LETTERS TO THE EDITOR

Electrical Resistivity Increase during Annealing of Cold-Worked or Irradiated Niobium

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There have been a few investigations on low temperature recovery of the body-centred cubic refractory metals^{(1)~(7)}. However, the mechanism of recovery has not as yet been clarified and it is believed that a more extensive study should be done, especially in the case of cold-work experiments. In the present investigation, the author has tried to find out whether the behaviour of low temperature recovery of niobium is affected by the content of interstitial impurity atoms.

Niobium wires of 0.5mm and 0.3mm in diameter were used for the specimens in the cold-work and irradiation experiments, respectively. Nominal values (ppm by weight) of the content of main impurities are as follows: Ta 900, Fe 300, Ti 100, O 100, N 50, C 100, H 10. It is believed that the contents of metallic impurities hardly change during the annealing for specimen preparation. The contents of interstitial impurities were calculated from the value of electrical resistivity of each specimen. This will be described later. Electrical resistivity was measured at liquid nitrogen temperature by means of the ordinary potentiometric technique, in order to follow the recovery process. Recovery anneals were conducted in the bath of the isopentane-liquid nitrogen and the petroleum-benzene-liquid nitrogen mixtures. The latter was used for the annealing at -120°C to room temperature, and the former for that at liquid nitrogen temperature to -120°C . The silicone oil bath was used for the annealing treatments above room temperature. All the specimens were annealed in vacuo (2×10^{-6} mmHg) at 1300°C for two hours before cold-work or irradiation, in order to bring them to a standard state.

Figure 1 shows the isochronal annealing curves for niobium specimens which were deformed by torsion in liquid nitrogen. The degree of cold-work which was represented by surface shear strain was 3.0% for the specimen A and 2.7% for B. The values of the ratio, $R(20)/R(LNT)$ are 4.55 for A and 4.17 for B. Here, $R(20)$ and $R(LNT)$ represent the resistance at 20°C and at liquid nitrogen temperature, respectively. From these values and from the results concerning the relation between the content of interstitial impurity atoms (chemical analysis) and the above values which have

Fig. 1 Isochronal annealing curves for samples deformed by torsion at liquid nitrogen temperature. Degree of cold-work was determined by the equation, degree of cold-work (%) = $100 (r \theta / l)$, where r , l are the radius and length of a sample, respectively. θ is the angle of torsion in unit of radian.

been already obtained by the present author⁽⁸⁾, it is believed that the interstitial impurity contents of A and B are about 280 and 700 ppm by weight, respectively. The curve A shows a small amount of recovery in the vicinity of -80°C , while the corresponding recovery is observed at -60°C in the case of B. Though the mechanism of these recoveries has not been clarified at present, it must be related to the interaction between point defects and impurity atoms. It has been sometimes reported that the range of recovery or recrystallization temperature shifts to a higher region because of the existence of the larger amount of impurities, especially in the case of face-centred cubic metals and iron^{(9)~(11)}.

It should be noted that a resistivity increase was observed in the specimen B which contains a larger amount of interstitial impurity atoms. From this fact it cannot be denied that there is a possibility that a certain impurity effect exists in this temperature range, although the reason why the higher purity specimen

- (1) M. W. Thompson : *Phil. Mag.*, **5** (1960), 278.
- (2) J. Nihoul : *phys. stat. sol.*, **2** (1962), 308.
- (3) C. Minier-Cassayre and D. Dautreppe : *Compt. rend.*, **254** (1963), 2368.
- (4) R. Pichon, C. Minier-Cassayre, V. Hivert and P. Moser : *phys. stat. sol.*, **17** (1966), K 33.
- (5) G. Burger, K. Isebeck, R. Kerler, J. Volkl, H. Wezel, H. H. Kuhlmann and H. Schultz : *Phys. Letters*, **20** (1966), 470.

