A Literature Review of Radiation Damage Data for Copper

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I. Introduction

Copper and copper-base alloys have been widely used in basic studies of radiation induced defects in metals. Although more information exists on radiation damage in copper than in most other metals, the data are scattered throughout the literature. The purpose of this paper is to summarize and tabulate available data on void swelling and dislocation loop formation in copper and copper alloys, at room temperature and above. The review is organized according to the type of radiation used to produce the damage. Individual sections are devoted to the formation of voids and dislocation loops under neutron irradiation, ion bombardment, and electron bombardment, respectively.

Void and loop defects have been characterized according to the dependence of measurable defect properties (number density, size distribution, and macroscopic void swelling) on both irradiation and materials parameters. Irradiation parameters include the irradiation temperature, dose, and dose rate, in addition to the energy and type of bombarding particle. Radiation dose was measured either as particle fluence, or as dpa (displacements per atom), which is the average number of times an atom is knocked from its lattice site during irradiation. The materials parameters in the studies reviewed here were mainly specimen purity and dislocation density.

II. Neutron Irradiations

A. Void Formation

The formation of voids in high purity copper by fast neutron irradiation has been investigated for fluences ranging from $5.5 \times 10^{18}/cm^2$ to $1.3 \times 10^{22}/cm^2$, over a temperature range of about 220°C to 550°C [1-6]. Some work has been devoted to the effects of dislocation density and to the

Table 1. Void & Dislocation Loop Studies in Neutron Irradiated Copper and Copper-Base Alloys

Specimen purity*	Neutron energy (Mev)	Dose ($10^{-20}cm^{-2}$)	Dose rate ($10^{13}cm^{-2}sec^{-1}$)	Irradiation temperature, °C	Defect **	Mean defect size (Å)	Defect density ($10^{14}cm^{-3}$)	Swelling ΔV/V%	Comments	Ref.
5N	> 1	1.2	-	260	V	230	3	.17	Octahedral voids, bounded by (111) planes	61
4N	> .1	5	25	220	V	50	-	~0		
"	"	5	25	250	V	230	3.5	.16		
"	"	5	25	335	V	560	0.27	.32		
"	"	5	25	435	V	>1500	10^{-6}	.003		
"	"	5	25	600	V	0	0	0		2,
Slightly CW	"	5	25	250	V	-	-	.31	Effect of coldwork	6
Heavily CW	"	5	25	250	V	-	-	.14		
5N	"	130	-	175	L	-	-	0		65
5N	> 1	.055	.4-.9	285	L,V	121	.7	.0061	Effect of fluence	
"	"	.088	.4-.9	285	L,V	130	1.0	.011		64
"	"	.133	.4-.9	285	L,V	159	1.2	.024		
"	"	.160	.4-.9	285	L,V	168	1.6	.038		
"	"	.240	.4-.9	285	L,V	187	2.2	.074		
"	"	1.27	.4-.9	260	L,V	287	3.2	.38		

Table 1. Continued

Specimen purity*	Neutron energy (Mev)	Dose ($10^{-20}cm^{-2}$)	Dose rate ($10^{13}cm^{-2}sec^{-1}$)	Irradiation temperature, °C	Defect **	Mean defect size (Å)	Defect density ($10^{14}cm^{-3}$)	Swelling ΔV/V%	Comments	Ref.
4N	> .1	5	28	220	V?	< 50	~ 0	~ 0		
				250	V	275	2.2	.16	Octahedral voids bounded by (111) planes	
				335	V	670	.17	.32		
				435	V	~3800	.0008	.23		3
				550	-	-	0	~ 0		
4N	> .1	6.5	8	220	L	-	-	-		
		6.5	8	250	V	270	3.1	.32		
		6.5	8	335	V	570	.36	.35		
		6.5	8	435	V	820	.08	.25		
		6.5	8	550	-	-	0	0		
$Cu-O_2$	> .1	5	25	250	V	410	.9	.28		
$Cu-H_2$		5	25	250	V	610	.2	.31		
Cu-1% Al		5	25	250	-	-	-	0	Al, Ge lower the stacking fault energy	6
Cu-7% Al		5	25	220, 250, 350	-	-	-	0		
Cu-2.5% Ge		5	25	250	V	465	.2	~ .1		

Table 1. Continued

Specimen purity*	Neutron energy (Mev)	Dose ($10^{20}cm^{-2}$)	Dose rate ($10^{13}cm^{-2}sec^{-1}$)	Irradiation temperature, °C	Defect**	Mean defect size (A)	Defect density ($10^{14}cm^{-3}$)	Swelling $\Delta V/V\%$	Comments	Ref.
Cu-5% Ge	> .1	5	25	250	V	500	$< 10^{-6}$	~ 0		6
Cu-10% Al	"	130	-	175	L,V	to 3500	$\sim 10^{-3}$	?		5
Cu-2% Ni	> 1	.24	.4-.9	285	V	300	0.1	.01		4
Cu-20% Ni	"	.24	.4-.9	285	-	-	-	0		
Cu-1% Ge	> .1	5	30	250	V	480	.025	.10	These solutes lower the stacking fault energy	3
Cu-3% Ge		5	30	250		600	few	~ 0		
Cu-1% Si		5	30	250		120	few	~ 0		
Cu-1% Al		5	30	250		-	few	~ 0		
Cu-3% Al		5	30	250		-	0	0		
Cu-5% Al		5	30	250		-	0	0		
Cu-.0001% Be, to Cu-1% Be	> 1	.005	1	40	L			-	Addition of Be decreases interstitial loop conc.	15

* All specimens are in the annealed state unless otherwise indicated. 5N = "five nines" = 99.999% purity, and so on.

