HEDL--7639

DE90 001131

Effects of Neutron Irradiation to 63 dpa on the Properties of Various Commercial Copper Alloys

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April 1986

Prepared for the U.S. Department of Energy
Assistant Secretary for Nuclear Energy

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U.S. Department of Energy

NOTICE

EFFECTS OF NEUTRON IRRADIATION TO 63 dpa ON THE PROPERTIES OF VARIOUS COMMERCIAL COPPER ALLOYS - H. R. Brager (Westinghouse Hanford Company)

OBJECTIVE

The objective of this effort is to determine the effect of high neutron fluence on the properties of high purity copper and of a range of conventional commercial high-conductivity, high-strength, copper-base alloys.

SUMMARY

High purity copper and six commercial copper alloys were neutron irradiated to 47 and 63 dpa at about 450°C in the FFTF. Immersion density measurements showed a wide range of swelling behavior after irradiation to 63 dpa. At one extreme was CuBe in the aged and tempered (AT) condition which had densified slightly. At the other extreme was 20% CW Cu-0.1% Ag which swelled over 45%. Electrical resistivity measurements of high-conductivity alloys followed trends similar to previously published results for the same alloys irradiated to 16 dpa, namely a continued reduction in conductivity with fluence which appears to relate to transmutation products and, somewhat, to void formation and defect cluster development. At 63 dpa, the electrical conductivity of zone-refined copper had decreased significantly. The reduction was to a value comparable with that of the irradiated Cu-Al25 -- the Al_2O_3 dispersion strengthened alloy. Conversely, for the moderate conductivity alloy CuBe, the electrical conductivity was unaffected for irradiation greater than 16 dpa. These results of the irradiated material were compared with electrical conductivity of unirradiated alloys examined after aging for 10,000 hours.

The most irradiation resistant high-conductivity, high-strength copper alloy examined after 63 dpa is Cu-Al25 followed by MZC. Cu-2.0Be, only a moderate-conductivity alloy, exhibits very consistent irradiation resistant properties. Thus, Cu-Al25 and MZC appear to be acceptable candidates for high heat flux materials in fusion reactor applications.

PROGRESS AND STATUS

Introduction

In an earlier paper,[1] presented at ICFRM-1, the swelling, electrical conductivity and tensile properties of pure copper and six commercial copper alloys were described. These materials had been neutron irradiated at approximately 450°C to the lowest neutron fluence attained by specimens in this irradiation series -- 16 dpa. The microstructure of the specimen of pure copper and of the three high-strength, high-conductivity alloys which showed the most resistance to irradiation after 16 dpa was characterized.[2] The current paper presents information on the same commercial copper alloys which now have been neutron irradiated to the next two higher neutron fluence levels -- approximately 47 and 63 dpa. A fourth, and final, set of specimens in this series is still being irradiated in the FFTF.

Experimental procedure

The alloys listed in Table 1 were irradiated in the form of miniature tensile specimens and standard microscopy disks, both of which were punched from the same sheet stock. The discs were used for changes in density, electrical conductivity, and microscopy and were all measured at room temperature. Tensile specimens were also subjected to thermal aging at 300 to 600°C for 10,000 hours. The specimens were irradiated in 4 mm diameter helium-filled subcapsules and were tightly packed with the copper specimens separated by aluminum foil spacers and with specially machined copper bars included to improve the thermal conductivity in the subcapsules and minimize the specimen's irradiation temperature. The aluminum was included in an attempt to eliminate self-welding of the copper specimens. The copper specimens span four classes: pure metal, and solution-strengthened, precipitation-hardened and dispersion-strengthened alloys.

Results

Swelling

The 16 dpa swelling data shown on Table 1 were derived from the miniature tensile specimens; the higher fluence data were extracted from TEM disks. There was often more than one disk, allowing for an estimate of the variability of swelling. The miniature tensile specimens in the second irradiation exhibited considerable self-welding and have been set aside for later examination.

Figure 1 shows the swelling behavior observed for those alloys which exhibit a moderate-to-high amount of swelling. Pure copper reaches 31% after 63 dpa. Consistent with its swelling behavior at lower fluence[1], copper with 0.1 wt% silver exhibits the greatest amount of swelling. Its swelling rate is compared, Fig. 1, with a 1% per dpa line. This line represents the peak swelling rate reported for reactor

Table 1. Swelling of various commercial copper alloys at -450°C (irradiated in MOTA/FFTF)

Alloy	Alloy Composition (wt%)	Condition	Swelling (%) Neutron Fluence 16.2 dpa	47.2 dpa	63.3 dpa
Cu (MARZ)	Cu (99.999%)	annealed	6.5	22.2, 23.3	30.1, 31.3 33.2
CuAg	Cu-0.1 Ag	20% CW	16.6	35.4, 38.2	47.4
CuAgP	Cu-0.3 Ag-0.06 P-0.08 Mg	20% CW	7.9	16.0, 16.2	17.1
CuNiBe (½ HT)*	Cu-1.8 Ni-0.3 Be	20% CW and aged (3 h at 480°C)	1.70	13.9, 14.6	22.3, 24.6
CuNiBe (AT)*	Cu-1.8 Ni-0.3 Be	20% CW and aged (3 h at 480°C)	0.29	3.05	5.73, 6.59
CuBe (½ HT)	Cu-2.0 Be	20% CW and aged (2 h at 320°C)	-0.18	0.18, 1.11 1.71	1.09, 1.61
CuBe (AT)	Cu-2.0 Be	annealed and aged (2 h at 320°C)	-0.66	-0.45 -0.24 +0.12	-0.43 -0.25
MZC	Cu-0.9 Cr-0.1 Zr-0.05 Mg	90% CW, aged ½ h at 470°C	1.03	0.79	5.15, 7.90
Cu-Al25 (CW)	Cu-0.25 Al (as Al_2O_3)	20% CW	0.13	0.23, 0.36 0.86	0.28
Cu-Al25 (CWA)	Cu-0.25 Al (as Al_2O_3)	20% CW + aged 1 h at 550°C	---	-0.18, 0.05 0.52	0.04,1.45 1.85
Ni-Be	Ni-1.9Be	Annealed and aged 1½ h @ 500°C	-0.37	0.05	-0.11
AISI 316	Fe-18Cr-13Ni-2.5Mo	Annealed	-0.20	1.30	2.28

*½ HT and AT are industry designations for half-hard and tempered, and annealed and tempered, respectively.

irradiated fcc alloys.[3] At higher fluences, the swelling rate decreases with the swelling reaching 47% at 63 dpa. The copper alloy CuAgP with three times as much silver and small amount of phosphorus and magnesium swells less but with a pronounced S-shaped behavior. CuNiBe swelled less than pure copper or CuAg, the amount depending on the preirradiation heat treatment.

