradiated by 1×10^{18} n/cm^2 at 30°C. Both the superconducting and normal (driven normal by a magnetic field) thermal resistivity of the Nb increased after irradiation, but only the superconducting thermal resistivity of the V increased. These investigators proposed that the exposure to the fast neutrons resulted in the formation of vacancy-interstitial pairs which condense into dislocation loops. The strain fields around the dislocations act as phonon scatterers. A possible difference between the Nb and V is that, at the 30°K measurement temperature, both interstitials and vacancies can migrate in the lower melting V, but only vacancies migrate in Nb.

Swartz and coworkers[18] observed no effect of fast neutron irradiation (to levels as high as 1.5×10^{18} n/cm^2) on the magnetization of arc cast Nb and Nb70%Ta30% alloys. Under the same conditions, however, these investigators did detect changes in the intermetallic superconductors Nb_3Sn, Nb_3Al, V_3Ga and V_3Si. The differences were attributed to the difference in the degree of order between these two classes of materials.

But later Kernohan and Sekula[19] found that almost ideal irreversible type II behavior in the magnetization of single crystal Nb could be realized by fast neutron irradiation of 2×10^{19} n/cm^2 (at 40°C). Effects were also observed at the lower irradiation levels employed by Swartz and coworkers,[18] so that the differences observed by these two groups must be attributed to the difference in the nature of the arc cast Nb as compared to annealed single crystal Nb. As is observed in the compound superconductors, the irradiation of Nb to the 2×10^{19} n/cm^2 level resulted in relatively little change in the T_c ($\sim$ 1% decrease). It is interesting to note that the neutron induced flux pinning centers are more effective in Nb than inhomogeneities introduced by mechanical deformation. Essentially irreversible behavior has not been achieved in Nb by cold working.

Tucker and Ohr[20] have observed neutron induced effects in polycrystalline Nb by transmission electron microscopy. These investigators find evidence to show that the neutron induced spots are indeed dislocation loops. The damage spots were found to be near the foil surfaces, even though the sample appears to have been thinned after irradiation.

These investigators do not relate the directly observed defect structure with superconducting properties.

THE EFFECT OF IRRADIATION ON THE PROPERTIES OF THE BETA-TUNGSTEN SUPERCONDUCTORS

A number of groups have been active in investigating the influence of irradiation on the superconducting properties of the beta-tungsten compounds. Before summarizing this work, it is important to point out that the microstructure of these hard, brittle materials is very much influenced by the method of preparation. Particularly in investigations such as these, where the physical perfection is an important variable, one expects to see differences in the effect of irradiation for materials prepared by the different methods. For example, in vapor deposited Nb_3Sn, very small preparative variables yield slightly off stoichiometric material which behaves radically differently than the stoichiometric material after exposure to fast neutron fluxes. The investigators at the General Electric Research Center (Swartz et al.[18]; Bean et al.[21]) have used, for the most part, arc cast material. At the Westinghouse Research Laboratories (Coffey et al.[13]), Nb_3Sn vapor deposited by RCA on a Hastelloy substrate (Hanak[22]; Hanak et al.[23]) has been employed. The Siemens investigators (Bode and Wohlleben[24]) have prepared Nb_3Sn by diffusion. At RCA (McEvoy et al.[15]; Cullen and Novak[25,26]; Cody, unpublished) vapor deposited Nb_3Sn on ceramic substrates (Cullen[27]), and single crystals prepared by a closed tube transport process (Hanak and Berman[28]) have been investigated.

Swartz and coworkers[18] detected changes in the magnetic hysteresis of arc cast Nb_3Sn, Nb_3Al, V_3Ga and V_3Si after an irradiation of 1.5×10^{18} n/cm^2. The magnitude of the changes observed is inversely proportional to the average atomic mass of the elements making up the compounds. The largest change in the calculated J_c was observed in V_3Si; $\Delta J_c = 7 \times 10^5$ A/cm^2 for 10^{18} n/cm^2. The Nb_3Sn was prepared by both arc casting and diffusion, and considerable differences were observed in the effect of irradiation between these two samples even though the unirradiated transition temperatures were very similar. The transition temperature is relatively insensitive to material changes which have large effects on the J_c. The largest change in the T_c observed in this investigation was -0.22°K for the arc cast Nb_3Al.

