boundaries of the twin. However, there appeared more new dislocations, stacking faults and so on, which were not present in crystal before detwinning. Thus, the crystal that had been subjected to twinning contains much more defects of crystal lattice than at the origin.

It is not out of place to mention that near the surface of crystal the number of dislocations, formed by twinning, is essentially more than in its depth. It may be connected with lower energy of formation of lattice defects near the surface of crystal than in the depth of it.

The phenomena described in this report were also observed by us in sodium nitrate crystals, which is a crystallographical analogue of calcite, and in metal crystals.

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Point Defect Clustering in Nickel*

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Point defects were introduced into nickel by neutron bombardment and quenching. Irradiations of 1×10^{18} nvt (total fast flux) were carried out at 70°C and 200°C, and the quenching treatments were varied by quenching to temperatures ranging from −10°C to above the Curie temperature. From the results obtained, it has been concluded that, because of local regions of damage which act as nucleation sites, prismatic dislocation loops are more easily formed in irradiated nickel than in quenched nickel.

Two methods of introducing point defects into a metal crystal are (1) by radiation with high energy particles (2) by quenching. Radiation produces both vacancies and interstitials in local regions of each encounter, whereas rapid quenching from high temperatures will result in a supersaturation of vacancies in a random distribution. Depending upon the temperature, dispersion of point defects, and the activation energy to be surmounted for the formation of various aggregates of point defects, the point defects will either remain dispersed, annihilate opposites, or form clusters of their own species. This investigation contrasts the point defect behavior in nickel produced by irradiation with high energy neutrons and by quenching. The major experimental technique is dependent upon the observations made with the electron microscope. Although single vacancies or interstitials have not been identified by electron microscopy, structures such as prismatic dislocation loops which are directly attributable to a supersaturation of point defects, have been observed in quenched and irradiated metals (see refs. 1–4). Since the energy of a small void below a critical size would be less than that of a prismatic dislocation loop[4], it is probable that voids exist before prismatic dislocations are formed. It is estimated that voids could be seen by electron microscopy because of a mass thickness contrast mechanism only when the void is greater than ten percent of the thickness of the foil. The experiments described are designed to attempt to make visible the structures which result from various neutron irradiation treatments and

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various quenching treatments.

Bulk specimens of a high purity nickel (Johnson and Matthey, 99.998%) were subjected to 1×10^{18} nvt (total fast flux) in the Brookhaven reactor. After the exposure, these specimens were thinned down to electron transparency and viewed in the electron microscope. A large number of irradiated nickel specimens were studied; however, no signs of any visual alterations directly attributable to the neutron bombardment have been seen although the physical and mechanical properties of the nickel are changed by similar irradiations[5]. In contrast to nickel, irradiated copper is found to contain dark spots which have been identified as prismatic dislocation loops. The cascade of point defects in the vicinity of a primary knock-on of a given energy will be about the same in nickel and copper. An estimate of the condition of the disturbed region can be made by considering the mean free path between the successive encounters[5]. If the Bohr radius is used for the determination of the screening constant, then the mean free path between displacements of various energies is shown in Fig. 1. If larger values of the Bohr radius are used, then the L_j curve is displaced downward. It is seen from Fig. 1 that the mean free paths for copper and nickel are similar. In addition, calculations of the number of vacancy interstitial pairs using the present theory[6] indicate that the number of defects originating from the same energy neutrons will be nearly the same for both metals. Thus, the initial stages of the knock-on in copper and nickel should be similar. The disparity in the observable structures, therefore, must be due to some other origin. One important factor that influences the formation of prismatic dislocation loops is the rate at which the point defects can come together and form a loop. The rate of diffusion of point defects is considerably different in copper and in nickel, and, therefore, elevated temperature experiments were carried out with irradiated nickel.

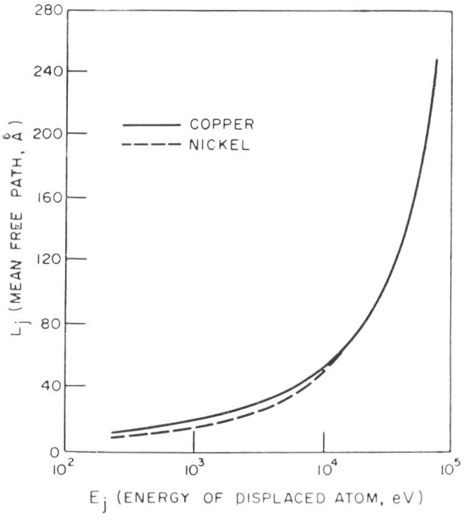

Fig. 1. Mean free path between encounters for energy E_j.