The low swelling alloys consisted of Cu-Al25, CuBe and MZC. The Cu-Al25 in the cold worked (CW) condition exhibited virtually no measurable swelling (0.28%) after 63 dpa, Fig. 2. The same material in the cold worked and aged (CWA) condition showed some scatter with swelling ranging from slight densification to nearly two percent swelling. Scatter of the density measurements could have been due to surface irregularities. Commercial grade pure aluminum foil was placed between the copper specimens to prevent self-welding. At 16 dpa,[1] this concept worked quite well. At the higher fluences reported here, some of the specimens had aluminum partially adhered to the surface. Removal of the aluminum could have been incomplete. The accuracy of each measurement is estimated to be ±0.16%.

The swelling of CuBe alloy in the hardened and tempered condition (½HT) measured swelling of about 1% after 63 dpa, Fig. 2. However, the same alloy in the aged and tempered condition (AT), on average, densified slightly.

The MZC alloy swelled about 1% after 16 dpa and was shown earlier to be the result of phase-related density changes and not due to void swelling.[2] Swelling of the alloy irradiated to 47 dpa showed practically no change while further irradiation to 63 dpa indicated swelling in the six to eight percent range.

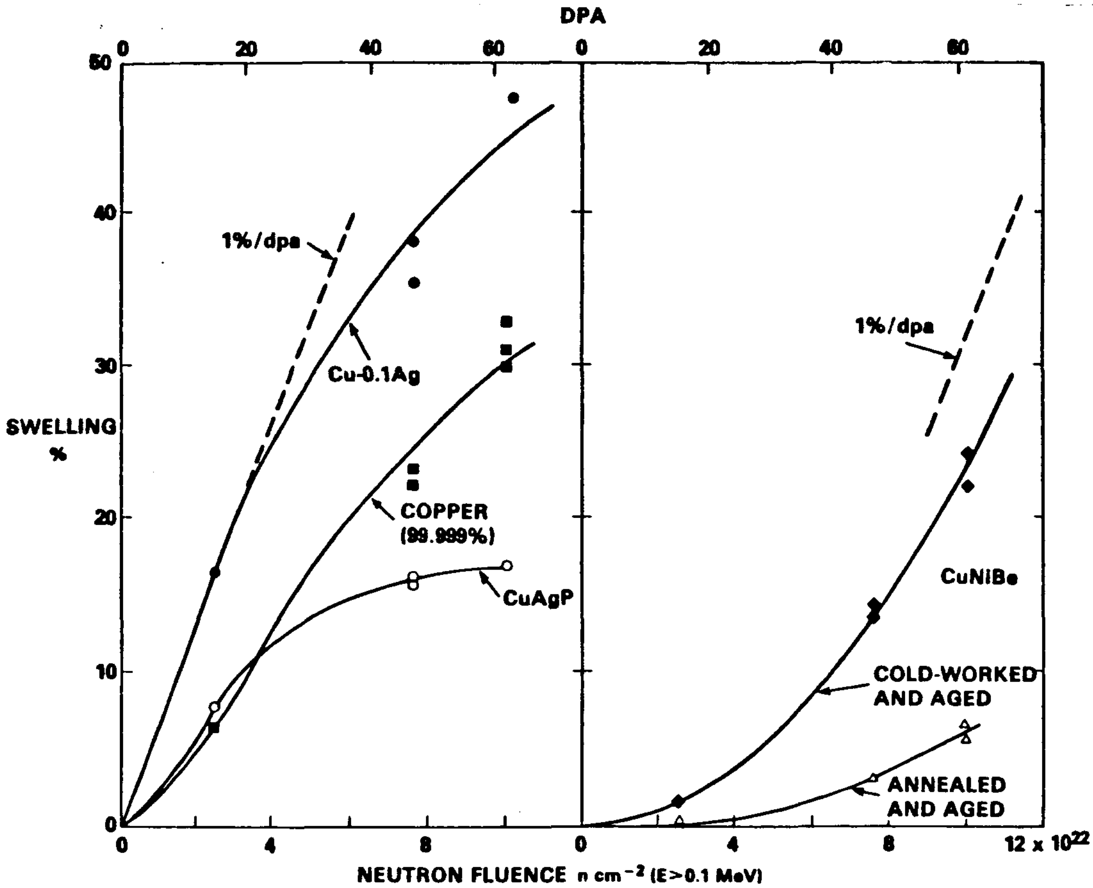

Fig. 1. Swelling behavior of zone-refined copper and copper alloys which exhibit a moderate to high amount of swelling.

The NiBe alloy was included in the experiment due to its high strength characteristics. Its potential use is as a structural reinforcing material although it has only limited current carrying characteristics. AISI 316 was included so as to reference the behavior of this well investigated alloy to other irradiation studies, if needed.

Electrical conductivity, and electron microscopy, measurements of this study focused on the three commercial copper alloys showing the most promise: Cu-Al25, MZC and CuBe. For comparison, the MARZ grade copper was also examined.

Electrical conductivity

The electrical conductivity measurements were all determined relative to that obtained for the unirradiated zone-refined copper specimen, which was assumed to have an International Annealed Copper Standard (IACS) value of 103%. The pre- and postirradiation conductivities were determined using a four point resistivity technique.