At the same laboratory, Bean and coworkers[21] investigated the effect of thermal neutron irradiation on the superconducting properties of Nb_3Al and V_3Si doped with fissionable uranium and boron. After exposure to a flux of 1.7×10^{18} n/cm^2 the material containing 0.321 at % U exhibited current densities as high as 2×10^6 A/cm^2 at 30 kOe. This represents an increase in the J_c by more than a factor of 100 over the preirradiated value, and is higher by a factor of $\sim \times 10$ than had been previously realized for these materials in the 30 kOe field. Above 10 kOe the J_c becomes relatively insensitive to the magnitude of the applied field, and thus the current carrying behavior of these samples does not adhere to the Lorentz force model. As in the investigations on the undoped materials, the increase in the J_c of the irradiated doped V_3Si is two to three times that of the Nb_3Al. Similar decreases in the transition temperatures were also observed as for the undoped samples, $\sim -0.22^oK$ for V_3Si, and $\sim -0.45^oK$ (below the preirradiated T_c) for the Nb_3Al.

Coffey and coworkers[13] have examined the effect of low temperature deuteron irradiation on the superconducting properties of vapor deposited Nb_3Sn on the Hastelloy ribbon substrate. The samples were exposed to a 1×10^{21} d/m^2 flux at 30^{o}K. Critical current measurements were made at temperatures between 5.1 and 12.2^{o}K. Appreciable differences were observed between two samples which exhibited different preirradiation current carrying capacities.

At 5.7^{o}K the J_c of the initially low J_c sample increased on irradiation from 6 to 10×10^8 A/m^2 in a 20 kOe field and remained at the higher J_c after annealing at 300^{o}K. At a measurement temperature of 10.7^{o}K, the J_c of the same sample decreased after irradiation, and exhibited recovery after the 300^{o}K anneal. The J_c was decreased at all measurement temperatures for a sample with a preirradiation J_c of $\sim 4 \times 10^9$ A/m^2 at 20 kOe. As with the low J_c sample, the deuteron induced behavior was stable to a 300^{o}K anneal for a 5.1^{o}K measuring temperature, but unstable at 12.2^{o}K. The transition temperatures were lowered and broadened by the deuteron irradiation, and 75-80% of the effect remained after a 300^{o}K anneal. A linear increase in the resistivity with increasing deuteron exposure was observed, of which $\sim$ 57% remained after annealing at 300^{o}K.

Bode and Wohlleben[24] have observed over 300% enhancement of the J_c of diffused Nb_3Sn after proton irradiation of 8×10^{16} p/cm^2 at temperatures between 100 and 200^{o}C. Above this irradiation level the J_c decreases. The postirradiation J_c is essentially independent of the applied magnetic field up to 50 kOe, thus the behavior of these samples does not follow the Lorentz force model. By comparing the levels of neutron (Cullen et al.[29]) and proton irradiation which lead to the same J_c enhancement, a ratio of effective levels of $N_p/N_n = (3\text{-}6) \times 10^{-2}$ was derived. These investigators calculate that at this ratio, for a displacement energy of 20 eV, the same concentration of defect clusters will be produced by either neutrons or protons. The proton induced J_c is not altered by a 12 hour anneal at 250^{o}C. The original J_c is restored by annealing at temperatures between 700 and 800^{o}C. A condensation of overlapping clusters is proposed as the mechanism to explain the decrease in the enhanced J_c at irradiation levels above 8×10^{16} p/cm^2.

THE EFFECT OF NEUTRON-INDUCED DEFECTS ON THE PROPERTIES OF Nb_3Sn: Investigations Carried Out at the RCA Laboratories

Various investigations have been carried out at the RCA Laboratories on the effect of fast neutron irradiation on the properties of polycrystalline and single crystal Nb_3Sn. The properties measured are: flux shielding, current carrying capacity, resistivity, transition temperature, and magnetization. The lattice expansion, and recovery of the lattice on annealing, has also been investigated. In an attempt to relate the electrical properties with structural changes, the neutron induced defects are now being directly observed by transmission electron microscopy.

