Effects of 14 MeV Nickel Ion Irradiation on Nickel-Copper Alloys Observed in Cross-Section

L.M. Wang, R.A. Dodd, G.L. Kulcinski

October 1987

UWFDM-731

. Presented at the 3rd International Conf. on Fusion Reactor Materials, 4–8 October 1987, Karlsruhe, FRG.

FUSION TECHNOLOGY INSTITUTE

UNIVERSITY OF WISCONSIN

MADISON WISCONSIN

Effects of 14 MeV Nickel Ion Irradiation on Nickel-Copper Alloys Observed in Cross-Section

L.M. Wang, R.A. Dodd, G.L. Kulcinski

Fusion Technology Institute
University of Wisconsin
1500 Engineering Drive
Madison, WI 53706

http://fti.neep.wisc.edu

October 1987

UWFDM-731

. Presented at the 3rd International Conf. on Fusion Reactor Materials, 4–8 October 1987, Karlsruhe, FRG.

EFFECTS OF 14 MeV NICKEL ION IRRADIATION ON NICKEL-COPPER ALLOYS OBSERVED IN CROSS-SECTION

L.M. WANG, R.A. DODD and G.L. KULCINSKI

Fusion Technology Institute, University of Wisconsin,
1500 Johnson Drive, Madison, WI 53706-1687, USA

ABSTRACT

Two Ni-Cu alloys, Ni-10 at.% Cu and Ni-50 at.% Cu, as well as pure Ni were irradiated with 14 MeV Ni ions at a homologous temperature of $T/T_m = 0.45$ up to 100 dpa at the peak damage depth. Most of the samples were pre-injected with 5 MeV oxygen ions at room temperature before Ni ion irradiation. The depth dependence of the ion damage structure was studied by TEM with the samples prepared in cross-section. The results obtained from the Ni-Cu alloys and pure Ni are compared.

While voids formed readily in the oxygen implanted Ni after Ni ion irradiation, most defect clusters in the irradiated Ni-Cu alloys were dislocation loops. Voids observed in Ni-10Cu alloy were mostly located in the oxygen implanted region, with only a few located at the peak damage depth. No voids were found in the Ni-50Cu alloy. The dislocation loop density in the Ni-50Cu samples was 5-7 times higher than that in the Ni-10Cu samples; however, the loop size was much larger in the latter. The mechanism of void suppression in Ni-Cu alloys is discussed in terms of the trapping of vacancies and gas atoms.

1. Introduction

The Ni-Cu system is one of the few simple alloy systems which form a complete solid solution over the entire composition range. While voids can easily be produced in both pure Ni and pure Cu by irradiation, the concentrated Ni-Cu alloys have been shown to be very resistant to void formation under neutron[1], ion[2-4] and electron[5] irradiations. However, the database for the irradiation of Ni-Cu is still quite small, and the cause of the suppressed void formation in the alloy remains uncertain[6]. Although Ni-Cu alloys are unlikely to be used as structural materials in future fusion reactors, the response of such a system to irradiation merits more detailed study in the view of the considerable importance attached to the understanding and control of void formation.

In the present study, we have investigated the effects of 14 MeV Ni ion irradiation on two Ni-Cu alloys, Ni-10Cu (atomic %) and Ni-50Cu, using the cross-section technique[7] which allows the entire ion damage region to be viewed at once by transmission electron microscopy (TEM). The effect of oxygen in the alloys was also investigated since oxygen has been shown to promote void formation in Cu and Ni both theoretically and experimentally[8-12].

2. Experimental Procedure

The two Ni-Cu alloys, Ni-10Cu and Ni-50Cu, were fabricated from Marz grade Ni (99.995 wt.% pure) and Cu (99.999 wt.% pure) in an arc melter. Before melting, the chamber of the melter was evacuated to 2.6 Pa then flushed with Ar gas five times. A Ti getter was used to absorb active gases during melting. The ingots were inverted and remelted for several times after the original melting, and then treated in flowing Ar at 1000°C for 24 hours to assure homogeneity. Analyses performed by Los Alamos National Laboratory, using a vacuum fusion technique, indicated the oxygen content in the alloys is about 100 appm. The ingots of the alloys were cold rolled with intermittent annealing in flowing Ar at 800°C to 0.5 mm thick foils. The foil samples were then mechanically polished with 0.3 μm alumina abrasive.

Three samples of each alloy were irradiated with 14 MeV Ni^{3+} ions at the University of Wisconsin Heavy-Ion Irradiation Facility with a flux of 3×10^{16} Ni^{3+}/m^2 s at a homologous temperature of T/T_m=0.45, i.e. 485°C for Ni-10Cu and 425°C for Ni-50Cu. The fluences were chosen according to a Monte Carlo calculation[13] to give peak damage levels of 20, 40 and 100 dpa. The samples with peak damage levels of 20 and 40 dpa were pre-injected with 5 MeV oxygen at room temperature to an average concentration of 100 appm in the region 1.3-2.0 μm below the surface. The distributions of the injected 5 MeV oxygen and 14 MeV Ni ions as well as the displacement damage caused by 14 MeV Ni ions in the Ni-10Cu alloy calculated by a Monte Carlo code, TAMIX, are shown in Fig. 1. One Ni sample irradiated earlier[11] with 14 MeV Ni ions to a peak damage of 15 dpa at 500°C, which is also 0.45 T_m, is also included in this study for comparison. The Ni sample had a bulk oxygen concentration of 75 appm and contains an additional 75 appm injected oxygen in the first ~1.2 μm region. After irradiation, all of the samples were prepared in cross-section for TEM observation and analyzed under a JEOL TEMSCAN-200CX electron microscope.

3. Results

The defect characteristics of all seven irradiated samples are summarized in Table 1. The void density, void size and dislocation loop density listed are all counted from the region of about 1.5 (1.3-1.8) μm from the irradiated surface unless noted in the table. This is the region where the injected oxygen ions come to rest and the effect of the injected Ni interstitials[14] would not be significant. It should be noticed that the dpa level at that depth is about half the peak level.