For zone refined copper, the electrical conductivity appears to decrease asymptodically with increasing neutron fluence, Fig. 3. The principal causes for the reduction in conductivity was expected to be due to void and defect cluster development and transmutation product formation. The principal transmutation products formed from copper irradiated in the FFTF are nickel and zinc.[4] The change in electrical conductivity was estimated from literature data[5] assuming that the nickel and zinc transmutation products are maintained in solution in the copper and was included in Fig. 3. These transmutation products appears to be the primary influence in the reduction in electrical conductivity of zone refined copper with increasing neutron fluence. The change due to void formation was estimated assuming that isotropic swelling decreased the conducting material between the probe point positions. The balance was attributed to the other transmutation products and defect clusters.

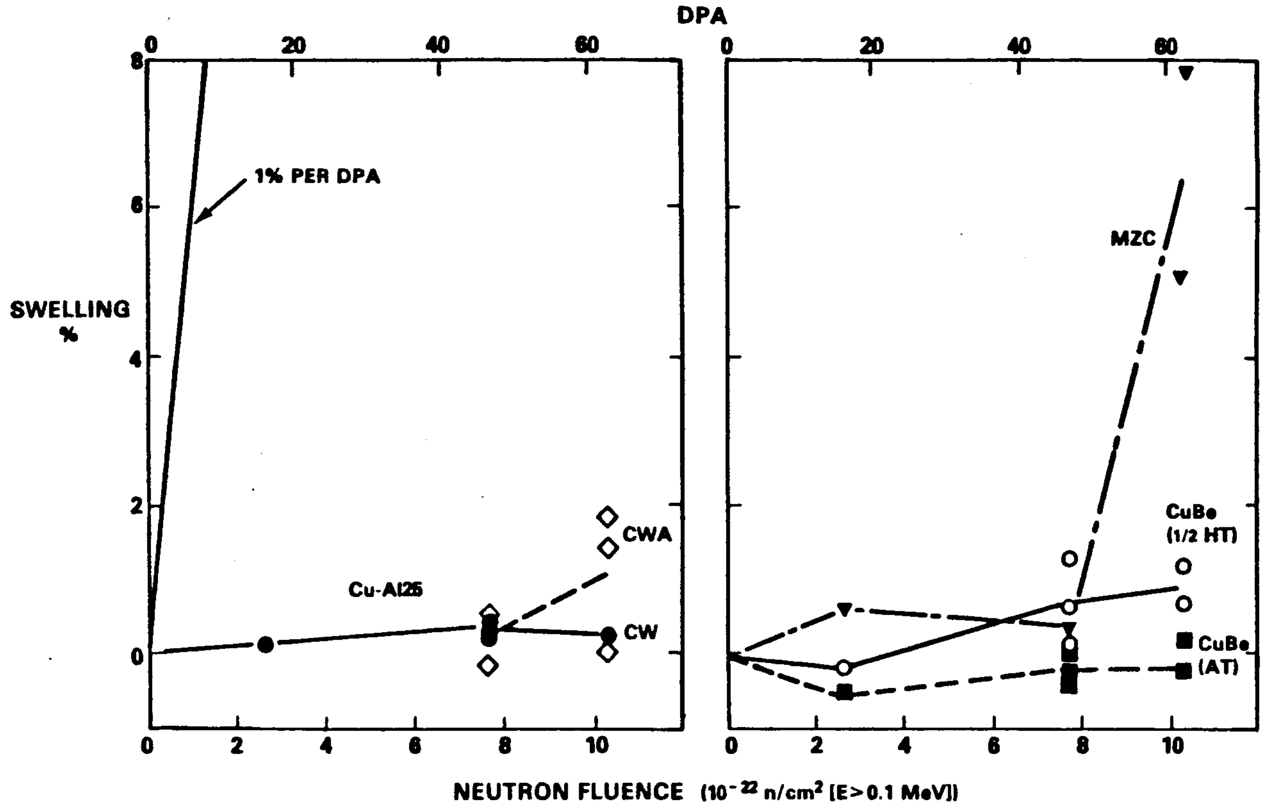

Fig. 2. Swelling behavior of copper alloys (Cu-Al25, MZC, and Cu-Be) which exhibit a low level of swelling.

The effect of neutron fluence on the electrical conductivity of the Cu-Al25 appears to follow the same trend as for zone-refined copper, Fig. 4. That is, a reduction in conductivity with increasing neutron fluence. Since Cu-Al25 consists of high-purity commercial grade copper with a low volume fraction of small sized Al_2O_3 particles, the nickel and zinc transmutation products should have a first order influence on the conductivity of the effectively single phase copper matrix. For the solution-strengthened, work-hardened MZC alloy, the general trend of a lower conductivity with increased neutron exposure was also observed. The MZC's conductivity at 63 dpa was 64% IACS or slightly lower than the 71% IACS value measured for the alloy irradiated to 16 dpa.

The effect of neutron irradiation on the electrical conductivity of the CuBe alloy was quite different from that of the single-phase, zone-refined copper. The conductivity of the unirradiated CuBe alloy is not high (about 18% IACS) and was shown to increase after irradiation to 16 dpa.[1] At higher fluences, the data of this study show that the conductivity appears to be unaffected, Fig. 5. This independence of conductivity with neutron exposure above 16 dpa is also shown to be independent of the two preirradiation thermal-mechanical-treatments given to the alloy. Both the aged and tempered (AT) and the hardened and tempered (½HT) conditions behave similarly. This behavior follows very closely the conductivity measurements of the unirradiated and aged CuBe alloy. Aging 10,000 hours at 300°C or at 500°C increased the IACS value from 18% to 25% and 33%, respectively. Both the irradiation at about 450°C and long-term aging would enhance the formation of second phase precipitates thereby reducing the amount of beryllium in solution in the matrix. This would result in an increase in conductivity of the CiBe alloy. Aging the unirradiated CuBe alloy at 600°C for 10,000 hours induced an IACS value of 22% indicating a significant resolution of beryllium back into the copper matrix at this temperature.