The magnetic flux shielding properties of polycrystalline vapor deposited Nb_3Sn on ceramic substrate tubes (Cullen[27]) was studied (McEvoy et al.[15]) by placing a field probe both inside and outside of the tube. Using this method originally suggested by Kim and coworkers,[6] the currents circulating in the tube which result in the flux shielding can be readily derived. The current densities derived from this method are in good agreement with direct current measurements on the strips of the same material (Cullen et al.[30]). The cylinders were exposed to a fast neutron flux of 10^{18} n/cm^2 at $\sim 50^{\circ}$C. The magnetization curves, H internal vs H external, were determined at 4.2°K. Prior to irradiation, no flux jumps were observed. But after irradiation, flux jumps occurred to such an extent that it was difficult to establish a postirradiation critical state curve. It was evident that the current density of a sample with a preirradiation $\alpha^* = 6.4 \times 10^6$ kG·A/cm^2 had been enhanced by at least 50%. Because of more extensive flux jumping, no estimate could be made of the increase in the current density after irradiation of a sample with a preirradiation $\alpha = 1.5 \times 10^6$ kG·A/cm^2. Although it was difficult to obtain quantitative results from this type of measurement, the increase in the superconducting current carrying capacity as a result of irradiation had been established.

Because of the difficulty in obtaining quantitative results from the flux shielding experiments, the more laborious direct measurement of the critical currents on strip samples were made (Cullen and Novak[25,26]). Current and potential contacts were soldered to nickle-plated lands on thin Nb_3Sn strips supported by a flat ceramic substrate. The adherence of the current carrying characteristics to the Lorentz force model (Kim et al.[6]) had previously been established on the Nb_3Sn ceramic supported strips. The critical current, both as a function of the applied field intensity, and the orientation of the current carrying axis in the field, is in excellent agreement with the Lorentz force model to less than 1% for fields as high as 100 kG (Cullen, Cody and McEvoy[30]; Cody, Cullen and McEvoy[31]; Cody and Cullen, to be published). The strip samples were exposed to fast neutron fluxes under the same conditions as had previously been employed for the tabular samples. The critical current densities in a transverse field at 4.2°K were measured as a function of the exposure to neutron fluxes as high as 1.4×10^{18} n/cm^2. A variety of samples were measured with various "as deposited" α's between 1.4 and 19×10^6 kG·A/cm^2. A summary of the results is shown in Table I.

The JH product (measured at 14 kG) of the sample with the lowest preirradiation α of 1.49 kG·A/cm^2 increased by more than an order of magnitude after irratiation of 14×10^{17} n/cm^2, while the JH of the highest initial α sample of 19.4 kG·A/cm^2 increased slightly after exposure to a flux of 3.4×10^{17} n/cm^2, and then decreased by more than an order of magnitude after an exposure of 7.2×10^{17} n/cm^2. The first of these samples is essentially stoichiometric Nb_3Sn, while the second sample is slightly Nb rich. This emphasizes that small differences in preparative variables can result in large differences in the way the superconducting properties are influenced by irradiation, and implies that the radiation induced defects interact strongly with heterogeneities already present in the sample. If the "as prepared" heterogeneities are larger than the irradiation induced damaged areas, as is undoubtedly the case, these defects may "short out" the irradiation induced damage, or the irradiation induced defects may condense on the larger heterogeneities and form larger and less effective pinning points. It is also possible that the manner in which the neutrons initially transfer energy to the lattice is strongly influenced by the presence of heterogeneities. It is interesting to note in this regard that Brimhall and Mastel[32] have observed a concentration of defect structures in twin boundaries and denuded zones around the boundaries of neutron irradiated Ni.

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*The current carrying characteristics of Nb_3Sn in an applied field are described in terms of α of the Kim et al.[6] relationship $J = \alpha/(H + B_o)$, where α is a constant dependent on the structure of the material. For low α specimens, $B_o \sim 600$ G.

TABLE I

Initial Sample Characteristics and Current Carrying Behavior as a Function of Irradiation

Sample	Composition (wt % Sn)	T_c midpoint (^oK)	ΔT_c (^oK)	(n/cm^2) x 10^{-17}	JH ($kG \cdot A/cm^2$) x 10^{-6} H = 10 kG	JH ($kG \cdot A/cm^2$) x 10^{-6} H = 14 kG	($kG \cdot A/cm^2$) x 10^{-6} α_1	α_2
FS-20(5)	29.5 ± 0.3	18.3	0.04	0	1.36	1.33	1.49	---
				3.4	5.30	6.46	6.58	14.3
				7.2	9.38	11.4	14.3	28.6
				10.5	13.0	16.8	24.1	90.5
				14.0	15.0	18.2	35.0	76.0
75(3)	28.0 ± 0.1	16.1	0.80	0	4.0	4.48	6.5	---
				3.3	6.6	7.84	12.1	---
				6.9	8.0	9.66	15.6	---
				10.1	6.2	7.56	10.1	19.5
74(4)	29.2 ± 0.1	16.9	0.80	0	11.5	13.3	19.4	27.9
				3.4	11.7	14.1	19.2	29.7
				7.2	0.89	1.3	1.18	2.32
Single Crystal	30.8 ± 0.01	18.0	0.10	0			0.15	
				1.0			0.50	