Voids are the only significant kind of the defect cluster observed in the irradiated Ni sample. The void distribution in the entire irradiated region in the sample is shown in Fig. 2. The high density of smaller voids in the first ~1 .2 μm region, which contains 75 appm injected oxygen, gives strong evidence of the effect of oxygen in promoting void formation.

Figs. 3 and 4 show the entire damage region of the two Ni-Cu alloys irradiated to the peak damage level of 20 dpa. In the Ni-10Cu sample, most defect clusters are dislocation loops (Fig. 3(a)), although some voids are also observed by tilting the loops out of contrast (Fig. 3(b)). The voids are mainly located in the oxygen implanted region, with only a few voids with an average diameter of 8 nm occurring at the peak damage depth. In the Ni-50Cu sample, dislocation loops with much smaller size and much higher density are observed (Fig. 4(a)), and no voids were found when the loops were tilted out of contrast (Fig. 4(b)). The latter fact remains true even after a careful examination for all the three irradiated Ni-50Cu samples at a magnification of 100,000x.

It should be mentioned that a surface layer of ~0.3 μm thick was removed from all samples during the process of cross-section specimen preparation to assure good bonding at the interface, so the actual depth from the irradiated surface is 0.3 μm more than the depth from the interface indicated in the cross-section micrographs (Figs. 2-4). Also, the injected oxygen region in the Ni sample is 0.8-1.0 μm closer to the interface than in the alloys because of a special operation after the pre-injection[11].

In the Ni-10Cu sample irradiated to 40 dpa at the peak, the void distribution was rather heterogeneous. Some larger voids (~50 nm in diameter) surrounded by many smaller voids (~5 nm in diameter) were observed in the oxygen implanted region, which implies the agglomeration of smaller voids during the continuous irradiation. Only one larger void (125 nm in diameter) was found at the damage peak region. Some voids were also found in the Ni-10Cu sample irradiated to 100 dpa at the peak without oxygen pre-injection, but they were all located in the peak damage depth (~2.2 μm from the original surface). In Fig. 5 the void structures in the irradiated Ni and Ni-10Cu samples are compared.

Fig. 6 gives a comparison of the dislocation structures in the Ni-10Cu alloy with various irradiation conditions, and Fig. 7 gives that comparison for the Ni-50Cu alloy. In Fig. 8, the distributions of the dislocation loop size in the six Ni-Cu alloy samples are compared. Through the above comparisons, it is quite clear that higher doses generally produce larger loops in both alloys, and that the loop density in the Ni-50Cu alloy is 5-7 times higher than that in the Ni-10Cu alloy under the same irradiation conditions, while the loop size is much larger in the latter.

4. Discussion

The results of this study support the previous findings that voids are increasingly more difficult to form with increasing Cu content for the Ni-based Ni-Cu alloys[2, 5]. The reason for the void suppression is of great interest. Brimhall and Kissinger[1] have excluded the possibility of void suppression in Ni-Cu alloys due to a stacking fault energy effect or differences in diffusion between the alloys and the pure metals, because the stacking fault energy is 50% higher in Ni-50Cu as compared to pure Cu[15], and the effective migration energies of point defects in the alloys change monotonically and continuously between values for pure Ni and pure Cu[16]. However, their explanation based on trapping of point defects by single solute atoms in the solution breaks down for the Ni-50Cu alloy. Mazey and Menzinger[2] proposed the possibility of trapping of vacancies and interstitials at the boundaries of fine-scaled clusters having compositions different from the matrix. Their explanation seems more plausible, but they did not give further elaboration of the mechanism.

More information has now become available in the literature which seems to be strong evidence suggesting that clustering takes place in Ni-Cu alloys during irradiation[17-19]. The clustering in the alloy is also justified by thermodynamic considerations. A miscibility gap has been included in the Cu-Ni phase diagram[20] based on a calculation of Elford et al.[21], although it could not be experimentally verified because of the low temperature[22]. In addition, the positive value of the heat of mixing of the Ni-Cu system[23] suggests a repulsive interaction between unlike atoms based on a regular solution assumption[24]. In this case, it means $E_{Cu\text{-}Ni} > 1/2(E_{Cu\text{-}Cu} + E_{Ni\text{-}Ni})$ where E is the near-neighbor bonding energy. Thus, there is a tendency for clustering of like atoms to occur in Ni-Cu alloys, as long as the entropy change due to clustering is not important, which is true at lower temperatures[24]. The boundaries of clusters might trap vacancies and gas atoms to reduce the high bonding energy as well as the strain energy. The traps can operate as nucleation sites for vacancy clusters. When a high density of this kind of trap is present, the arrival rate of irradiation produced vacancies at each site will be low, so the small vacancy clusters will not grow fast enough to reach the critical size of the void embryo before collapsing into dislocation loops. This inhibits void formation in the alloys. Although the vacancy/interstitial nature of the dislocation loops observed in this study has not been determined by experimental work at this stage, it seems to be reasonable to assume that at least most of the smaller loops are vacancy type by comparing with the work of Leister[3]. On the other hand, it is apparent that Ni-50Cu will contain more fine-scaled clusters of like atoms than Ni-10Cu; in other words, more vacancy traps are present in Ni-50Cu than in Ni-10Cu. Therefore, the higher resistance to void formation and the higher density of dislocation loops observed in the Ni-50Cu can be explained.

5. Summary

The resistance to void formation of concentrated Ni-Cu alloys is confirmed by TEM cross-section observation of the 14 MeV Ni ion irradiated Ni-10Cu and Ni-50Cu alloys with damage levels up to 100 dpa at the peak.

Irradiation produced a substantial number of dislocation loops in both alloys, but the loop size is much smaller and their density is 5-7 times higher in Ni-50Cu than in Ni-10Cu.

Pre-injection of 100 appm oxygen before Ni ion irradiation promotes void formation in Ni-10Cu, but does not show any apparent effect in the case of Ni-50Cu.

Trapping of vacancies and gas atoms by fine-scaled clusters of like atoms is considered the mechanism responsible for the void resistant property of the alloys.

Acknowledgement

The authors wish to thank S. Han for performing the calculation of dpa and injected ion distributions in the Ni-Cu alloy using his new computer code. This research is supported by the U.S. Department of Energy, Office of Fusion Energy.