Electron microscopy

Electron microscopy examination was conducted on thin foils of irradiated pure copper and on the two swelling resistent high-strength, high-conductivity commercial copper alloys -- Cu-Al25 and MZC.

Zone-refined copper. The zone refined copper (99.999%) was in the solution annealed condition. The irradiation was conducted at approximately 450°C which represents a homologous temperature of 0.53. For a pure fcc metal in the solution annealed condition, one would expect a significant level of vacancy mobility at this temperature and a relatively low void density. Figure 6 shows that only a low density

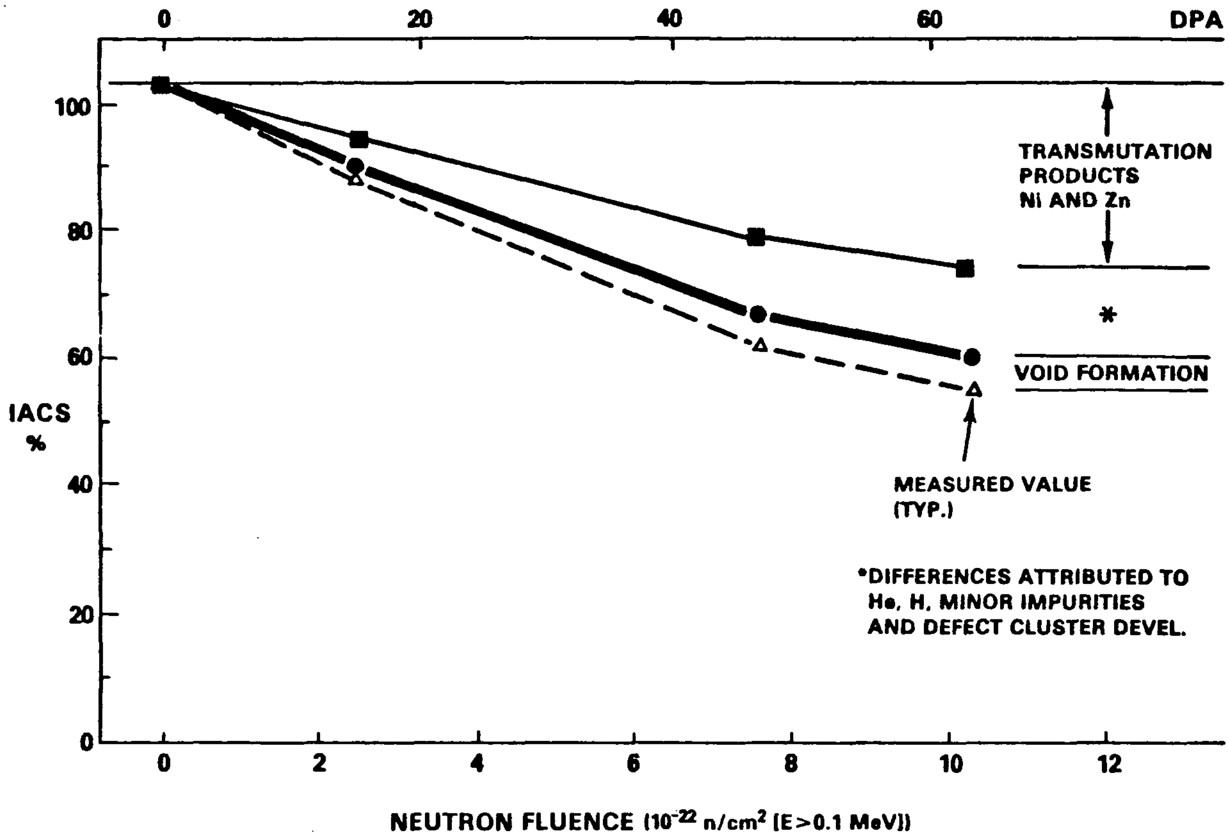

Fig. 3. Electrical conductivity measurements of zone-refined copper irradiated to a neutron fluence of up to 63 dpa. The estimated affect of transmutation products and defect cluster development on electrical conductivity of pure copper is shown.

(approximately 4 x 10^{12} cm^{-3}) of quite large and faceted voids were observed. The average diameter of these voids is nearly 500 nm. The local swelling in the region shown in Fig. 6 is approximately 20% compared to the measured change in bulk density of approximately 30%. The difference is probably associated with the difficulty in measuring voids in very thick foils.

A low density of small unidentified defect clusters is also present. These defects might be associated with the estimated 0.5 wt% Ni formed by transmutation of the copper.

Al_2O_3 dispersion-strengthened copper. The commercial alloy Cu-Al25 was irradiated in the 20% cold-worked (CW) and the cold-worked and aged (CWA) conditions and is essentially pure copper strengthened with a high number density of very small alumina particles formed by internal oxidation of a small amount of aluminum solute. In contrast to the pure copper, which had large grains on the order of tens of microns, Cu-Al25 contains grains and subgrains of micron and submicron sizes. In this particular alloy, the Al_2O_3 is 0.25 percent by weight and in the as-fabricated condition is dispersed in particles with a mean of approximately 7 nm and with a density of approximately 3 x 10^{16} cm^{-3}.

An examination of the microstructure after irradiation showed that this alloy was remarkably insensitive to irradiation, with only a low density of small cavities observed and a high density of small objects which exhibit fringe contrast that are independent of the reciprocal lattice vector, Fig. 7. The small cavities could well be helium bubbles which would represent a portion of the approximately 20 appm helium formed in the copper after 63 dpa irradiation in the FFTF.[4] To a lesser extent than for results at 16 dpa,[2] when different diffraction vectors are used to image the Al_2O_3 precipitates, only a small number of black-white contrast images with vectors parallel to the diffraction vector are visible. This result indicates that the normal radially-symmetric strain field around the Al_2O_3 particles formed during alloy preparation and observed after 16 dpa irradiation[2] is decreased after the 63 dpa neutron irradiation. However, the high concentration of small Al_2O_3 particles uniformly dispersed throughout the matrix appears to be maintained, Fig. 8.