As the critical current density is enhanced by either neutron irradiation or the introduction of chemical heterogeneities, the current carrying behavior cannot be described by the Lorentz force current field relationship. A change in the α takes place at ~ 10 kG; above this applied field level the J_c is less dependent on the applied field. An α for below 10 kG, and an α for above 10 kG, are given for these samples in Table I, but the current carrying behavior is better described by the JH products at 10 kG and at 14 kG.

The sample resistivities at 300^{o}K and 77^{o}K were measured as a function of the exposure to the neutron flux. The residual resistivities were derived from the R_{300^oK}/R_{77^oK} ratio by an empirical relationship established by Woodard and Cody.[33]

An average change in the residual resistivity with the neutron flux $d\rho_o/d\varphi$ is ~ 5.7 x 10^{-24} $\Omega \cdot cm^3/n$. This value is independent of the level of the flux exposure, and is within the range of that measured in other metals.

Very little change in the transition temperature was observed (Cooper[34]) as the result of neutron irradiation of these Nb_3Sn samples. For a sample with an unirradiated T_c (start) of 18.33^{o}K, and a ΔT_c of 0.05^{o}K, no change in magnitude or width of the transition was observed after exposure to a flux of 4.7 x 10^{17} n/cm^2. After an exposure of 2.7 x 10^{18} n/cm^2 the transition temperature decreased by 0.18^{o}K ± 0.02^{o}K, with no change in width.

Magnetization studies (Cody, unpublished) have been carried out on cylinders cut from single crystals of Nb_3Sn (Hanak and Berman[28]). The α's for the single crystal material are commonly a factor of 10 less than the lowest α of the polycrystalline materials. At 4.2^{o}K, the magnetization curves are irreversible, and are appreciably shifted by exposure to a neutron flux of 1 x 10^{16} n/cm^2. This radiation level is lower than the lowest exposure used for the polycrystalline material. A flux exposure of 1×10^{17} n/cm^2 typically increases the α (measured at 4.2°K from 0.15 to 0.50 kG·A/cm^2. The $d\alpha/d\varphi$ for the single crystal material is slightly higher than that measured on the lowest α polycrystalline material ($\sim 3 \times 10^{-12}$ as compared to 2.5×10^{-12} kG·A/n).

This is consistent with the observations made on the polycrystalline material which show that the effect of the neutron damage on J_c is inversely proportional to the initial sample α.

The effect of neutron irradiation on the electrical properties of Nb_3Sn may be summarized as follows:

1) The degree to which neutron irradiation influences the current carrying capacity of Nb_3Sn is a strong function of the initial sample characteristics. The $d\alpha/d\varphi$ is inversely proportional to the initial α. On this basis the changes realized on single crystal material are in good agreement with changes observed in polycrystalline material.

2) The highest α measured to date on Nb_3Sn was obtained by irradiation of an initially low α sample.

3) Above a certain initial α level, the current carrying capacity of the material is decreased by irradiation. Thus the maximum α obtainable by irradiation is also a function of the initial sample characteristics.

4) The JH product, measured at 14 kG, has been increased by as much as a factor of 15 by neutron irradiation.

5) The $d\rho/d\varphi$ is independent of the level of irradiation to a flux level of $\sim 10^{18}$ n/cm^2.

6) The transition temperature is decreased very little at irradiation levels that have a large effect on the current carrying properties.