Since point defects are certain to be present in irradiated nickel, further annealing could produce defect agglomeration which may result in an observable structure. Annealing treatments were carried out on nickel that was irradiated at pile temperature (less than 70°C). The temperatures of the anneals were 148°C, 180°C, 200°C, 250°C, and 400°C. The results at various times are shown in Table I.

The lower temperature annealing treatments did not produce any observable struc-

Table I

Annealing Temp.°C	Time (sec.)	Loop Density (cm^{-3})	Diffusion distance (cm)	
			$v_1 = 10^{-4}$ *	$v_1 = 10^{-2}$
148	7.2×10^3	no loops	4×10^{-10}	4×10^{-9}
	6.0×10^5	no loops	4×10^{-9}	4×10^{-8}
180	1.4×10^4	no loops	2×10^{-8}	2×10^{-7}
200	3.5×10^5	6×10^{13}	1×10^{-7}	1×10^{-6}
250	1.4×10^4	—	1×10^{-7}	1×10^{-6}
400	2.3×10^4	1.4×10^{14}	2×10^{-6}	2×10^{-5}

* v_1 is the density of vacancies, assumed at the two indicated levels.

ture which could be associated with neutron irradiation. After the annealing treatments at 200°C and 400°C, however, some agglomeration in the form of prismatic dislocation loops was apparent in the thinned foils. Fig. 2 is a photomicrograph of the resulting structure after annealing at 200°C for 3.5×10^5 sec. Loops were not discernible in the 250°C anneal; however, surface roughness of these particular specimens may have hidden any fine structures.

If the mobility of the vacancies are considered at the various annealing temperatures, the diffusion length, L_D, can be calculated for the above treatments. The

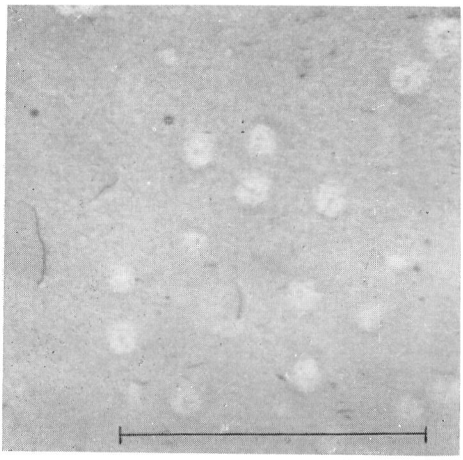

Fig. 2. Nickel irradiated at about 70°C and annealed at 200°C for 3.5×10^5 sec. Note prismatic dislocation loops.

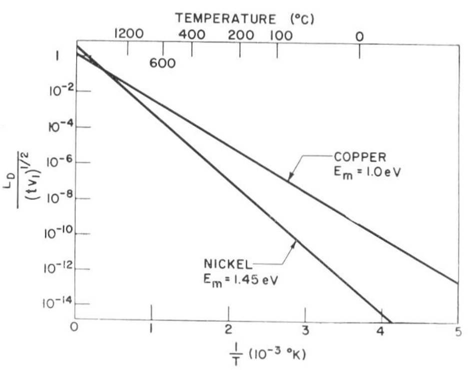

Fig. 3. $\frac{\text{Diffusion length}}{(\text{time}\times\text{fraction vacancies})^{1/2}}$ as a function of $1/T$.
For copper[8] $D=0.34\exp(-2.0/kT)$; nickel[9] $D=1.27\exp(-2.9/kT)$. E_m is assumed to equal E_f and thus $E_m=1/2\,E_D$ where E_f=activation energy of formation and E_D=activation energy for self diffusion.