References

[1] J.L. Brimhall and H.E. Kissinger, Rad. Eff. 15(1972)259.

[2] D.J. Mazey and F. Menzinger, J. Nucl. Mater. 48(1973)15.

[3] K-H. Leister, PhD Thesis, Kernforschungszentrum Karlsruhe (May, 1983).

[4] P. Dauben and R.P. Wahi, Progress Report No. 2 (1981-1984), Reports of Hahn-Meitner-Institute.

[5] P. Barlow, PhD Thesis, University of Sussex (April, 1977).

[6] S.J. Zinkle, R.A. Dodd, G.L. Kulcinski and K. Farrell, J. Nucl. Mater. 117(1983)213.

[7] S.J. Zinkle and R.L. Sindelar, Nucl. Instr. and Meth. B16(1986)154.

[8] L.D. Glowinski and C. Fiche, J. Nucl. Mater. 61(1976)29.

[9] S.J. Zinkle, W.G. Wolfer, G.L. Kulcinski and L.E. Seitzman, Phil. Mag. A55(1987)127.

[10] S.J. Zinkle, PhD Thesis, University of Wisconsin (May, 1985).

[11] L.E. Seitzman, L.M. Wang, G.L. Kulcinski and R.A. Dodd, J. Nucl. Mater. 141-143(1986)738.

[12] L.M. Wang, R.A. Dodd and G.L. Kulcinski, J. Nucl. Mater. 141-143(1986)713.

[13] S. Han and G.L. Kulcinski, to be published in: Fusion Reactor Materials, DOE/ER-0313/2.

[14] B. Badger, Jr., D.L. Plumton, S.J. Zinkle, R.L. Sindelar, G.L. Kulcinski, R.A. Dodd and W.G. Wolfer, ASTM STP 870 (1985) p. 297.

[15] P.C. J. Gallagher, Met. Trans. 1(1970)2429.

[16] F. Lihl and H. Wildhack, Z. Metallk. 62(1971)143.

[17] W. Schule, P. Spindler and E. Lang, Z. Metallk. 66(1975)50.

[18] R. Poerschke and H. Wollenberger, Thin Solid Films 25(1975)50.

[19] R. Poerschke and H. Wollenberger, Rad. Effects 49(1980)225.

[20] Metals Handbook, 8th edition (American Society for Metals), Vol. 8 (1973) p. 294.

[21] L. Elford, F. Muller and O. Kubaschwski, Ber Bunsenges Physik Chem. 73(1969)601.

[22] M. Hansen, Constitution of Binary Alloys, 2nd edition (McGraw-Hill, 1958).

[23] INCRA Monograph on the Metallurgy of Copper, I. Selected Thermodynamic Values and Phase Diagrams for Copper and Some of Its Binary Alloys (International Copper Research Association, Inc., 1971, Eds. R. Hultgren and P.D. Desai) p. 126.

[24] R.A. Swalin, Thermodynamics of Solids (John Wiley & Sons, New York, 1972) p.146.

Table 1
Defect characteristics of 14 MeV Ni ion irradiated Ni-Cu alloys

No.	Material	Oxygen pre-injected (appm)	dpa (peak)	dpa (1.5 μm)	Voids* density (m^{-3})	Voids* average size (nm)	Dislocation loops* density (m^{-3})
(1)	Ni	75	15	7	~$1x10^{21}$	29	——
(2)	Ni-10Cu	100	20	10	~$7x10^{19}$	12	~$1x10^{21}$
(3)	Ni-10Cu	100	40	20	~$1x10^{20}$	5 (90%) 53 (10%)	~$1x10^{21}$
(4)	Ni-10Cu	none	100	50	not observed at 1.5 μm ~$9x10^{19}$ (peak damage region)	14 (peak damage region)	~$1x10^{21}$
(5)	Ni-50Cu	100	20	10	not observed		~$7x10^{21}$
(6)	Ni-50Cu	100	40	20	not observed		~$5x10^{21}$
(7)	Ni-50Cu	none	100	50	not observed		~$5x10^{21}$

* Counted in a region of 1.5 (1.3~1.8) μm from the irradiated surface unless noted.