The lattice expansion has been measured of polycrystalline vapor deposited samples which were pulverized and encased in sealed quartz X-ray capillary tubes and exposed to neutron irradiation under the conditions previously described. Lattice expansions typically $\Delta a/a_o \sim 3 \times 10^{-4}$ were measured after exposure of the samples to a fast neutron flux of 1×10^{17} n/cm^2. After the initial exposure the lattice expansion is linear to a value of $\Delta a/a_o = 14 \times 10^{-4}$ after an irradiation of 1.4×10^{19} n/cm^2. Although the expansion showed no indication of leveling off at this irradiation level, further measurements were not carried out because of the periods of exposure needed for higher radiation levels. The samples were annealed at various temperatures, for a period of an hour, until the starting lattice constant of 5.2895 Å was obtained. Between the temperatures of 300 and 650°K, the relaxation in the lattice constant is linear and would extrapolate to a complete anneal at ~ 1050°K. However, above 650°K the sample anneals more rapidly, and the original cell constant is achieved at 800°K in one hour. More recent experiments indicate that the samples can be completely annealed at 650°K in two hours. The X-ray diffraction lines sharpen in the back reflection region as the sample is annealed, as is expected if a range of lattice spacings are observed as the result of changes in spacing with distance from a damaged area. The expansion in the lattice is consistent with the formation of an area of decreased density resulting from a thermal spike, as has been proposed (Silcox and Hirsch[35]) for the neutron irradiated copper. It is surprising, however, that measurable lattice changes are observed in this material which has a total damaged volume of ~ 0.1% (as seen by electron microscopy). The magnitude of the damage, and annealing behavior, are similar to that observed for neutron irradiated copper. The damage is retained at higher temperatures than would be anticipated by comparing the melting points of Cu and Nb_3Sn, but this may qualitatively be accounted for by the highly ordered structure of the intermetallic Nb_3Sn.

Direct Observation of Neutron Damage in Nb_3Sn by Transmission Electron Microscopy

Three different types of Nb_3Sn samples have been employed for transmission electron microscopy:

1) Single crystal Nb_3Sn which was irradiated and subsequently thinned by chemical etching.
2) Polycrystalline Nb_3Sn which was irradiated and thinned by low angle ion bombardment.
3) Polycrystalline Nb_3Sn which was thinned by low angle ion bombardment and then irradiated.

Initially the Nb_3Sn samples were thinned exclusively by chemical etching. This procedure posed serious problems because the polycrystalline material etches rapidly at high energy grain boundaries and at the interfaces caused by the columnar growth. Therefore it was extremely difficult to obtain thin edges useful for transmission electron microscopy. The physically homogeneous single crystal material may be thinned by chemical etching, but an uncertainty arose when it was noted that the planar density of the dark areas observed by microscopy after irradiation do not appear to be a function of the thickness of the samples. It has been established that the dark spots observed are indeed associated with exposure to fast neutrons, and not preparation surface artifacts, but the lack of change in density with thickness presents the possibility of an interaction with defects near the surface with the chemical thinning procedure. This would be easier to explain if the damage areas were lighter (on positive prints of electron micrographs) than the matrix, which could be associated with pits. Tucker and Ohr[20] have concluded, by observation of neutron irradiated Nb foils in bright-field and dark-field electron microscopy, that the dark spots they have observed result from defects lying close to the surfaces of the sample. Since the samples were irradiated prior to electrochemical thinning, this implies an interaction between the defects and the thinning method.

Both of these problems have been obviated by thinning by low angle ion bombardment. The method was developed recently by Professor Paulus of CNRS, France. Since the removed material is not knocked into the sample, but leaves at a low angle, no observable damage occurs on thinning. Samples that contain high energy areas can be thinned uniformly by this physical technique.* The polycrystalline Nb_3Sn is now routinely thinned by this method. Wedge shape areas of irradiated material have now been observed in which the planar density of defect spots is a function of the sample thickness.

In the chemically thinned single crystal Nb_3Sn samples, 100 Å diameter defect spots were observed after exposure of the samples to a 10^{18} n/cm^2 flux.[36] The density of the spots is $\sim 5 \times 10^{15}$/cc. This amounts to a 0.1% volume damage of the material. Considering that the film thickness is little more than double the distance between the spots, the volume density changes very little if the assumption is made that the

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*The details of the low angle ion bombardment technique have been discussed only in internal reports of CNRS, Bellevue, France. A thinning apparatus has been marketed by Alba Engineers, Asnières, France. A modification of this apparatus has been employed at the RCA Laboratories to thin the Nb_3Sn samples. A thinning apparatus similar to that modified at the RCA Laboratories will be available in the near future from the Materials Research Corporation, Orangeburg, New York.

observed areas lie close to the two surfaces, rather than uniformly throughout the bulk of the sample. To date attempts to resolve the structure of the spots by the various microscopic techniques have been unsuccessful, and it must be concluded that the damaged areas are amorphous.

The spot size and density observed in ion beam thinned polycrystalline samples after the same level of irradiation have been in excellent agreement with those observed in the single crystal material. Because of the interaction between the "as prepared" defects and the neutron induced defects, as shown by the electrical data, attempts are now being made to thin the sample prior to irradiation, and thus examine specifically identified areas both before and after irradiation, and after annealing. The first attempt was unsuccessful because of the formation of a thin oxide on the surface of the sample during the irradiation which obscured the defect structure. This result is not unexpected since a continuous microscopic oxide film which may serve as the insulator in a tunnel diode structure may be formed by heating Nb_3Sn in air at 100^oC. The samples are now irradiated in an atmosphere of a pure inert gas.