** V = Voids, L = Dislocation Loops

addition of metallic alloying elements. There was little mention of the effects of gaseous impurities or other transmutation products on the nucleation and growth of voids. Most studies systematically investigated the effect of only one or two variables. The results of these studies are summarized in Table 1.

Because these experiments were performed in various reactors, only a rough comparison of the damage (dpa) level from one study to another can be made. The neutron energy spectrum, and hence the value of the dpa per unit fluence, varies from one reactor to another and also depends on position within a reactor. As an approximation, a fluence of 10^{21} neutrons/cm^2 (E = 1 MeV) corresponds to about 1.5 dpa [7]. The doses reported in most of these studies are therefore less than 1 dpa.

In high purity copper the variation of void swelling with temperature is similar to that in many other pure metals. Swelling occurs at intermediate temperatures of about .35 Tmp to .57 Tmp, with a broad peak situated near the middle of this range. In copper irradiated in a flux ($E > .1$ MeV) of $\sim 2.5 \times 10^{14}$/cm^{2}sec, up to a dose of 5×10^{20}/cm^2, voids were observed by Adda [6], Levy et al. [2], and Labbe [3] at temperatures of 220°C to 500°C. Peak swelling of about .32% occurred at ~ 340°C. The mean void diameter increased from ~ 50 Å to more than 1500 Å over this temperature range, while void concentration decreased rapidly from a maximum of 3.5×10^{14}/cm^3, showing that higher temperature inhibits nucleation but favors growth. One study [3] displayed the effect of a lower dose rate in shifting the swelling maximum to lower temperatures. The peak swelling temperature was reduced 40°C in specimens that were irradiated to the same fluence as above, but at a dose-rate four times lower. The voids observed here and in other work [1,4] were octahedra bounded by {111} planes, often truncated at the corners.

The dependence of void nucleation and growth on neutron fluence was studied by Brimhall and Mastel [4], at a temperature of 285°C. No threshold fluence for swelling was observed, although a plot of swelling vs. fluence suggested a threshold at doses lower than $\sim 5 \times 10^{18} cm^{-2}$. Void nucleation continued up to doses of at least 1.2×10^{20} n/cm^2, although the void density began to saturate at fluences above $\sim 3 \times 10^{19}$ cm^{-2}. Below this fluence the void density increased approximately linearly with dose.

Several interesting observations of the relation between dislocation structure and void formation were made. In the low-fluence study discussed above, Brimhall and Mastel [1] noted that voids nucleated concurrently with dislocation loops, but not subsequent to loop formation. The dislocation structure, which consisted of loops and tangles, increased in density as fluence increased, then saturated at the same dose where void nucleation ceased. There was no spatial correlation between voids and dislocations. When dislocations were introduced by pre-irradiation cold-working of specimens [3,6], there appeared to be an optimum dislocation density for swelling. Slightly cold-worked specimens irradiated at 250°C swelled more than annealed specimens but heavily cold-worked specimens swelled less.

Work on copper alloys centered on determining the effect of the stacking fault (SF) energy on void formation. Metallic solutes often lower the SF energy, which, in theory [4], makes formation of three-dimensional voids less favorable energetically. In Cu-1 wt% Al alloys irradiated at 220-350°C, no voids or very few voids were found under conditions that produced .16-.32% swelling in pure Cu [2,3,5]. Such alloys have SF energies ranging from < 5 to

45 ergs/cm^2, compared to 55 ergs/cm^2, for pure Cu [3]. However, Wolfenden [5] did observe voids (~ 10^{11}/cm^3) and other damage in Cu-10% Al (SF energy ~ 2 ergs/cm^2) irradiated at 175°C, to a fluence 26 times higher than for the Cu-Al discussed above. Large voids formed in the α-phase of the alloy, and were associated with dislocations, tiny particles, or coherent twin boundaries, and had a variety of shapes. In pure Cu irradiated under the same conditions, only dislocation loops and tangles, but no voids, formed. An explanation for this was a higher vacancy mobility in the Cu-Al than in the Cu allowed void formation in the alloy [6]. In Cu-Ge irradiated at 250°C, swelling occurred (.10%) for 1 and 2.5 wt% Ge, while measurable swelling did not occur in the 3-5% Ge alloys, which have a lower SF energy. In Cu-Ni alloys, where SF energy is not significantly reduced by Ni, some swelling occurred for the 2 wt% Ni alloy, but no swelling was evident in the Cu-20% Ni [4]. Interstitial trapping by the Ni was the most likely explanation for this void suppression, in agreement with the HVEM work of Barlow and Leffers described later.

B. Loop Formation

Some studies of neutron irradiated Cu involved fluences or irradiation temperatures too low for void formation [8-14]; nevertheless, their findings on defect cluster and dislocation loop formation are important. Irradiations in the temperature range of 20-80°C and fluence range of 3 x 10^{16} to 1 x 10^{20} n/cm^2 [9,11,13,14], produced dislocation tangles, defect clusters, and vacancy and interstitial loops lying on $\{111\}$ planes. The loops were present in overall densities of 10^{15}/cm^3 - 10^{16}/cm^3 and ranged in size from < 20 Å to ~ 200 Å. The smaller loops tended to be vacancy in nature while the larger ones were interstitial [9]. Studies of the annealing behavior of these defects indicated that interstitial loops become unstable at ~ 325°C, and that vacancy clusters or voids formed before annealing was complete [12]. In pure Cu exposed to 1.1 x 10^{20} cm^{-2} fast neutrons at 60°C, annealing at 500°C for one hour removed all visible defects [13]. One room-temperature study [11] compared the damage structures from equal fluences (3 x $10^{16}/cm^2$) of 14 MeV and fission neutrons. The 14 MeV neutrons produced interstitial and vacancy loops that were larger and ~ 5 times denser than those produced by the fission spectrum. The defect structure resulting from higher temperature irradiation was quite different from that at room temperature. In Cu exposed to $10^{18}/cm^2$ fast neutrons at nominally 400°C, Hulett et al. [8] found the damage confined to "defect regions" 10-100 μm in size, separated by apparently perfect crystal. These regions contained dislocation tangles, vacancy clusters $\lesssim$ 200 Å diameter (possibly voids), sessile vacancy loops 100-500 Å diameter, and large prismatic loops that were predominantly interstitial. Higher annealing temperatures (500-800°C) than for room temperature irradiations were needed to remove this damage. Larson and Young [10], using anomalous x-ray transmission techniques, found that such defect regions form at irradiation temperatures between about 210°C to 370°C, with corresponding number densities of 2 x 10^{11} cm^{-3} to 1 x 10^6 cm^{-3}.