diffusion length[7] is equal to $2\,(Dt)^{\frac{1}{2}}$, where

$$D=Cv_1\exp(-E_m/kT)$$

and D=diffusion coefficient, t=time of diffusion, C=constant, v_1=fraction of vacancies, E_m=activation energy for the movement of vacancies, and T=the absolute temperature. In Fig. 3, $L_D/(tv_1)^{\frac{1}{2}}$ is plotted against T^{-1}. From this graph, the diffusion length for the various annealing treatments can be obtained if the vacancy concentration is known. Although the increase in the average vacancy concentration in nickel for a given neutron exposure can be calculated, it is difficult to estimate the local concentration of vacancies in the vicinity of the knock-on because of the unknown shape and size of the cascade and the uncertainty of the amount of recombination of some of the vacancies and interstitials. However, it is reasonable to assume values for v_1 between 10^{-2} and 10^{-4}. If the loops could be associated with the coalescence of vacancies, then for a concentration of vacancies of 10^{-2}, $L_D=10^{-6}$ cm for an observable density of 6×10^{13} cm^{-3} and $L_D=2\times 10^{-5}$ cm for an observable density of 14×10^{13} cm^{-3}. The values of L_D for $v_1=10^{-4}$ are listed in Table I. Apparently, the vacancies did not travel far before agglomeration products were formed. From these experiments one can conclude that some of the originally-produced clusters of vacancies have remained dispersed throughout the specimen for a long time subsequent to the irradiation; and, after the proper heat treatment, either the interstitials or the vacancies agglomerated. However, it is significant that for the greatest L_D the loop density is about 1/10 of that obtained with irradiated copper. Apparently, some annihilation of vacancies and interstitials had taken place between the time of irradiation and the formation of the prismatic dislocations.

In a further series of experiments, nickel was irradiated at an elevated temperature where the diffusion length of the vacancies is about the same as the diffusion length of the vacancies in copper at a pile temperature of 70°C. From Fig. 3 an equivalent diffusion length is found at approximately 200°C. A high temperature hole was obtained at the Brookhaven reactor, and the nickel bulk specimens were irradiated at 200°C. Thin films were made from these bulk specimens,

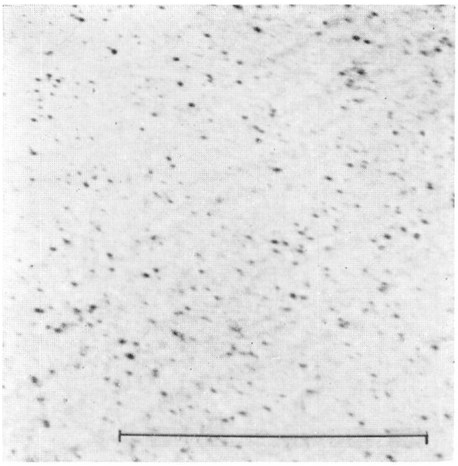

Fig. 4. Nickel irradiated at 200°C.

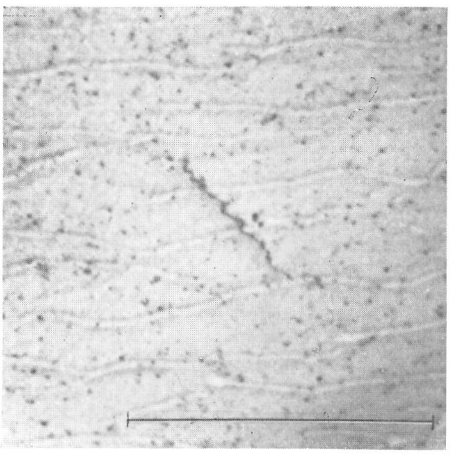

Fig. 5. Nickel irradiated at 200°C. Note the kinked appearance of the glide dislocations.

and a typical structure is shown in Fig. 4. The many dark spots that have appeared in this photo-micrograph are definitely a product of the neutron irradiation. The density of these spots is of the order of $2.3 \times 10^{15}/cm^3$ and is of the same magnitude as that of the loop density in the irradiated copper. In Fig. 5, the interaction of these spots with dislocations show kinked portions of the dislocations similar to the configurations seen in irradiated copper.

For the irradiation treatment at 70°C—in contrast to the irradiation at 200°C— it may be concluded that the lack of observable structures may be a result of a temperature too low for either (1) sufficient diffusion of point defects, or (2) overcoming an activation energy of nucleation. The predicted configuration of vacancies and interstitials around a knock-on consists of a region in which the central portion contains a high concentration of vacancies surrounded by an interstitial "shell." Consequently, it would be expected that for cases in which the diffusion distances for vacancies, interstitials, or both are comparable to the size of the knock-on region, there would be a large cancellation of the vacancies with the interstitials. If however stable aggregates of similar point defects are nucleated rapidly, there would be a smaller chance for large amounts of recombination. Moreover, when the point-defect clusters remain in the lattice for a length of time, a great deal of annihilation can occur. This may explain why fewer loops are formed after annealing of irradiated samples than are formed in samples irradiated at 200°C. Makin[10] has proposed that interstitial loops are formed during the irradiation of copper; but since interstitials are more mobile than vacancies, the 70°C irradiation of nickel should have produced some loops. These were not seen, and it is therefore inferred that interstitial prismatic loops do not form during neutron bombardment of nickel.