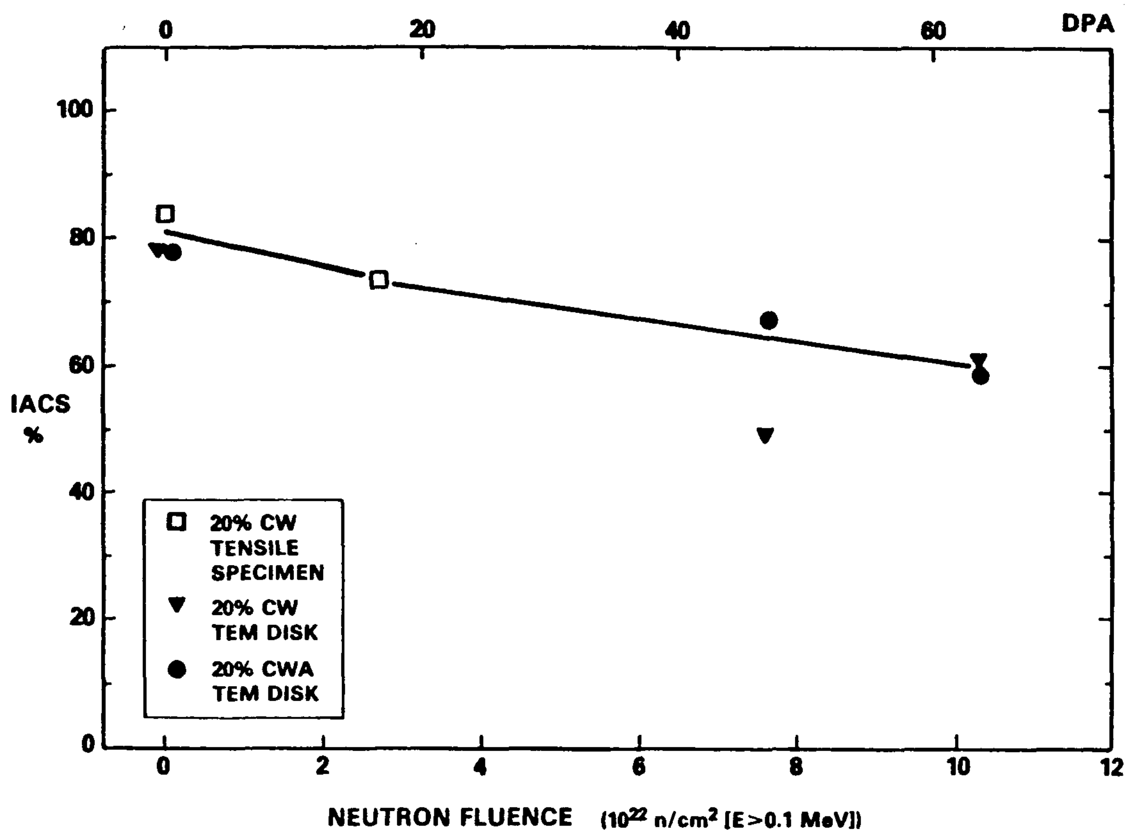

Fig. 4. The effect of neutron irradiation on the electrical conductivity of Cu-Al25 dispersion strengthened alloy.

MZC (precipitation-strengthened cold-worked alloy). The MZC copper-base alloy contains small amounts of magnesium, zirconium and chromium which provide both solid solution strengthening and precipitation hardening. When combined with work hardening, this alloy provides a good combination of high strength and high conductivity. The properties of the alloy are somewhat dependent on thermal-mechanical treatment. The recommended treatments are directed toward production of a high concentration of small precipitates. The purpose of introducing these precipitates is to stabilize the dislocation network at high temperatures.

After a less detailed examination than that employed for the Cu-Al25 alloy, it appeared that few, if any, large voids and a low density of cavities had formed in the irradiated MZC alloy, Fig. 9. This apparent absence of significant void volume in the MZC specimen is inconsistent with the measured value of about 7% swelling by immersion density change. Previously, no voidage was observed in this alloy after irradiation to 16 dpa that had a 1.0% density change.[2] While it is suspected that at least a part of this apparent swelling is principally a consequence of a lattice parameter change of the matrix arising from precipitation, a more thorough examination is required to settle this discrepancy. The possibility of having aluminum on the specimen surface and this influencing the immersion density measurements will be reviewed. While Fig. 9 also shows a high number density ($>10^{15}$/cc) of precipitates with sizes in the range 2-10 nm which exist after irradiation to 63 dpa, there is still a second population of larger (~50 nm) precipitates at approximately 10^{14} cm^{-3} which existed after 16 dpa irradiation.

Discussion

The results of neutron irradiation at near 450°C to 63 dpa of a series of commercial copper alloys have shown a mixed response. The behavior of the zone-refined copper was, in general, consistent with expectations of a pure fcc metal irradiated at a high homologeous temperature. After 16 dpa, a moderate density of large voids formed. Irradiation further to 63 dpa resulted in a substantial increase in swelling but with over an order of magnitude reduction in void density (from about 1×10^{14} cm^{-3} to about 4×10^{12} cm^{-3}). The void size increase to nearly 500 nm diameter would have occurred by both void growth and coalescence.