III. Charged-Particle Irradiations

In this section, ion irradiation experiments are discussed separately from high-voltage electron microscope (HVEM) experiments. The ion work is subdivided into two parts, one dealing with the understanding of fundamental aspects of radiation damage other than void formation, and the other dealing with void formation.

A. Ion Bombardment

1. Fundamental Studies

In general, these investigations [14,16-36] involved the irradiation of high purity copper specimens with 30-150 keV Cu^+ ions at, or somewhat above, room temperature. Copper ions in this energy-range are similar to the primary knock-on's produced by fast neutron irradiation of copper. The specimens were thin films or foils ($\lesssim$ 3000 Å thick), so surface effects played a key role. Analysis of the radiation damage was done by electron microscopy. A summary of these studies is presented in Table 2. A somewhat more complete summary of early work (pre-1969) has been compiled by Ruhle [23].

Because the experimental conditions varied from one study to another, only broad conclusions can be drawn from this work. Room temperature irradiation produced vacancy loops 20-80 Å in diameter with Burgers vector $\vec{b}$ = a/3 <111> [24,25,27,29]. The loops were often faulted or dissociated, and resulted from the collapse of the vacancy-rich center of the displacement cascade. They tended to be superimposed on a background of irresolvable "black spot" defect clusters. Few interstitial loops were observed because the combination of thin specimens and shallow ion ranges led to a high loss-rate of interstitials to the surface [29]. At somewhat higher irradiation temperatures unfaulted loops with $\vec{b}$ = a/2 <110> formed, and stacking fault tetrahedra were also observed [29]. Above 300°C these loops shrunk rapidly after forming. English and Eyre [29,30] accounted for this shrinkage with a thermal vacancy emission model.

Material purity had a variable effect on the density or nature of defects in self-ion irradiated copper at room temperature [14,31]; e.g. in Cu-10% Al or Cu-16% Al the lower stacking fault energy caused dislocation loops to

Table 2. Radiation Effects in Ion Bombarded Cu

Purity	Energy (KeV)&Ion	Dose (cm^{-2})	T°C	Defect: Type*	Defect: Size (Å)	Defect: Density (cm^{-3})	Comments	Ref.
h.p.	38,000/He	1.4E17	~200	iL v.clusters	220 20	E9-E10 E10-E11	Vac. clusters anneal into bubbles or voids.	16
5N	1-5/Ar	E14-E16	~ 20	iL	<100	6E11	Thin film target.	17-19
h.p.	700/H 1000/He	5.6 E16 7 E15	20 20	v.cluster "	24 "	< E16 "	Vac. clusters form directly in cascade.	20
4N8	60/H 20/H	3.5 E16- 1.1 E17	70 100 200 250 300	iL	200 350 300-1000 750-2000 500-3000	7.6E9 4.4E9 1.7E9 1.9E8 1E8	Hexagonal, faulted interstitial loops on (111) planes.	21
h.p.	30/Cu	1 E12	20	vL	50	-	Frank sessile vac. loops on (111) planes.	24
h.p.	30/Cu 90/Cu	5E10-2E12 " "	~ 20 20	vL vL	20-80 "	- -	~ 1 cluster forms per ion. ~ 3 " " " "	25,27
5N	40/Cu	1 E11	~ 20	L	10-75	-		14
h.p.	≤ 5/Ar	E 15-E 17	20	iL	10-40	-	$\bar{b} = \frac{a}{2} < 110 >$; loops may be Ar clusters.	26
h.p.	150/Cu 350/Cu	1 E16	-130-350		-	-	Damage extended up to 16x proj. range in channelling directions.	28
5N	30/Cu "	1 E12 "	20-300 350-400	vL vL,SFT	~ 46 55	2 E11 2 E10	At T ≥ 300, loops shrink rapidly after forming due to thermal emission.	29 30

Table 2. Continued

Purity	Energy (KeV)&Ion	Dose (cm^{-2})	T°C	Defect Type*	Defect Size (Å)	Defect Density (cm^{-3})	Comments	Ref.
5N	30/Cu	2 E11	~ 20	vL	-	-		31
h.p.	30/Cu	.2-5 E11	-173-227	vL	43	-	Thin foil.	32,33
5N	1000/H	1E16	20	iL	-	1-7.7E18	Defect density vs. depth obtained by cross-section technique.	34
5N	4000/Ni 60,000/Ni	5E12 1.3E13	20 20	L L	10-120 "	E15-4E16	Disagreement between observed heavy ion damage distribution and LSS theory. Only 6% of displaced atoms retained as obs. defects.	35
5N	1000/He 5000-38000/Cu 4000/Ni 58000/Ni	2E15 5E12 1E13	25 25 25	vL, iL " "	- - -	- - -		36
Cu-16% Al	40/Cu	1E11	20	L	10-75	-	Same type of damage as in pure Cu.	14
Cu-.6%O Cu-10%Al	30/Cu "	2E11 "	~ 20 "	vL "	- -	- -	Damage not greatly affected by impurities; in Cu-Al Some loops → stacking fault tet.	31

* iL, vL ≡ interstitial, vacancy loops, respectively

dissociate more easily into SF tetrahedra. However, the basic damage structure remained similar to that in pure copper. Bombardment with gas ions, which acted as impurities in the target, led to interstitial loop formation often accompanied by small vacancy clusters. For example, bombardment with 20-60 keV H^+ and 38 MeV He^{++} resulted in large interstitial loops and 20 Å diameter vacancy clusters [16,30].