The quenching experiments have been conducted in the following manner: Strips of polycrystalline nickel (Johnson and Matthey nickel as described above) contained in an evacuated quartz tube were quenched from 1250°C and 1430°C into iced brine. The examination of the thinned specimens yielded negative results; namely, with the exception of a small number of dislocations and a few singular large loops, the expected magnitude of loop density was not found. Since the quenching in the above experiment is considered to be slow quench and since loops were only seen in irradiated nickel when irradiation was carried out at 200°C, a more versatile apparatus was devised for rapid quenching with various temperature quenching baths. In order to cover a temperature range from −10°C to above the Curie temperature of nickel, two separate devices were constructed and are illustrated in Fig. 6.

For this series of experiments zone melted nickel strips $10 \times 3 \times 0.7$ mm were quenched from about 1225°C to various temperatures

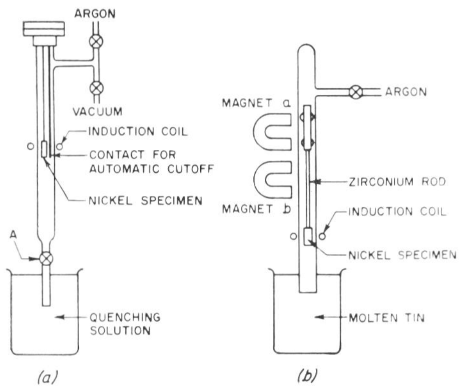

Fig. 6. (a) Quenching from above 1200°C to temperatures from −10°C to 200°C. Iced brine and LiBr solutions used for quenching bath. (1) Specimen is heated in argon to about 1225°C; (2) the pressure of the argon is reduced; (3) valve A is opened and the liquid is drawn up to the specimen; (4) just before specimen is quenched, the induction furnace is automatically cut off by the liquid.
(b) Quenching from 1225°C to 333°C and 380°C. (1) High purity argon is bubbled through the molten tin and purified by heating the zirconium rod; (2) The specimen is heated and dropped into the tin by removing magnet a; (3) Magnet b is used to remove the specimen from the tin.

(−10°C to 380°C). Few prismatic loops were found in the series of quenches from −10°C to 200°C. In the high temperature quenches below and above the Curie point (333°C and 380°C), a large number of spherical spots were seen which are either voids or small loops of about 100 to 500 Å in diameter. The structures below and above the Curie point, however, were essentially alike. The suggestion by Mader, Seeger and Simsch[11] that prismatic loops are difficult to form below the Curie temperature because of demagnetization effects does not seem to be relevant. In addition, since the zone-melted nickel used in these experiments was purer than the nickel previously used, it appears that the change in impurities did not affect the results.

If the quenching results are contrasted with the irradiation and annealing information, it is seen that, for comparable annealing times, loops are formed in the irradiated nickel and not in the quenched nickel. Thus, it appears that, in addition to the dependence of the diffusion length, the formation of loops are dependent upon the local distribution of defects.

The dislocation patterns in neutron irradiated, deformed nickel have been discussed in an earlier paper[12]. It was found that the dislocations were extremely irregular and that many small dislocation loops were distributed throughout the volume through which dislocations had moved. In addition, upon further examination of thin foils made from neutron irradiated and deformed nickel strips ($50\times3\times0.5$mm), cross-slip was frequently observed. Cross-slip also occurred in specimens which were taken from samples after their exposure to a fast flux of 10^{18} nvt and in others which were annealed for 1 hour at 200°C after neutron bombardment. In Fig. 7 it can be seen that

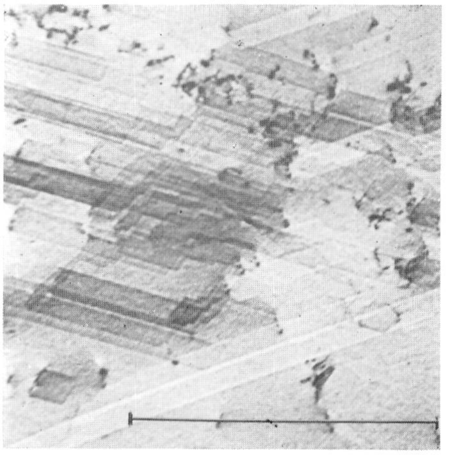

Fig. 7. Cross slip in nickel irradiated at 70°C.

dislocations have moved in the foil during observation in the electron microscope leaving trails which indicate the path travelled by them. Obviously, many dislocations have cross-slipped repeatedly. This phenomenon had been predicted to occur in crystals with excess vacancies[13].