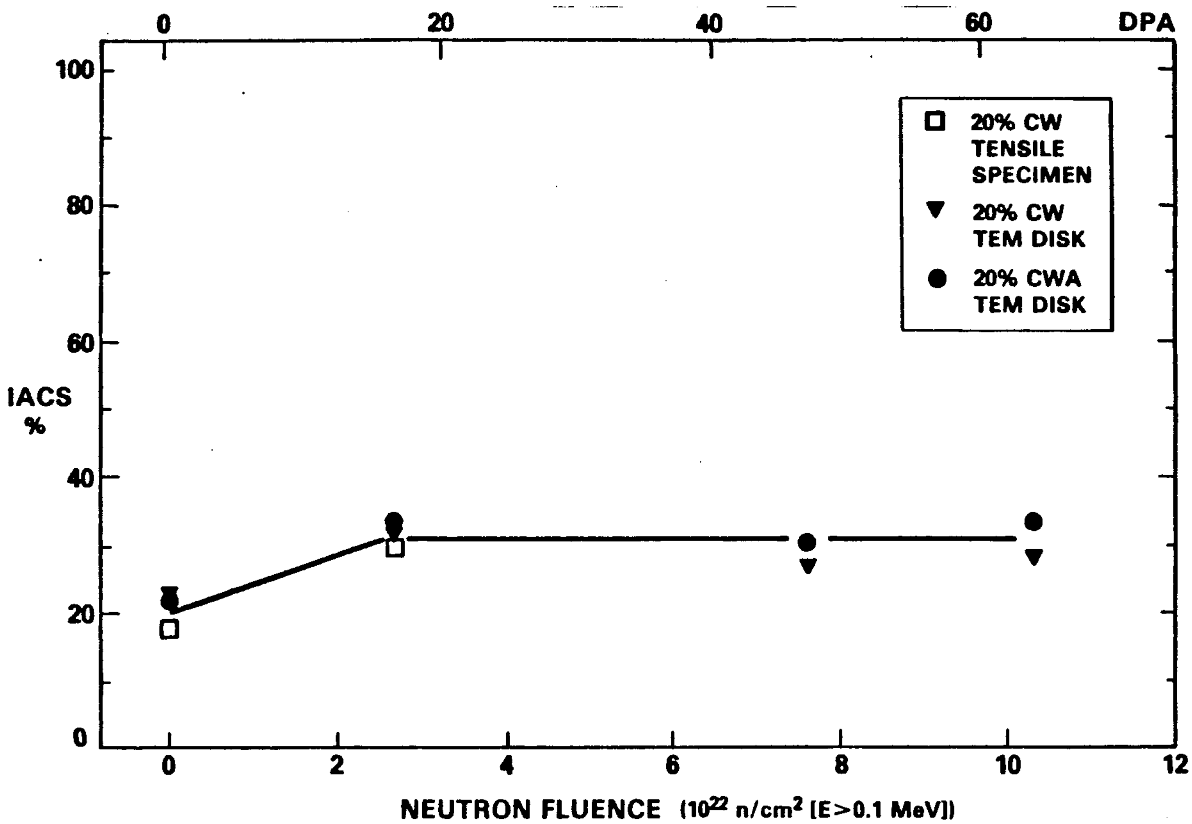

Fig. 5. The effect of neutron irradiation on the electrical conductivity of Cu-Be alloy. The conductivity appears to be unaffected by exposure above 2.7 x 10^{22} n/cm^2 (16 dpa) and by pre-irradiation thermal mechanical treatment.

The electrical conductivity of the zone-refined copper alloy was quite drastically reduced to about 60% IACS after 63 dpa. It would appear that zone refined copper should only be considered in applications with fusion reactors which will irradiate material to less than about 10 dpa. In addition, the spectral effect on transmutation products need be evaluated to estimate their effect on altering the type and amount of elements formed. In single phase materials, the effect of alloying addition on electrical conductivity should be cumulative.[5] The addition of a small (0.25%) amount of Al_2O_3 in the form of a high density (>10^{16}/cm^3) of small stable particles (~7 nm diameter) uniformly distributed in the matrix substantially improves the irradiation response of copper. This alloy, Cu-Al25, appears to be the most irradiation-resistant, high-conductivity, high-strength alloy examined in this study.

Comparison of the electrical conductivity of the zone-refined copper, Fig. 3, and of the Cu-Al25 dispersion strengthened alloy, Fig. 4, after 63 dpa shows that both materials have similar values --near 60% IACS. For applications designed for high neutron fluence -- greater than about 50 dpa, the use of the Cu-Al25 alloy appears to be clearly superior to that of pure copper.

A more thorough examination is required to better evaluate the irradiation response of the MZC alloy with its apparent resistance to void formation. This alloy appears to have high-conductivity values, maintain its high-strength at elevated temperatures and can be welded.

The CuBe alloys show excellent swelling resistant but have low conductivity. It is interesting to note that the Cu-Ni-Be alloy, with 1.8%Ni and 0.3%Be for both the ½HT and the AT conditions, exhibited poor irradiation resistance to void formation at 16 dpa.[2] The inferior behavior of this beryllium bearing alloy became very pronounced at the high neutron fluence of 63 dpa.

CONCLUSIONS

High purity copper and six commercial copper alloys were neutron irradiated to 47 and 63 dpa at about 450°C in the FFTF. Immersion density measurements showed a wide range of swelling behavior after irradiation to 63 dpa. At one extreme was CuBe in the aged and tempered (AT) condition which had densified