One group of studies was quite different from the work described above, in that the specimens were viewed in cross-section in the electron microscope, in the direction perpendicular to the bombarding ion beam. Narayan et al. [34-36] used this technique to view the displacement damage along the entire range of the bombarding ions. Their purpose was to compare the theoretical depth distribution of damage with that actually observed, and to compute the fraction of displaced atoms retained as visible defects. Here, single-crystal copper specimens were irradiated at room temperature with 1 MeV protons or alpha particles; 5, 16, 27, or 38 MeV Cu^+ ions; or 4 or 58 MeV Ni ions. Subsequently the specimens were electroplated with about 1 mm of copper, then cross-sectioned and thinned for electron microscopy.

In the 1 MeV proton-irradiated specimens, the range of the ions as indicated by the cutoff in the defect clusters, and the overall profile of the damage distribution, was in good agreement with that predicted by LSS theory. The agreement with theory was not as good for the Cu and Ni ion bombarded specimens. The experimental damage profiles were compared with calculated EDEP-1 damage energy profiles, using various forms for the electronic stopping. From this the correct electronic stopping powers as a function of energy were deduced. LSS theory, with the LSS predicted values of the proportionality constant k, consistently underestimated the peak damage position for

Cu and Ni ions incident on copper. Disagreement was greatest (~ 25%) for low energy ions, but improved to within a few precent of the observed results for the highest energy ions. Agreement with LSS calculations was obtained by reducing the value of the proportionality constant k in the electronic stopping formula. For the higher energies it was necessary to use an electronic stopping power of the form $d\varepsilon/d\rho = k_2 \varepsilon^{1/2} - C$ to obtain agreement. Hence, the electronic stopping of the Cu and Ni ions in copper is not proportional to the ion velocity as predicted by LSS theory.

2. Void Formation Studies

Only a few ion bombardment simulation studies of void formation in copper have been performed [6,37-40]; however, they were done systematically and contain a great deal of information. All were conducted under the auspices of the French Commissariate a l' Energie Atomique between 1970-1975. Early results of this work were sketched by Adda [6], and the completed work was reported in detail by Glowinski et al. [37-40]. This work examined the influence of various irradiation and materials variables on the nucleation and growth of voids and dislocation loops in high purity copper foils, which were irradiated with 500 keV self-ions. Specifically, the influence of irradiation temperature, dose rate, dose, foil thickness (effect of free surfaces), dislocation structure, and gas content of the specimens was studied. The experimental results are summarized in Table 3.

Void swelling occurred over a narrower temperature range in ion bombarded Cu than in neutron bombarded Cu, although the shape of the swelling curve was similar (Fig. 1). In annealed, non-degassed Cu irradiated at a dose rate of 2×10^{-4} dpa/sec, there was measurable void swelling between temperatures of 400-500°C, with a narrow peak at 450°C [38]. Void size increased with

Table 3. Void formation in ion bombarded copper and copper alloys (irradiated with .5 Mev Cu ions unless otherwise noted).

Purity and pre-irradiation treatment	Dose (dpa)	Dose rate (10^{-4}dpa/sec)	Irrad. temperature (°C)	Defect: Type[a]	Defect: Mean size(Å)	Defect: Density ($10^{13}cm^{-3}$)	Swelling ΔV/V%	Comments	Ref.
h.p., nondegassed	4	2	300	-	-	-	0	Increasing dose	6
	4	2	400	V	-	-	.7	rate shifts swelling	
	40	20	300	-	-	-	0	to higher temperature.	
	40	20	400	-	-	-	0		
	40	20	450	V	-	-	4		
h.p. as rolled	40	20	450	V	-	-	.5	High sink density	6
h.p., Kr^{85} doped	40	20	450	-	-	-	0	→ lower swelling.	
h.p., nondegassed	3	2.9	350	vL	-	-	0	In thin regions of	38
	3	2.9	400	V	300	8	.13	the foil (500-2000 Å)	
	3	2.9	450	V	900	8	3.2	only blackspots form.	
	3	2.9	500	-	-	-	0	Voids are visible in	
	30	29	400	vL	-	-	0	thicker regions or	
	30	29	450	V	1000	6	3.4	near dislocations.	
	30	29	500	V	2100	2	9		
	30	29	530	V	2200	.6	3.2		
	30	29	550	V	0	0	0		
h.p., degassed at: 450°C	30	29	450	vL, iL, V	1000	6	3.4	Degassing at high T	38
600°C	30	29	450	V	750&1300	6	1	reduces or eliminates	
700°C	30	29	450	vL	-	-	~0	void formation.	
4N, He doped	30	30	450	V	750	8	4.1	Presence of He	38
1 E14/cm^2	30	30	530	V	1900	2	12	increased void density.	
4N, nondegassed,	.83	30	450	V	190	32	.16	Effect of dose. Inter-	39
thick foils	1.7	30	450	V	270	34	.43	stitial loops also	
	3	30	450	V	340	40	.88	noted. Loops, voids	
	10	30	450	V	420	32	1.41	lie on or near dislo-	
	30	30	450	V	660	18	3	Line disl. density is	
prethinned foil→	30	30	450	V	1000	6	3.4	0.8-7.0 E9 cm^{-2}	
degassed 1 hr., 750°C at 6E-9 torr	.83	30	450	Blackspots and some vacancy loops			0	Neither voids, int. loops or disl. networks form.	39
	1.67	30	450				0		