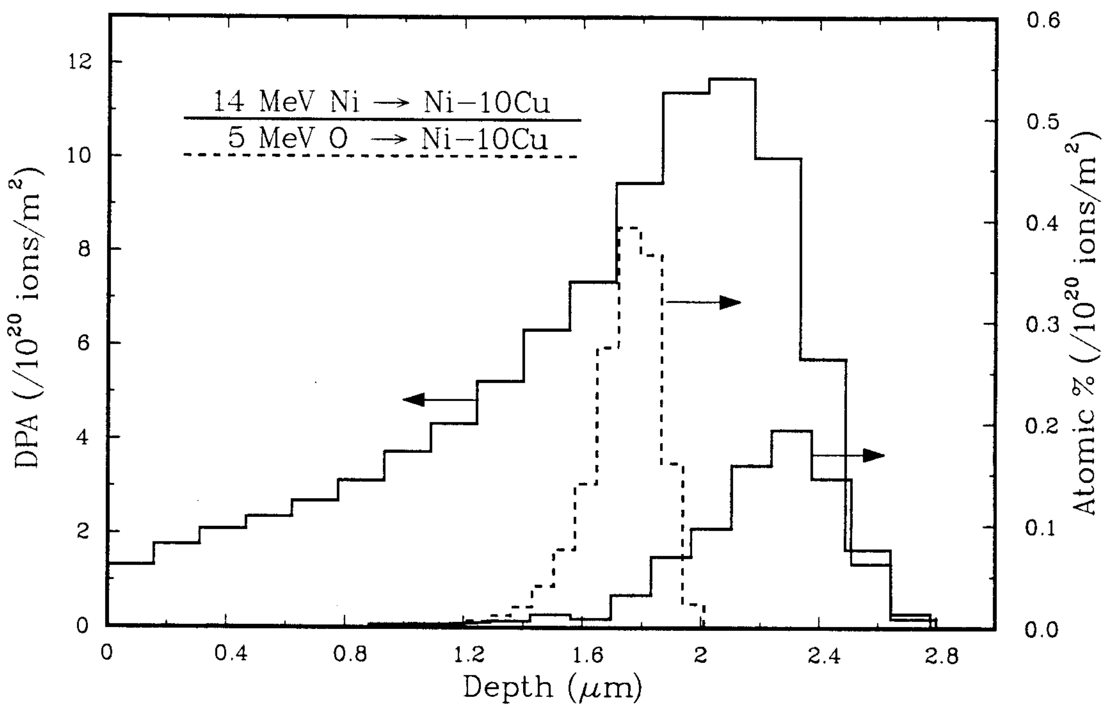

Fig. 1 Displacement damage (by 14 MeV Ni ions only) and injected ion distribution (14 MeV Ni ions and 5 MeV oxygen ions) in Ni-10Cu calculated by using the TAMIX code[13].

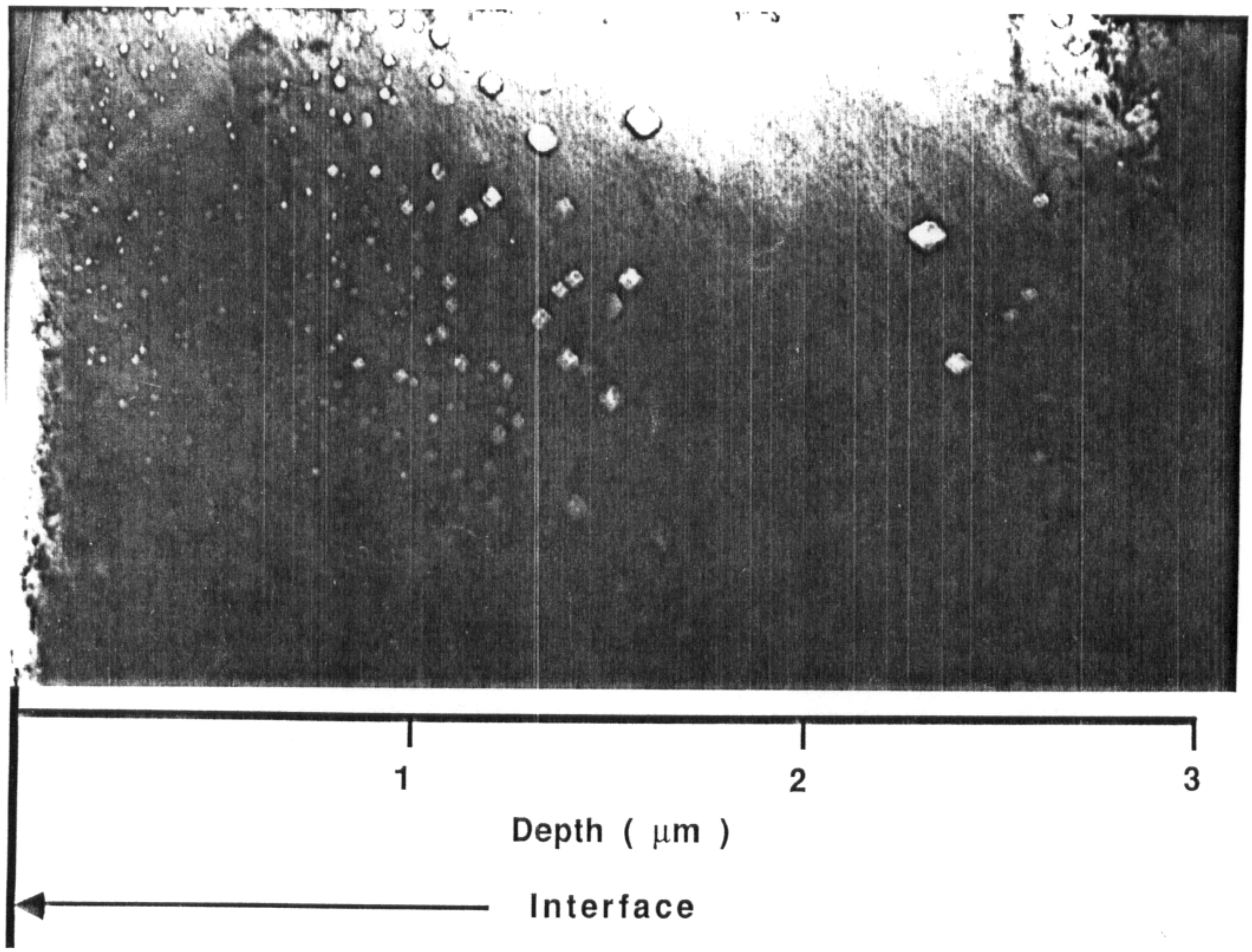

Fig. 2 TEM cross-section micrograph showing void distribution in 14 MeV Ni ion irradiated Ni. Damage level at peak damage depth (~2μm) is 15 dpa. 75 appm oxygen was pre-injected in the first 1.3 μm region. Since about 0.3 μm was removed from the original surface, the actual distance from the original irradiated surface should be the distance from the interface plus 0.3 μm.