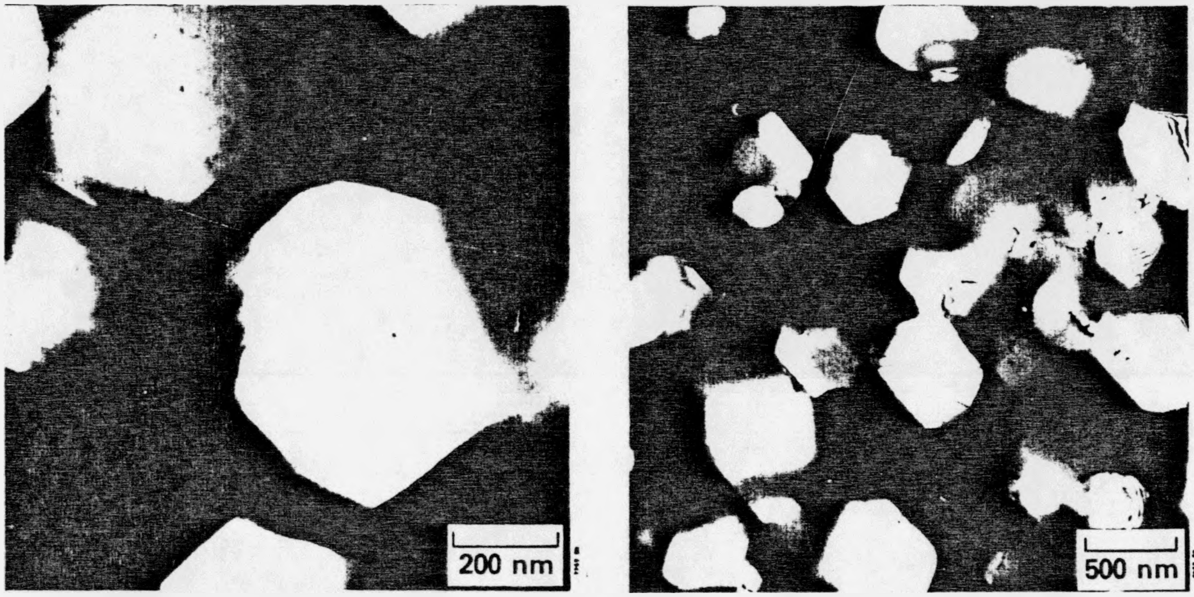

Fig. 6. A low density (~4 x 10^{12} cm^{-3}) of large voids (mean value nears 500 mm) formed in zone-refined copper irradiated at ~450°C to 63 dpa.

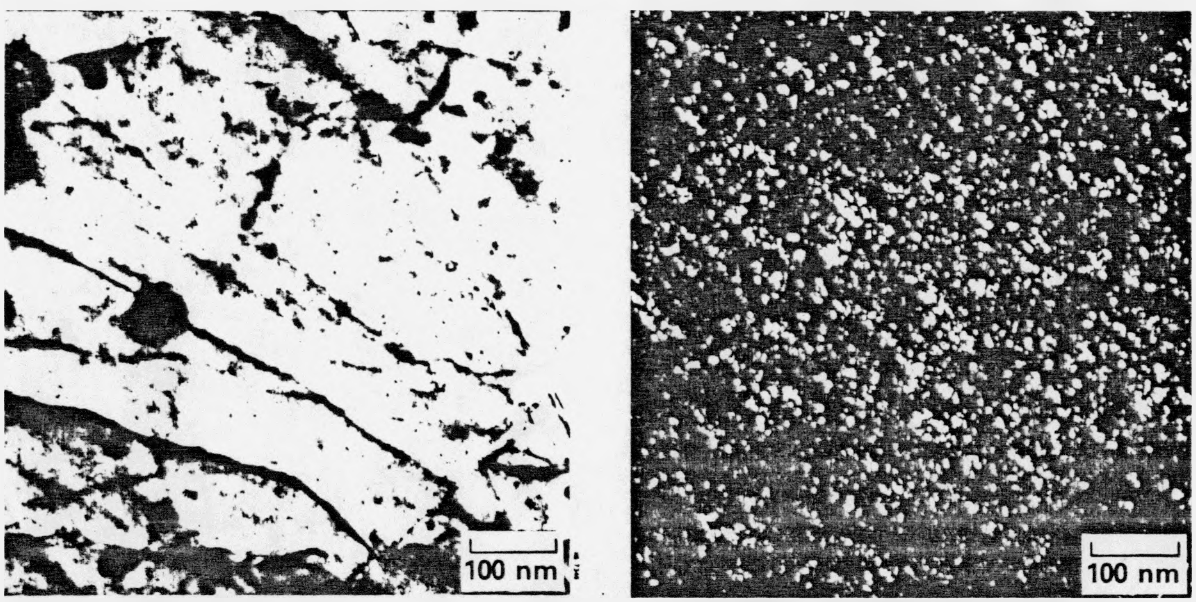

Fig. 7. Bright field and dark field micrographs of Cu-Al25 alloy which exhibit a high resistance to neutron damage of 63 dpa.

slightly. At the other extreme was 20% CW Cu-0.1% Ag which swelled over 45%. Electrical resistivity measurements of high-conductivity alloys followed trends similar to previously published results for the same alloys irradiated to 16 dpa, namely a continued reduction in conductivity with fluence which appears to relate to transmutation products and, somewhat, to void formation and defect cluster development. At 63 dpa, the electrical conductivity of zone-refined copper had decreased significantly. The reduction was to a value comparable with that of the irradiated Cu-Al25 -- the Al_2O_3 dispersion strengthened alloy. Conversely, for the moderate conductivity alloy CuBe, the electrical conductivity was unaffected for irradiation greater than 16 dpa. The most irradiation resistant high-conductivity, high-strength copper alloy examined after 63 dpa is Cu-Al25 followed by MZC. Cu-2.0Be, only a moderate-conductivity alloy, exhibits very consistent irradiation resistant properties. Thus, Cu-Al25 and MZC appear to be acceptable candidates for high heat flux materials in fusion reactor applications.