Table 3. Continued

Purity and pre-irradiation treatment	Dose (dpa)	Dose rate (10^{-4} dpa/sec)	Irrad. temperature (°C)	Defect Type[a]	Defect Mean size (Å)	Defect Density (10^{13} cm^{-3})	Swelling ΔV/V%	Comments	Ref.
4N, degassed, doped w/ 1ppm He	32	30	450	V	1150	3	2.5	Dislocation density, ρ_d, varies from 1.8E9 to 4E9/cm^2	40
5 "	32	30	450	V	1050	6	4		
15 "	32	30	450	V	930	9	4.5		
30 "	32	30	450	V	900	10	5		
100 "	32	30	450	V	950	4	1.5		
30 "	32	30	500	-	-	0	0	ρ_d = 6E8 to 3E9/cm^2	40
50 "	32	30	500	V	2100	1	5.7		
100 "	32	30	500	V	1500	6	14		
7ppm O	32	30	450	V	1350	3	4	ρ_d = 1.7 to 5.3E9 1cm^2	40
40 "	32	30	450	V	1300	3	3.7		
105 "	32	30	450	V	1200	2.7	2.5		
30 "	32	30	500	-	-	0	0	ρ_d = 3.5 to 5.5E9/cm^2	40
70 "	32	30	500	V	2450	.74	6.3		
100 "	32	30	500	V	2200	1.5	10		
nondegassed, 100ppmH	32	30	450	-	-	-	0	No voids or dislocation networks.	40
degassed, 100ppmH	32	30	450	-	-	-	0		
", deformed, 100ppmH	32	30	450	-	-	-	0		
degassed, 30ppmC	32	30	450	blackspots; small vL			0	No voids, disl. networks. C inhibits vac. cluster formation.	40
h.p., doped 10ppmHe	b	-	400	V	-	-	-	Void formation inhibited in Cu-Ni by trapping at solute atoms or clusters.	41
Cu-2%Ni "	b	-	400	V	--	-	-		
Cu-20%Ni "	b	-	500	-	-	-	-		
Cu	c		500	V			.6		42
Cu-.7%Mg	c		480	V			.2		
Cu-.7%In	c		480	V			.13		

c Bombarded with 150 KeV Cu^+ to 160 dpa
b Bombarded with 46.5 Mev Ni^+ to 2.5E16 ions/cm^2
a Defect type: vL, iL, V = vacancy loops, int. loops, voids respectively

temperature, from a mean diameter of 300 Å at 400°C to 900 Å at 450°C, while void density remained about the same. Below the temperature of the onset of swelling, only vacancy loops and black spots were observed. Above the maximum temperature for swelling no irradiation defects were observed.

The effect of an increase in dose-rate was to shift the temperature range of swelling to higher temepratures. Compared with neutron irradiations [3] that occurred at a dose-rate of 2×10^{-7} dpa/sec, the peak swelling temperature for the ion bombarded specimens (at 2×10^{-4} dpa/sec) was increased by about 115°C. An order-of-magnitude increase in the ion bombardment rate to 2×10^{-3} dpa/sec shifted the swelling range upward by 50°C; that is, the onset of swelling occurred at 450°C and peak swelling was observed at 500°C. In this higher dose-rate case, void size increased while void density dropped by a factor of 10, as temperature increased from 450 to 530°C.

At a constant temperature and constant dose-rate, an increase in fluence caused void swelling to increase through void growth [39]. In specimens irradiated at 450°C to fluences ranging from 0.83 to 30 dpa, swelling increased from 0.15% to 3%. Void density remained at 3×10^{14} cm^{-3} over this range but mean diameter increased from 190 Å to 660 Å. Below a fluence of 3 dpa, swelling as a function of fluence increased at more than a linear rate; for fluences greater than 3 dpa the swelling rate was less than linear.

The effect of the proximity of a free surface, i.e., of specimen thickness, on the defect structure was observed in bombarded specimens that had been thinned and perforated (for post-irradiation electron microscopy analysis) prior to irradiation [38]. In such foils the specimen thickness varied from less than 500 Å to much greater than 5000 Å, so the distance of the back surface to the region of maximum energy deposition varied from zero to effectively infinity. The void swelling described in the previous paragraph was observed in regions thicker than 1500-2500 Å. In very thin ($\lesssim$ 500 Å) regions no defects were found, while only black spots formed in the intermediate thicknesses. The absence of defect clusters in the very thin foils had two possible causes: the depression of point defect concentrations due to loss to the surface; or, the loss of dislocations to the surface, thus decreasing the dislocation density in these regions below the level required for void formation.

Several general conclusions were reached regarding the experimental evidence for the role of dislocations in void formation. First, voids almost always nucleated near interstitial loops or dislocation lines, on the compression side of the dislocation [37-39]. Secondly, some minimum dislocation density was necessary for void formation, and there was a direct correlation between void number density and dislocation density [39]. Finally, void growth was affected by the vicinity of a dislocation. This last point was connected with the finding that void size increased very rapidly during the early stages of void growth (at fluences $\lesssim$ 3 dpa), when all voids were in the close proximity of dislocations. All the observations are evidence that dislocations act as biased sinks absorbing interstitials preferentially to vacancies, thereby creating an excess of vacancies that precipitate into voids.