Nickel has a relatively small stacking fault energy which is given in the literature as about 90 ergs/cm^2 [14),15)]. An extended dislocation may possibly cross-slip if it is subjected to rather high stresses as may be prevalent in Stage III of the stress-strain curve. This condition is not satisfied when dislocation motion in thin foils is induced by a high intensity electron beam. It was concluded that the phenomenon of cross-slip in nickel was due to the interaction of vacancies with dislocations. If the number of vacancies in a crystal exceeds the equilibrium concentration, an atmosphere of vacancies will be formed around moving dislocations[16]. The effect of vacancies on dislocations is to reduce the core energy, and moreover, on extended dislocations to cause jogs for which constrictions are a geometrical necessity. As had been pointed out earlier[16], vacancy atmospheres will be formed only around slow moving dislocations, and this condition is exactly fulfilled in our experiment. The above result is in accordance with observations of cross-slip in foils of other f.c.c. crystals having a low stacking fault energy; it was reported in neutron irradiated foils of stainless steel[17] and in foils of quenched gold[18].

Summary

"Low temperature" irradiation or various quenching treatments from above 1225°C to temperatures ranging from −10°C to 200°C did not directly produce any associated structures. After annealing treatments at 200°C and 400°C, prismatic dislocation loops were seen in the irradiated nickel; whereas for annealing treatments up to 300°C, no loops were noted in the quenched nickel. It has been reported, however, that prismatic dislocation loops have been seen after annealing above the Curie temperature[11]. Apparently, prismatic dislocation loops are more readily formed in a material which has been bombarded with high energy neutrons. The relative ease of formation can be attributed to regions of high local damage which act as nucleation sites for loops. The exact form and size of the damaged regions cannot be accurately evaluated because they are too small to be observed by the electron microscope. Large amounts of cross slip due to the vacancy concentration are seen in dislocations moving in foils of irradiated nickel.

Dark spots are observed in nickel that was irradiated at 200°C, a temperature at which the vacancies in nickel have about the same mobility as the vacancies in copper that is irradiated between 30°C and 70°C. The resultant visible defects are found to be similar in the two metals. Quenching to high temperatures above and below the Curie temperature resulted in similar structures refusing the concept that magnetization effects are of prime importance with regard to the agglomeration of point defects in nickel.

Acknowledgements

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DISCUSSION

Cahn, R. W.: At Birmingham recently we have done some tensile experiments to look for quench-hardening in nickel. After quenching from 800°C, there was no detectable increase in flow stress of pure (carbonyl) nickel, not even after a short subsequent anneal at 200°C. Can Dr. Wilsdorf offer any explanation of this negative result?

Wilsdorf, H. G. F.: On first sight there seem to be two reasons why nickel specimens quenched from 800°C do not show a measurable increase of the flow stress as compared with that obtained from annealed crystals: (i) a temperature of 800°C appears to be too low for introducing a significant vacancy concentration. (ii) It is known from other metals, for example copper, that heat treatments are necessary to bring out quench hardening. Presumably, a temperature of 200°C is too low for the development of quench hardening.

Brandon, D. G.: I would like to ask two questions on the interpretation of thin film observations. Firstly, how do you distinguish between surface graininess, which is very apparent in nickel, and bulk diffraction contrast? Secondly, to what extent do you think dislocation movement observed in films of 1000 Å thickness or less is typical of bulk material and what significance do you attach to the observation of stacking faults in these thin films?

Wilsdorf, H. G. F.: Dr. Brandon's question regarding the influence of surface "graininess" on the reliability of observations due to diffraction contrast is very appropriate. Thin nickel specimens are indeed difficult to prepare and often show a surface roughness in the electron microscope. However, this surface structure is the same for annealed, quenched and neutron irradiated specimens, and, from experiences over a period of three years, we believe that contrast due to surface roughness as compared to that caused by lattice strains, *i.e.* prismatic dislocation loops etc., can be distinguished unambiguously. Moreover, "bulk contrast" is most sensitive to tilting the specimen while the change of contrast due to the surface structure is less sensitive and never disappears completely. Answering the second question, I will restrict myself to discussing the observations of stacking faults and cross-slip in the context of the paper. The presence of large stacking faults, frequently seen when glide dislocations move through thin foils prepared from annealed nickel, was quoted in order to contrast the occurrence of cross-slip in neutron irradiated material. While the production of large stacking faults will not occur in bulk specimens, the contraction of extended dislocations due to the influence of point defects is expected to take place in thick crystals.