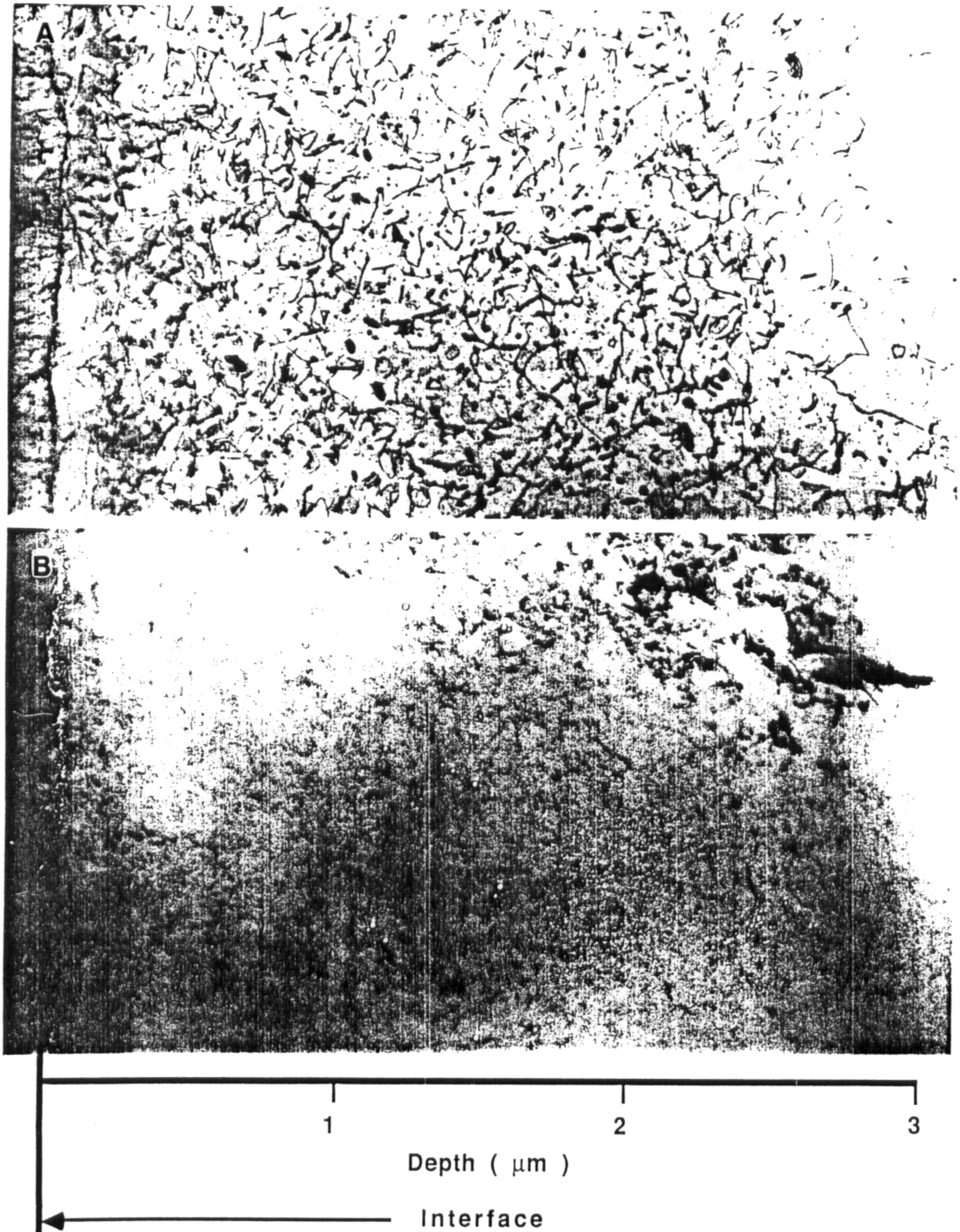

Fig. 3 TEM cross-section micrographs showing (a)dislocation loop and (b)void distribution in a Ni-10Cu sample with a peak damage level of 20 dpa and 100 appm oxygen pre-injected in the region of 1.5-2 μm from the original surface. (b) was taken by tilting the dislocation loops out of contrast. Since about 0.3 μm was removed from the original surface, the actual distance from the original irradiated surface should be the distance from the interface plus 0.3 μm.