In addition to the importance of the dislocation structure for void formation in copper, these experiments showed that gas (impurity) atoms must be present for voids to nucleate. The void formation described previously [38,39] occurred in high purity specimens that were annealed at 900°C in a vacuum that was insufficient for complete outgassing of the copper. Following the anneal some specimens were again annealed in situ in the high vacuum (10^{-8} torr) target chamber of the accelerator at either 450°, 600°, or 700°C for 1/2 hour, then irradiated at 450°C to 30 dpa [38]. In those annealed at 450°C the damage microstructure was quite similar to that in specimens not annealed in high vacuum. However, in the 600°C specimens the damage was markedly different, i.e. the void size distribution was double-peaked (at 750 Å and 1300 Å), swelling decreased from 3.4 to 1%, and vacancy loops were present in even the thinnest regions of foil. In a later study [39] specimens annealed in high vacuum (6×10^{-9} torr) at 700°C for 1 hour, then irradiated at 450°C to 0.83 - 30 dpa showed black spots and some vacancy loops, but no voids, interstitial loops or dislocation networks. The most probable reason for the absence of void formation was the removal during the high vacuum annealing of residual gas* necessary for void nucleation [37-40].

To determine if gaseous impurities were necessary for void formation, experiments were conducted [38,40] in which high purity Cu specimens were ion-implanted with various doses of oxygen, helium, or hydrogen, then irradiated at 450-550°C to 30 dpa. The specimens had been degassed at 700°C in a vacuum of 2×10^{-8} torr before implantation. Voids did form in specimens that had been implanted with helium [38,39,40] or oxygen [40], in contrast to copper that had been degassed but not ion-implanted. The presence of helium enhanced void swelling relative to conventional non-degassed, non-implanted specimens in Ref. [38]; the magnitude of swelling increased, the temperature domain of swelling was widened, and the peak-swelling temperature was shifted upwards.

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*The initial gas content of specimens used in Ref. [37] was not specified, but those in Refs. [38-40] contained less than 48 ppm O, 12.4 ppm H, 14 ppm N, 14 ppm N, and 48 ppm C.

The behavior of swelling with respect to gas content was different for the oxygen and helium injected specimens. For concentrations less than 30 ppm, helium was somewhat more efficient in nucleating both voids and interstitial loops, but for higher concentrations void density decreased for helium but remained constant for oxygen. This was explained in terms of the different solubilities of the two gases in copper. Also, these results suggested that of three possible explanations for the role of gases in void formation: formation of microbubbles, lowering of surface energy, or stabilization of vacancy clusters, the last explanation was most likely. The reasoning was that oxygen is soluble in Cu at the concentrations used, so microbubbles could not form; also helium does not appreciably affect the surface energy [37].

Swelling did not occur in specimens that had been implanted with hydrogen prior to irradiation. Three types of samples were implanted with hydrogen: non-degassed, degassed, and degassed, then work-hardened copper. None of the specimens contained voids or dislocation networks. Either the hydrogen diffused out of the specimens, or it had no effect on damage formation. The absence of voids in the non-degassed copper was not explained.

Several degassed specimens that were implanted with carbon prior to irradiation contained neither voids nor dislocation networks [40]. Specimens implanted with oxygen or helium and also with carbon exhibited less swelling than if the carbon was absent. This indicated that the carbon acted as a point-defect trap.

B. High-Voltage Electron Microscope (HVEM) Irradiations

1. Loop Formation

HVEM irradiation offers the advantage of direct observation of the defect structure as it evolves during irradiation. The mode of damage production differs from ion or neutron irradiation in that isolated point defects rather than collision cascades are produced. Displacement damage in pure copper was first observed by Makin [43] during irradiation with an intense 600 keV electron beam at approximately room temperature. He verified that a beam threshold energy of 500-600 keV, depending on crystal orientation, was necessary for the production of visible defect clusters. These clusters consisted mainly of perfect dislocation loops (interstitial) that grew from black spot clusters, which had nucleated during the first few minutes of irradiation. Details of this study are given in Table 4.

Ipohorski and Spring [44] and then Fisher [46] expanded upon Makin's work by examining in detail the various factors influencing loop formation. It was found that loop density decreased and size increased as irradiation temperature increased, until at 400°C only a few large ($\gtrsim$ 1 μm) loops formed. Denuded zones at surfaces (600 Å deep at ~ 20°C) and at grain boundaries increased in width with temperature. Barlow [49] observed continuous nucleation of two types of interstitial loops during irradiation: Frank faulted loops lying on {111} planes ($\vec{b}$ = a/3 [111]), and glissile prismatic loops on variable habit planes with $\vec{b}$ = a/2 [110]. The apparent activation energy for this loop growth was measured at .35 eV [51].

2. Void Formation

Void nucleation and growth characteristics in HVEM irradiated Cu [45-50] (Table 4) were found to be qualitatively similar to those in ion bombarded Cu. In general, voids were observed [46-50] in the temperature range of ~ 250-550°C, although one study [45] reported voids at 100-250°C also. Peak swelling usually occurred at 450-500°C depending on dose rate. The variation of swelling with temperature was asymmetric with respect to the peak swelling

Table 4. Summary of Some Previous HVEM Studies in Copper and Copper Alloys

Purity and preirradiation treatment	Electron energy (KeV)	Max. dose*	Dose rate*	Irradiation temperature (°C)	Defect** Type	Mean size(Å)	Density (cm^{-3})	Swelling ΔV/V%	Comments	Ref.
h.p.	600	1.4E21 cm^{-2}	3E18/ cm^2sec	~ 20°C	iL?	50-150	~8E14 to ~4E14	-	Only ~ 0.5% of defects end up as visible loops. Total loop area is ∝ to dose.	43
h.p., previously irrad. to produce int. loops and vac. clusters	580	1E22 cm^{-2}	"	"	iL	initially 200	-	-	Int. loops grow initially. Later vac. clusters form also.	43
h.p., either quenched or deformed	"	0.7E22 cm^{-2}	"	"	iL?	-	very high	-	Very rapid loop growth, coalescing into dense disloc. tangles	43
4N8	600	?	1.2E19/ cm^2sec	"	iL	up to 10^4	-		No defects in foil > 1000 Å thick; 600 Å denuded zone near surface. Loops on (111) planes.	44
5N	1000	65	1.1E18/ cm^2sec 6.2E-3 dpa	250	V	-	5E14	10	1600 Å denuded zone at surfaces	45
5N#	"	95	"	250	V	-	1E15	17		
Cu-1% Ag; Cu-1% Cd#	"	12	"	"	V	-		13	Enhanced swelling rate compared to pure Cu	