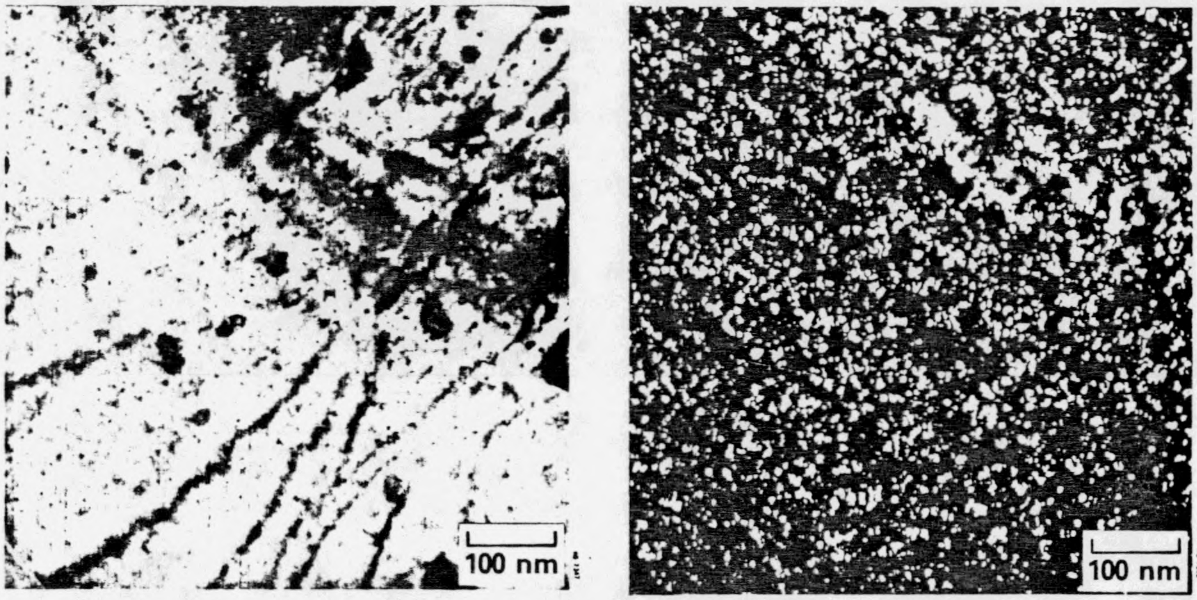

Fig. 8. Bright field and dark micrographs of Cu-Al25 alloy irradiated to 63 dpa and showing a high concentration of small, uniformly dispersed Al_2O_3 particles.

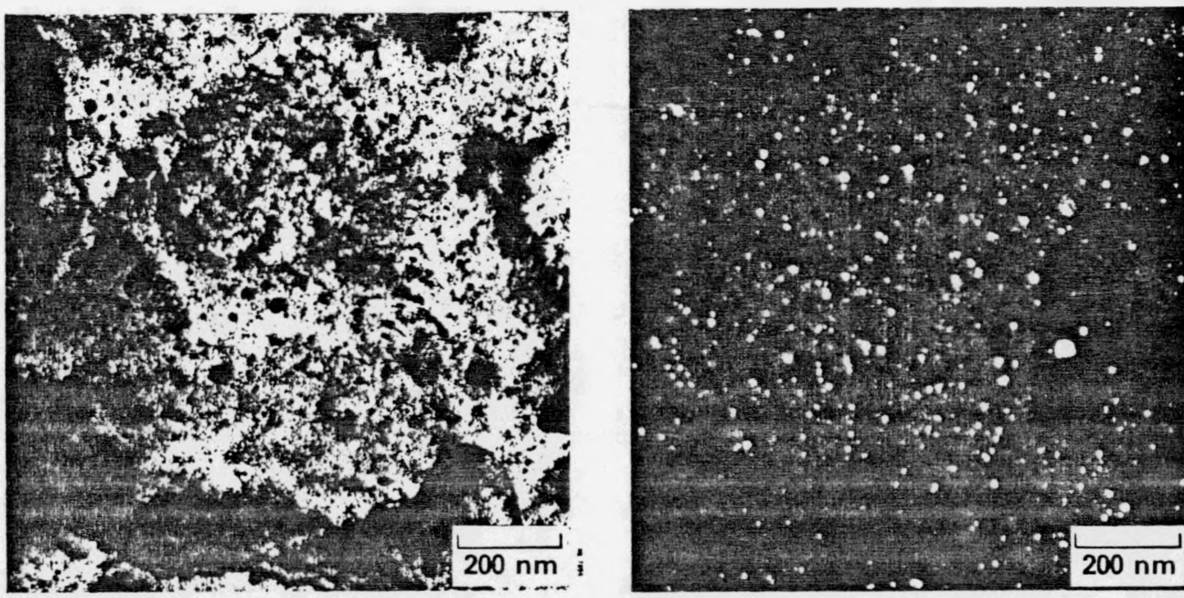

Fig. 9. Bright field and dark field micrographs of MZC alloy irradiated to 63 dpa. Preliminary examination showed no significant voidage was observed by stereographic analysis.

FUTURE WORK

The next higher fluence level, and the last of four sets, of the same copper alloy specimens irradiated in the FFTF has been discharged with MOTA 1D. These specimens, with a fluence in excess of 100 dpa, are being processed for examination covering the same topics described in the present report.

Based on the information generated by the current report, a second generation of copper alloy specimens have been prepared for irradiation. Four sets of specimens were prepared and inserted in MOTA 1E for irradiation. Details of this experiment are described elsewhere in this progress report.[6]

REFERENCES

1. H. R. Brager, H. L. Heinisch and F. A. Garner, J. Nucl. Mater. 133/134, 676-9 (1985).

2. H. R. Brager and F. A. Garner, "Microstructural Examination of Pure Copper and Three Copper Alloys Irradiated in FFTF", p. 63-70 in Damage Analysis and Fundamental Studies Quarterly Progress Report, July-September 1985, DOE/ER-0046/23, U. S. Department of Energy, Office of Fusion Energy.

3. F. A. Garner, J. Nucl. Mater. 122/123, 459-71 (1984).

4. F. M. Mann, "Transmutations in Fusion Test Facilities", p. 10-20 in Damage Analysis and Fundamental Studies Quarterly Progress Report, October-December 1985, DOE/ER-0046/24, U. S. Department of Energy, Office of Fusion Energy.

5. P. Gregory, A. J. Bangay and T. L. Bird, "The Electrical Conductivity of Copper", Metall. 71, 207-14 (1965).

6. H. R. Brager, "Neutron Irradiation of Copper Alloys", this progress report.