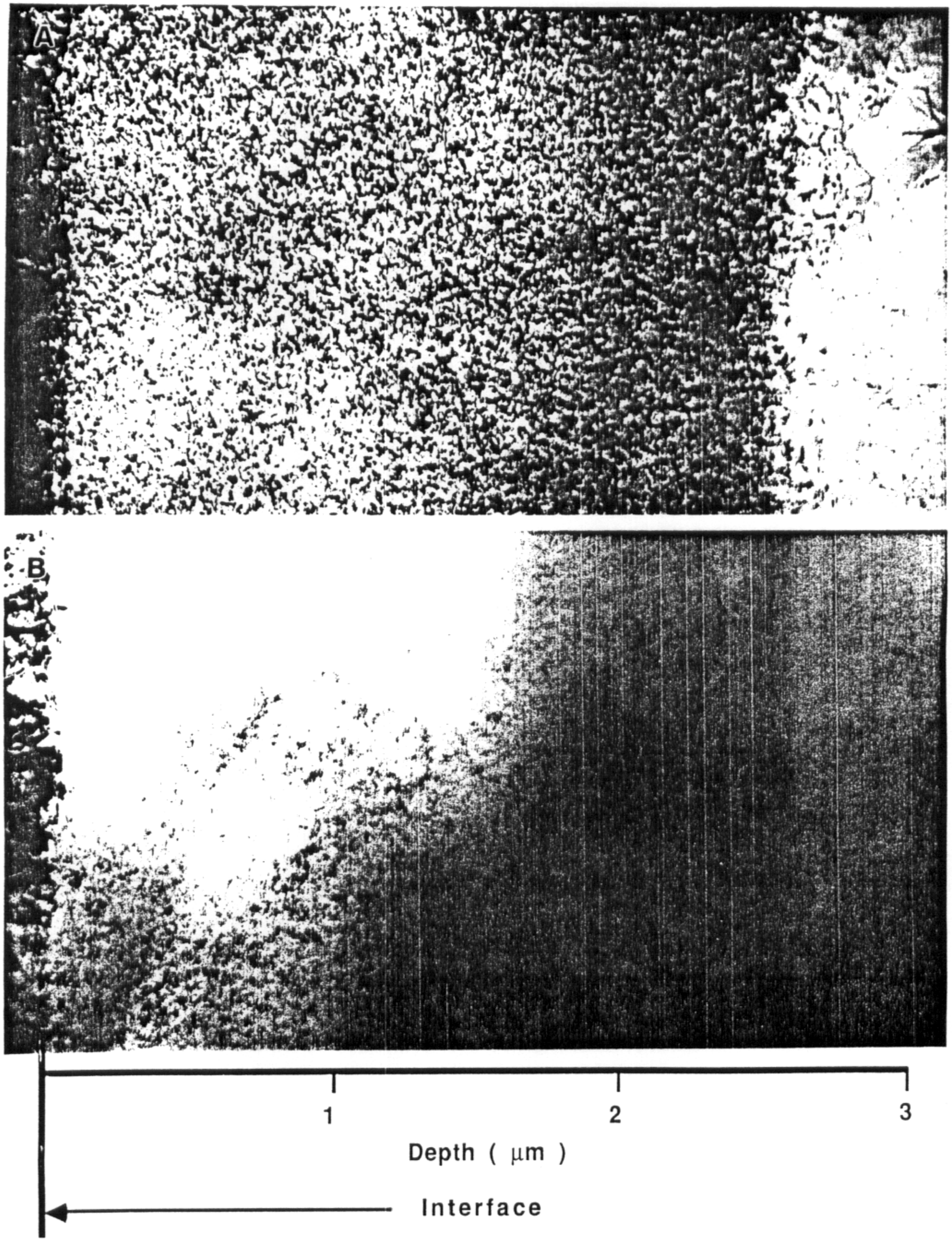

Fig. 4 TEM cross-section micrographs obtained from a Ni-50Cu sample with a peak damage level of 20 dpa and 100 appm oxygen pre-injected in the region of 1.5-2 μm from the original surface. (a) dislocation loop distribution; (b) loops tilted out of contrast showing absence of voids. Since about 0.3 μm was removed from the original surface, the actual distance from the original irradiated surface should be the distance from the interface plus 0.3 μm.

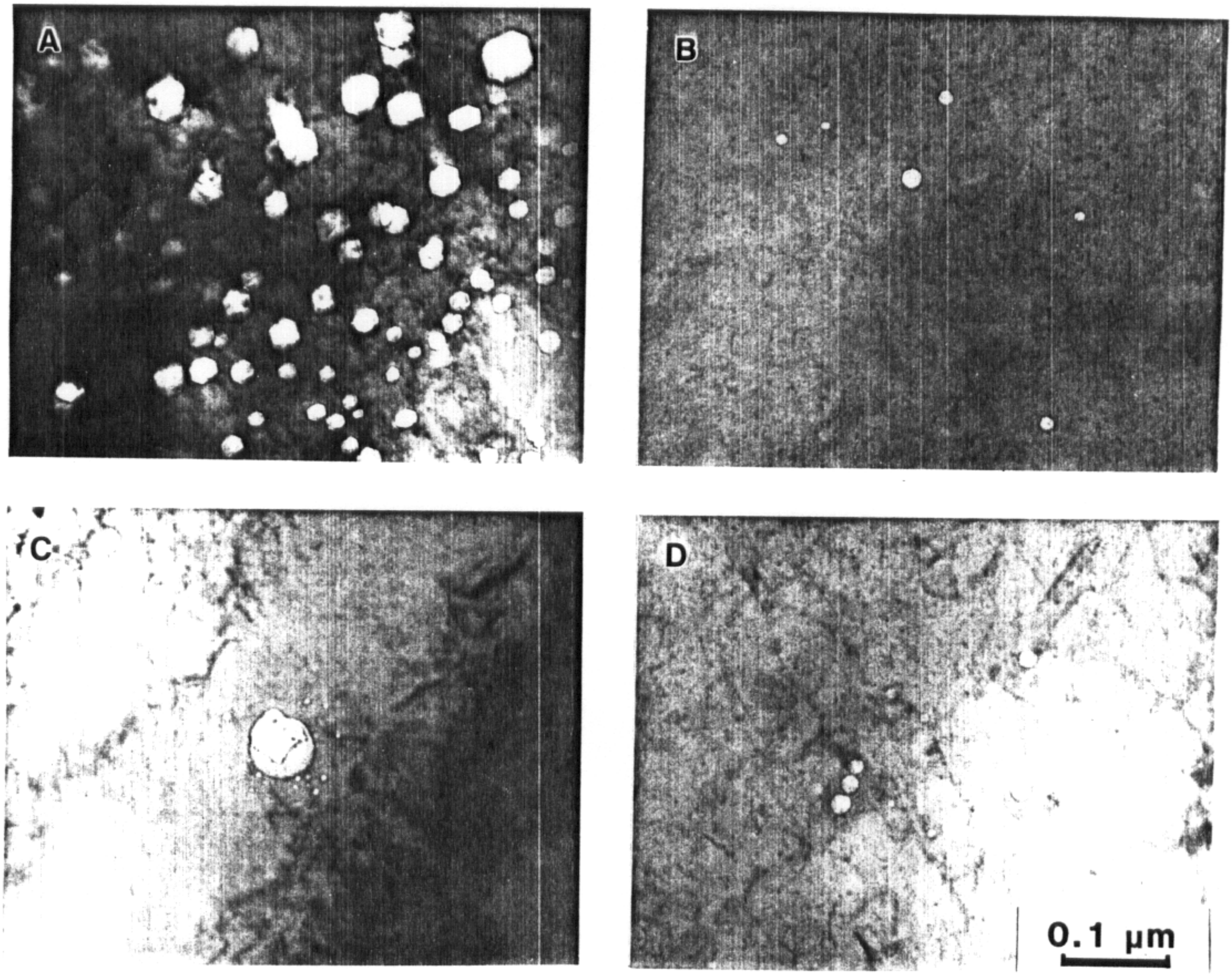

Fig. 5 Comparison of the void structures in irradiated Ni and Ni-10Cu samples. (a) Ni, 7 dpa, ~75 appm oxygen; (b) Ni-10Cu, 10 dpa, 100 appm oxygen; (c) Ni-10Cu, 20 dpa, 100 appm oxygen; (d) Ni-10Cu, 100 dpa. (a), (b) and (c) were taken at a 1.3-1.8 µm depth from samples (1), (2) and (3) respectively, and (d) was taken from the peak damage region of sample (4).