Table 4. Continued

Purity and preirradiation treatment	Electron energy (KeV)	Max. dose*	Dose rate*	Irradiation temperature (°C)	Defect** Type	Defect** Mean size (Å)	Defect** Density (cm^{-3})	Swelling ΔV/V%	Comments	Ref.
Cu-1.2at%Be#	1000	100	6.2E-3 dpa	250	-	-		0	No voids observed	45
4N5	"	7	3.1E-4	250	L,V	80	1.6E14	.004	Higher initial disloc. density increases void density	47
4N5,deformed	"	6	3.14E-4	250	L,V	60	1.6E14	.002		48
4N;non-degassed, irrad. to 1 dpa at 100°C to introduce dislocations	"	14 " " "	1.3E-3 " " "	400 450 500 550	iL,V " " "	- - - -	- - - -	2.2 4.7 5.8 0		48
4N;degassed at 700°C, ½ hr, 4E-8 torr		" " " " "	" " " " "	250 300 344 400 450	iL,V " " " "	 ~800 ~1200 - -	 6E13 2.5E13 - -	.64 1.7 2.8 1.8 0	Dislocation density decreases from 3E9 to 8E8 cm^{-2} with temp.	48
5N	"	90 30 30 30 30	~1E-2 " " " "	250 350 450 500 550	" " " " "	500 650 1900 2850 0	3E14 3E14 1E14 2E12 0	2 3.3 13.7 2.5 0		49, 50

Table 4. Continued

Purity and preirradiation treatment	Electron energy (KeV)	Max. dose*	Dose rate*	Irradiation temperature (°C)	Defect** Type	Mean size (Å)	Density (cm^{-3})	Swelling V/V%	Comments	Ref.
Cu-2wt%Ni	1000	90	~1E-2	250	iL,V	160	9E14	.1	Ni solute traps interstitials, reduces swelling	
		30	"	350	"	200	4E14	.13		
		30	"	450	"	1050	4E13	1.5		
		30	"	500	"	2200	3E13	9		
		30	"	550	"	1450	2.5E12	0.3		49
Cu-5wt%Ni		90	"	250	"	100	9.5E14	< .1		
		30	"	350	"	80	3.5E14	< .1		
		30	"	450	"	5550	.3E14	.3		
		30	"	500	"	1800	.2E14	4.5		50
		30	"	550	"	3450	2.5E12	3.5		
Cu-10wt%Ni		30	"	250-500	-	0	0	0		
		30	"	550		1200	3E12	.3		

*Dose, dose rate units are dpa, dpa/sec unless indicated

**iL = interstitial loop, V = void; values given for defect size, density, and void swelling correspond to the maximum dose case.

#Preinjected with 80 keV Ar^+, $10^{15}/cm^2$

temperature [48-50]; beyond the peak, swelling decreased abruptly, but below the peak it dropped off more slowly and exhibited a "tail" at low temperatures (Fig. 1). Behavior with respect to temperature was strongly dependent on the purity (concentration of gas or metallic solute) and the dislocation density of the specimens. By comparing the swelling in annealed, thoroughly degassed foils with swelling in non-degassed foils, Glowinski [48] found the peak swelling temperature, the width of the temperature domain, and the magnitude of swelling to be very dependent on the gas content of the foil (Fig. 2). In non-degassed, high purity Cu, swelling occurred between ~ 250-550°C, with a peak of 5.8% at 500°C. Foils that were degassed in high-vacuum before irradiation swelled only 3% (at the same dose of 14 dpa); the swelling peak shifted to 360°C, and no voids formed above 440°C. As in the Cu^+ ion studies [38,39], where no swelling was observed in degassed Cu, the gas was thought to aid void nucleation and enhance void growth by nucleating interstitial loops and stabilizing dislocation networks that were necessary to achieve a net interstitial bias.

The effects of gas were also explored by Makin [45]. Copper injected with 10^{15} Ar atoms/cm^2 showed the same swelling behavior with dose as pure Cu at 250°C, but void density was several times higher, indicating that gas in the matrix enhanced void nucleation. In Cu-2000 ppm He, where the He was precipitated into gas bubbles by a 500°C pre-irradiation anneal, no voids formed after 23 dpa at 250°C. The bubbles apparently suppressed swelling by acting as efficient point-defect sinks.

Dose-rate effects on void swelling in the HVEM apparently depended on specimen purity. Glowinski [48] observed a swelling maximum at 500°C in non-degassed Cu, and at ~ 345°C in degassed Cu, irradiated at a rate of 1.3×10^{-3}