- (6) Ehab M. Abd El-Salam and J. W. DeFord : *Phys. Rev.*, **161** (1967), 600.
- (7) S. Myhra and J. W. DeFord : *Phys. Rev.*, **188** (1969), 1093.
- (8) To be published.
- (9) R. W. Balluffi, J. S. Koehler and R. C. Simmons : *Recovery and Recrystallization of Metals*, Ed. by L. Himmel, Interscience, (1963), p. 1.
- (10) J. Talbot : *ibid.*, p. 269.
- (11) R. E. Reed-Hill : *Physical Metallurgy Principles*, Van Nostrand, (1964), p. 175.

does not show such behaviour is unknown.

Figure 2 shows the isochronal annealing curves for the specimens irradiated by fast neutrons ($E \geq 1$ Mev, $2 \times 10^{16}/\text{cm}^2$) at liquid helium temperature. After irradiation, the specimens were immersed in a liquid nitrogen bath. The values of ratio of resistance described above suggest that the contents of interstitial impurities are about 400 and 900 ppm by weight for the specimens C and D, respectively.

Fig. 2 Isochronal annealing curves for neutron irradiated samples. Annealing time is three minutes in both cases.

Though the behaviour of recovery is rather complicated, the resistivity increase is observed as in the case of a cold-worked specimen (the curve B in Fig. 1). From a comparison between this result and that of Pichon et al.⁽⁴⁾ or Bürger et al.⁽⁵⁾, it is very likely that the resistivity increase resulted from the existence of a larger amount of interstitial impurity atoms. A considerable recovery observed in the vicinity of 0°C is thought to be due to the formation of interstitial type loops. Tucker⁽¹²⁾ demonstrated that the loops were already formed in niobium immediately after neutron irradiation ($2 \sim 50 \times 10^{17}/\text{cm}^2$) at about 50°C. The fact is consistent with the interpretation above for the recovery near 0°C in the present experiments.

In order to investigate the resistivity increase above 100°C, the resistivity of full-annealed specimen was

measured after the heat treatment in a silicone oil bath in the same manner as that of recovery anneal for the irradiated specimens. The result shows that the resistivity increase, which is believed to originate in contamination from the silicone oil, was about $0.3 \times 10^{-9} \Omega\text{-cm}$ at 200°C and about $1.5 \times 10^{-9} \Omega\text{-cm}$ at 250°C. The resistivity increase shown in Fig. 2 is considerably larger than the values obtained above. From this, it can be considered that contamination from the silicone oil is more easily caused in the irradiated specimens. However, other reasons, e.g. the decomposition of cluster of interstitial impurities, can be also considered. According to Miura et al.⁽¹³⁾ who have studied the recovery of cold-worked niobium, niobium with a large content of oxygen showed the resistivity increase above 200°C, and they attributed it to the decomposition of oxygen cluster. Such behaviour was also observed by the present author⁽¹⁴⁾.

The role of metallic impurities was not referred to so far. However, there may be some possibilities that metallic impurities affect the behaviour of recovery. For example, it can be thought that a compound or complex of metallic and interstitial impurities is decomposed by cold-work or irradiation. This would be one of the reasons for the resistivity increase after cold-work or irradiation. It is also to be thought that there may be the possibility that a metallic impurity-point defect complex is formed. However, since only point defects (except the hydrogen atom) are mobile below room temperature, it is believed that point defects (and/or hydrogen atoms) play the most important role in the low temperature recovery of niobium. Moreover, though the contents of metallic impurities are considered to be nearly the same in specimens A and B, and C and D, the behaviour of resistivity change is different. This would suggest the importance of the role of interstitial impurities in the recovery process of niobium. However, it is difficult to correlate the present results with those obtained by Pichon et al.⁽⁴⁾, Bürger et al. and other workers⁽⁵⁾. More extensive experiments should be done using high-purity or ultra-high purity specimens.

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Motokuni Eto

Graduate School, University of Tokyo, Tokyo.
Present address : Japan Atomic Energy Research
Institute, Ibaraki, Japan.

(12) R. P. Tucker : ORNL-TM-2480 (1968).

(13) S. Miura, J. Takamura and M. Yamashita : Suiyōkwai-Shi, 15 (1965), 395.

(14) J. Mat. Sci., 7 (1972), 567.