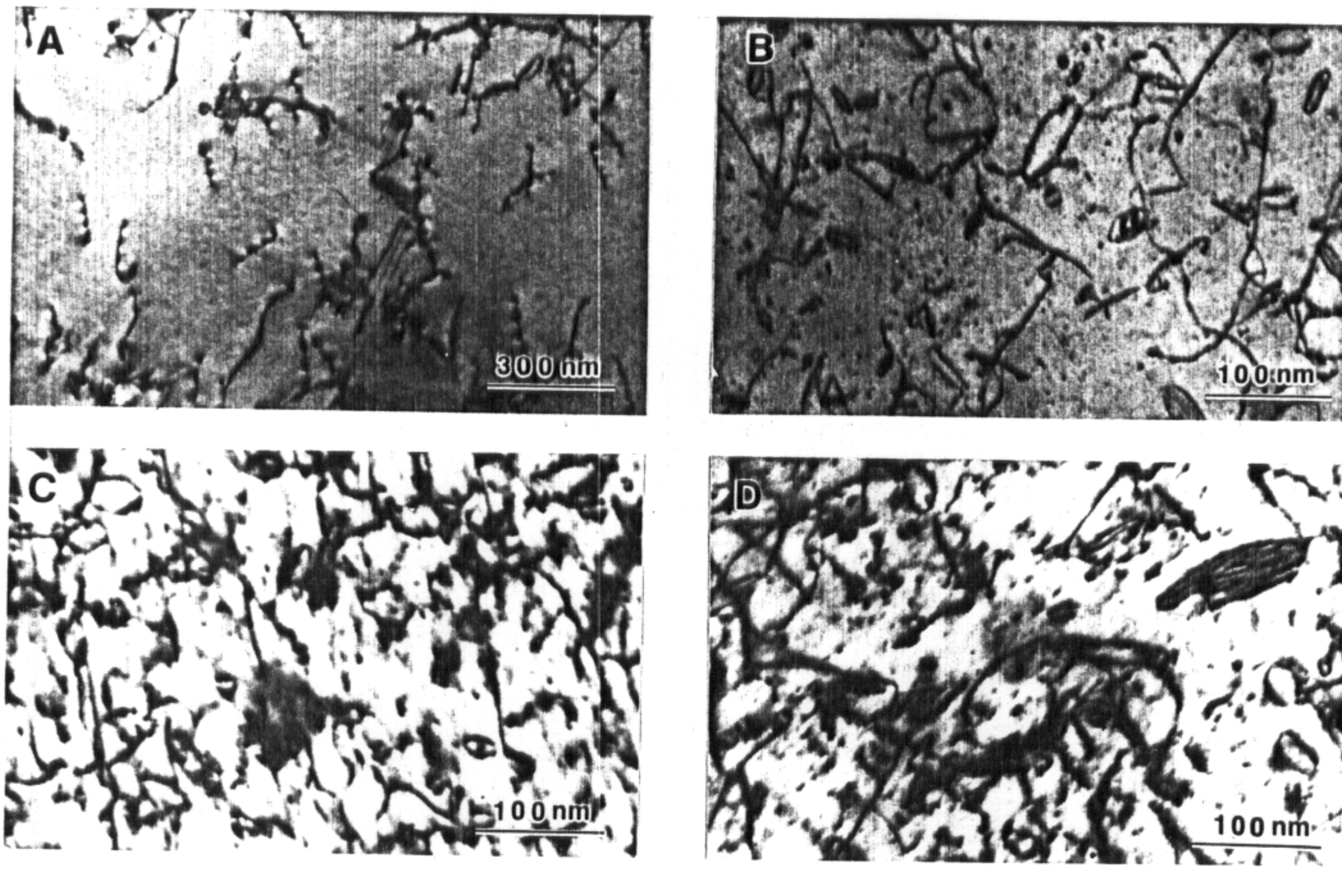

Fig. 6 Comparison of the dislocation structures in Ni-10Cu with various irradiation conditions. (a) Control region; (b) 10 dpa, 100 appm oxygen; (c) 20 dpa, 100 appm oxygen; (d) 50 dpa. (b), (c) and (d) were taken at a 1.3-1.8 μm depth from samples (2), (3) and (4) respectively.