Resolution of the fine structure within the damage spots would contribute to an understanding of the mechanism of the damage formation, but it is the size and spacing of the damage areas that is most important for understanding the effect of these heterogeneities on the current carrying properties. Future studies are directed toward establishing a relationship between the density of the damaged areas and the current carrying characteristics of the material. It is also important to examine the microstructure of material exposed to an irradiation level where further damage effects a decrease in the current carrying capability. If possible, the interaction between the complicated "as deposited" structure of polycrystalline material and the added neutron induced defects will be studied. At present, for one level of neutron exposure, the following summary can be offered:

Polycrystalline vapor deposited Nb_3Sn, as deposited
$\alpha = 1.5 \times 10^6$ kG·A/cm^2 exposed to a fast neutron flux of
1×10^{18} n/cm^2 at $\sim 50^oC$.

Damage spot density observed: 5×10^{15} spots/cm^3.

Spot area: ~ 100 Å.

$d\alpha/d\varphi = 2.5 \times 10^{12}$ kG·A/n.

$d\rho/d\varphi = 5.7 \times 10^{-24}$ Ω·cm/n.

$\Delta T_c = \sim -0.18^oK$, no change in transition width for irradiation level of 2.7×10^{18} n/cm^2.

CONCLUSIONS

An appreciable amount of work has been carried out during the last eight years on the effect of irradiation on the properties of the various superconducting materials. Both the "soft" and the "hard" superconductors have been studied. It is evident at this time that the greatest opportunity for arriving at a quantitative relationship between structural and electrical properties lies in correlating direct observations of the nature of the irradiation induced defect structure with the superconducting properties of the type II materials. The soft superconductors do not lend themselves to such studies because, for the most part, the irradiation induced properties anneal out at temperatures below room temperature and thus direct examination of the defect structures is impractical. Also, larger effects in these materials are realized by mechanical deformation than by irradiation. The NbZr and NbTi alloys, both cold worked and annealed, are very little affected by irradiation, while large effects on the current carrying properties of these alloys can be brought about by mechanical deformation. These deformed alloys have been examined by transmission electron microscopy, but the structure is complicated and difficult to analyze quantitatively. The superconducting properties of the beta-tungsten intermetallic compounds are more sensitive to structural defects introduced by irradiation than by chemical introduction of impurities or second phases. The irradiation induced enhancement of the critical current density in these materials is stable to temperatures well above room temperature and therefore it is feasible to undertake direct observation of the defect structure. Well-defined single phase material may now be prepared, and methods have recently been developed for thinning these refractory compounds. The nature (size, density, and distribution) of the irradiation induced defects is simple as compared to that observed in mechanically deformed materials, and the irradiation induced damage may be introduced at well-controlled levels. Therefore, quantitative correlations between the structure and electrical properties are possible.

The critical current density is more influenced by irradiation induced damage than the other superconducting properties. It has been observed in several beta-tungsten compounds that, at irradiation levels where the J_c is increased by more than an order of magnitude, the T_c is decreased by only $\sim$ 1%. It has also been observed in several compounds by various investigators that the current carrying behavior may be explained by a Lorentz force model prior to irradiation, but that the J_c is relatively insensitive to the magnitude of the applied field, above certain levels, after irradiation.

A key point that has been brought out by a number of investigators, and by comparing the results of several groups, is that the magnitude of the irradiation induced effects observed is highly sensitive to the initial structure of the material, and therefore sensitive to material preparative variables. This implies a strong interaction between the grown-in defect structure and the irradiation induced defects. The "as prepared" defects may "short out" the radiation induced defects, or the induced defects may condense on the grown-in heterogeneities to form a network of larger, fewer, and less effective flux pinning centers. A similar interaction may also take place as the density of the irradiation induced defects increases. Several investigators have observed a peak in the enhancement of the critical current density as a function of exposure to the irradiation.

The size and density of the irradiation induced defects observed by transmission electron microscopy at one level of irradiation fits well into the flux pinning model. Additional studies at increased levels of irradiation exposure should contribute further to the understanding of the flux pinning model and to an explanation of the effects of irradiation on the superconducting properties which have already been observed.

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