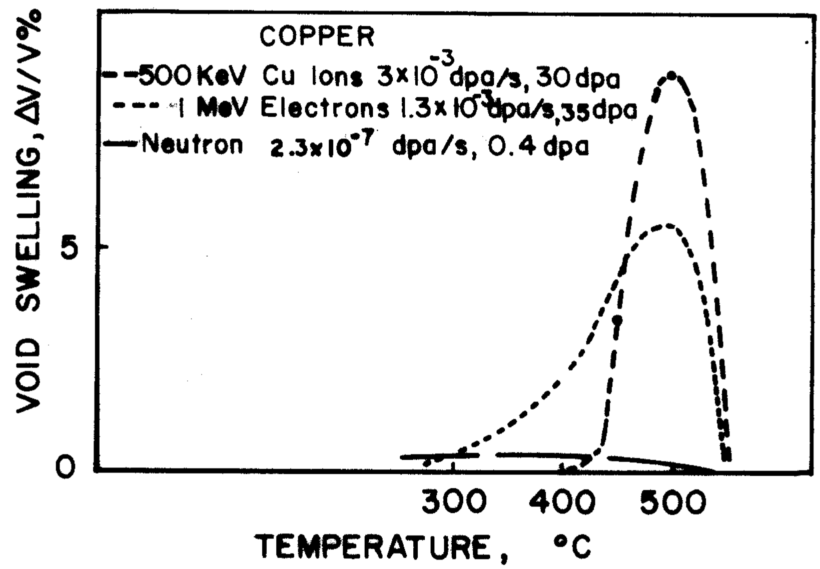

Fig. 1. (Ref. 37) Void swelling vs. temperature in copper irradiated with neutrons, electrons, and copper ions.

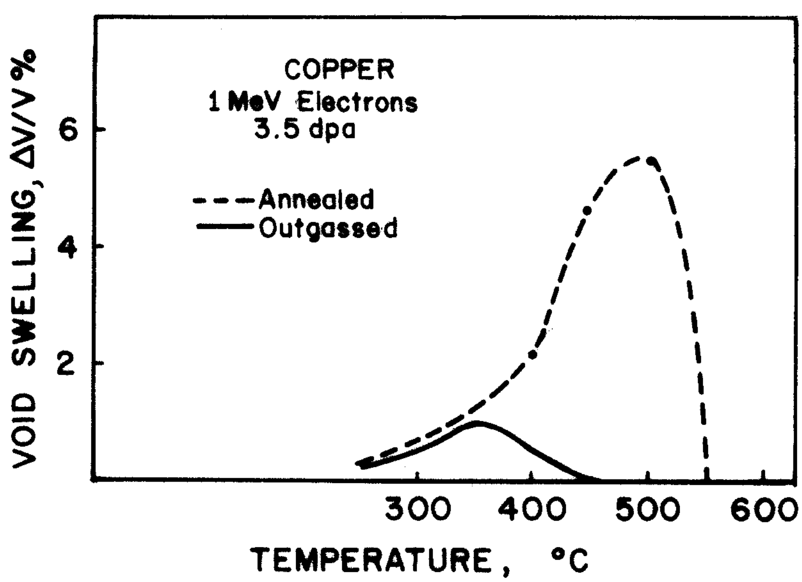

Fig. 2. (Ref. 37) Effect of outgassing on void swelling in copper.

dpa/sec. However, Barlow [49,50] found peak swelling at 450°C for a dose-rate of 1 x 10^{-2} dpa/sec. The effect of dose on void swelling characteristics depended on the gas content and dislocation density [45,47,48] of the specimen. In general, the rate of swelling increased more slowly at low fluences than at high fluence, in contrast to self-ion bombarded Cu [39]. In one very high fluence study [45], swelling saturated at doses > 75 dpa.

The influence of the dislocation structure on void formation was best summarized by the experimental observations of Kenik and Mitchell [47]: a) void nucleation (i.e. void density and the dose at which voids appear) is strongly influenced by the initial dislocation density and behavior under irradiation; b) void growth is related to the average dislocation density during irradiation; and c) above some dislocation density (2.5 x $10^9/cm^2$ here) dislocation motion is hindered and swelling decreases, indicating that the interstitial bias is reduced. In foils thin enough for most dislocations to escape (< 3000 Å) no voids formed at 300°C. In one study [45] voids formed only near dislocation walls above 350°C, while in Glowinski's work [48] voids formed above ~ 300°C only if the specimens were first irradiated at a lower temperature (100°C) to introduce a dislocation structure.

Void formation in copper-base alloys [45,49-52] was dependent on the nature and concentration of the solute as well as on the factors discussed previously for pure copper. Makin [45] examined Cu-1% Ag and Cu-1% Cd (pre-injected with Ar) during irradiation to 12 dpa at 250°C. The incubation period for the appearance of voids decreased and swelling increased greatly relative to pure Cu. However, in Cu-1% Be irradiated to 100 dpa at 250°C no voids formed. No reason was given for this void-suppressing ability of the Be solute. Barlow [49] also studied 0.1 wt% Ag and 1 wt% Ag alloys at various temperatures. The .1% alloy behaved like pure Cu at all temperatures, but the 1% alloy exhibited a higher swelling rate than pure Cu at 150-250°C, due to a higher void number density. At 350-450°C the swelling rate was the same as for pure Cu.

Barlow [49] and Leffers [50] extensively studied loop and void formation in Cu-Ni alloys (1, 2, 5, 10 wt% Ni) as a function of temperature and dose. At a given temperature void swelling increased linearly with dose at a rate dependent on Ni content. Plots of swelling vs. Ni content for different temperatures showed that swelling either decreased immediately, or else increased initially, then decreased with Ni concentration. In general, as temperature increased a greater Ni concentration was required to suppress void swelling. Reduced void growth rather than reduced void density was responsible for the decrease in swelling with composition. The most likely explanation [51] for this suppression of void growth was that tiny, non-equilibrium Ni clusters formed that acted as interstitial traps, i.e. as recombination centers.

Takeyama et al. [52] studied the effect of precipitation on void formation in Cu-1.5 wt% Fe at 250°C. Specimens were aged before HVEM irradiation to produce various concentrations of coherent or incoherent precipitates. Voids formed near precipitates during irradiation, and increased in size with increasing dose. Macroscopic void swelling increased with increasing aging time. Also, swelling was lowest in as-quenched samples, where most Fe was in solution, and highest in pure Cu samples. So, in general, void swelling increased as the amount of Fe in solution decreased.

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