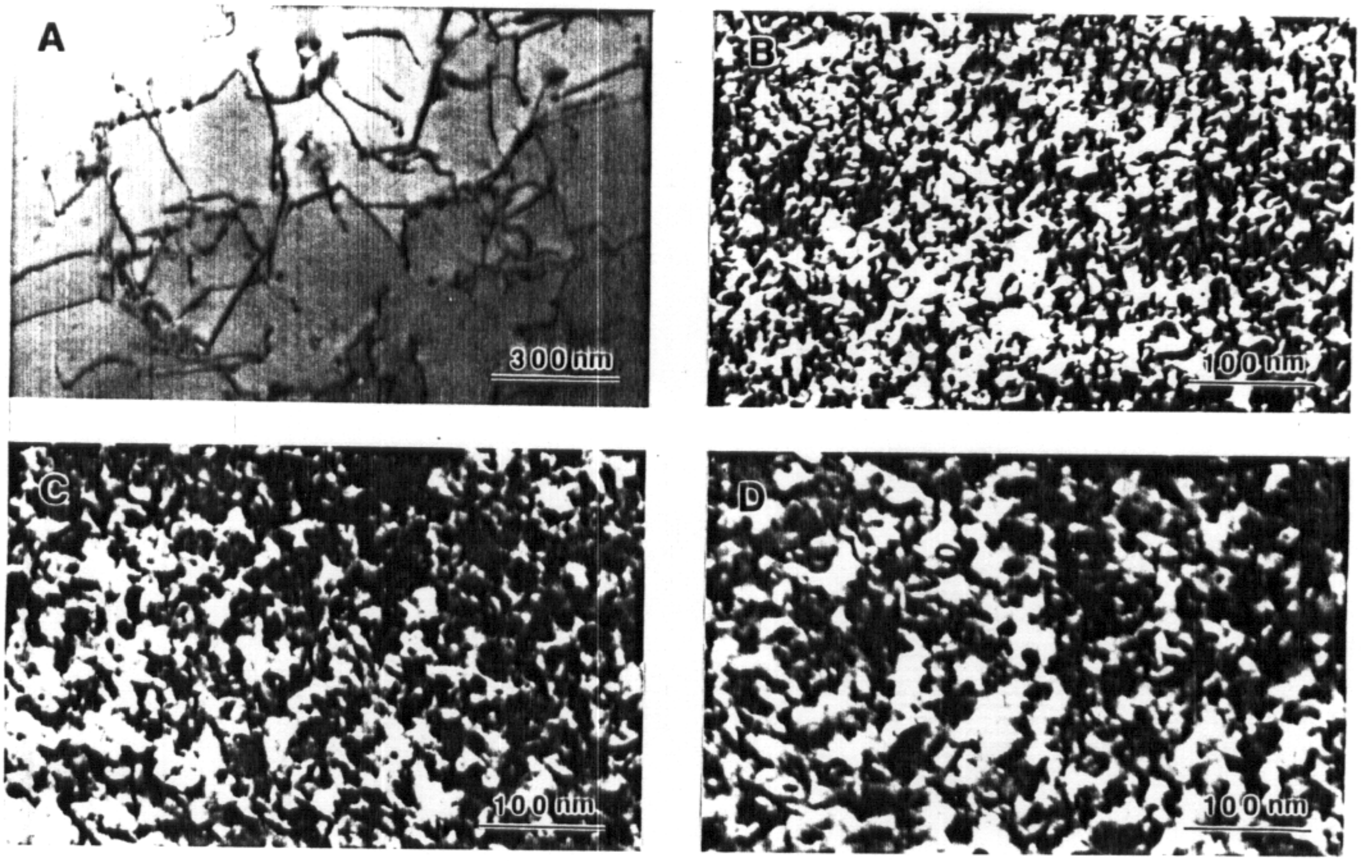

Fig. 7 Comparison of the dislocation structures in Ni-50Cu with various irradiation conditions. (a) Control region; (b) 10 dpa, 100 appm oxygen; (c) 20 dpa, 100 appm oxygen; (d) 50 dpa. (b), (c) and (d) were taken at a 1.3-1.8 μm depth from samples (5), (6) and (7) respectively.

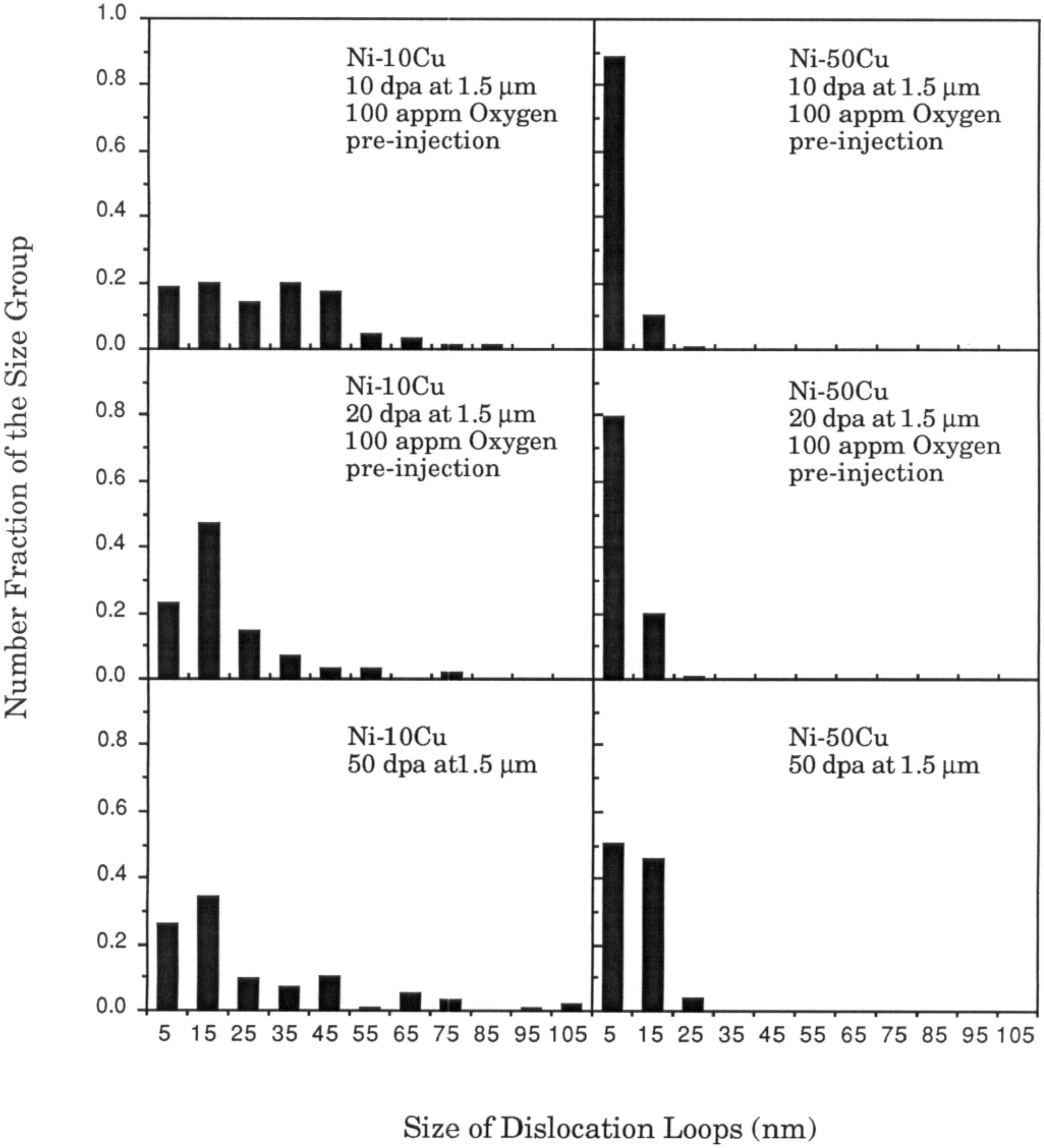

Fig. 8 Comparison of the dislocation loop size distribution in the six irradiated Ni-Cu alloy samples (data were obtained by counting the region at a depth of 1.3-1.8 μm from the irradiated surface).