CONF 9009264--2

PNL-SA--18576

DE91 001563

RADIATION RESISTANCE OF COPPER ALLOYS AT HIGH EXPOSURE LEVELS

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August 1990

Invited paper presented at the
International Conference on Effects of
Irradiation on Materials of Fusion Reactors
Leningrad, USSR
September 18-20, 1990

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830
with the Pacific Northwest Laboratory
and under Contract DE-AC05-84OR21400
with the Martin Marietta Energy
Systems, Inc.

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ABSTRACT

Copper alloys are currently being considered for high heat flux applications in fusion power devices. A review is presented of the results of two separate series of experiments on the radiation response of copper and copper alloys. One of these involved pure copper and boron-doped copper in the ORR mixed spectrum reactor. The other series included pure copper and a wide array of copper alloys irradiated in the FFTF fast reactor.

INTRODUCTION

A number of copper alloys have been suggested to serve as high heat flux materials to be employed in the diverter assembly of a fusion device. Data required for the use of these materials are mechanical properties, thermal conductivity and dimensional stability during neutron irradiation, all in the range of 25 to 500°C. Although relatively pure copper has been proposed for some high heat flux components, it also serves as a reference material in many studies, including those described in this report.

There have been several hundred published studies on the effects of radiation on copper over the last three to four decades.[1,2] Many of these studies employed charged particle irradiation and a smaller number involved the use of neutron irradiation. However, few of the neutron studies have explored the full temperature range of possible exposure during high heat flux application in a diverter. In addition, only a small number of the neutron studies at any temperature have explored displacement levels in excess of one displacement per atom (dpa). Exposures greater than 1 dpa are anticipated for various short-term and long-term fusion materials goals.

This paper presents an overview of two separate series of experiments. The first series was designed to define at ~1 dpa the full temperature range of swelling in pure copper, as well as the temperature dependence of microstructural evolution. The dependence of swelling and microstructure on helium was also studied. The second experimental series was designed to explore over a more limited temperature range the radiation response of pure copper and a wide variety of copper alloys. In this series the evolution of both microstructure and various design-relevant macroscopic properties were investigated to exposure levels ranging from 16 to 100 dpa. Each of these experiments has been documented in detail in recent publications. Only the highlights of each experiment will be presented in this paper.

Irradiation in the Oak Ridge Research Reactor (ORR)

In a recent series of studies Zinkle and Farrell irradiated both zone refined copper and copper containing ~116 appm boron resulting from dissolved B_4C powder.[3,4] The boron was isotopically enriched to 92% ^{10}B. Each of the two metals were irradiated in the form of standard microscopy disks after annealing for one hour at 550°C. Nine irradiation temperatures were employed between 182 and 500°C (± 5°C), with the specimens contained in helium-filled subcapsules. The specimens reached exposures of 1.2 to 1.5 dpa at a displacement rate of ~2 x 10^{-7} dpa/sec. In the ORR spectrum the ratio of thermal to fast ($E > 0.1$ MeV) neutrons is on the order of 1:1 and 99% of the displacement damage arises from the $E > 0.1$ MeV neutrons. The ^{10}B isotope was quickly converted to helium and lithium (~100 appm of each) at an initial rate of ~500 appm/dpa.

As shown in Figure 1 swelling of pure copper peaked in the range of 300-350°C. No voids were observed at 182 and 500°C at 1.3 and 1.2 dpa, respectively. At 182°C vacancies were found to produce stacking fault tetrahedra instead of voids. Figure 2 shows that early generation of ~100 appm each of helium and lithium enhanced void swelling at temperatures below that of the peak swelling temperature in pure copper. A bimodal size distribution of cavities was observed at all nine irradiation temperatures, along with

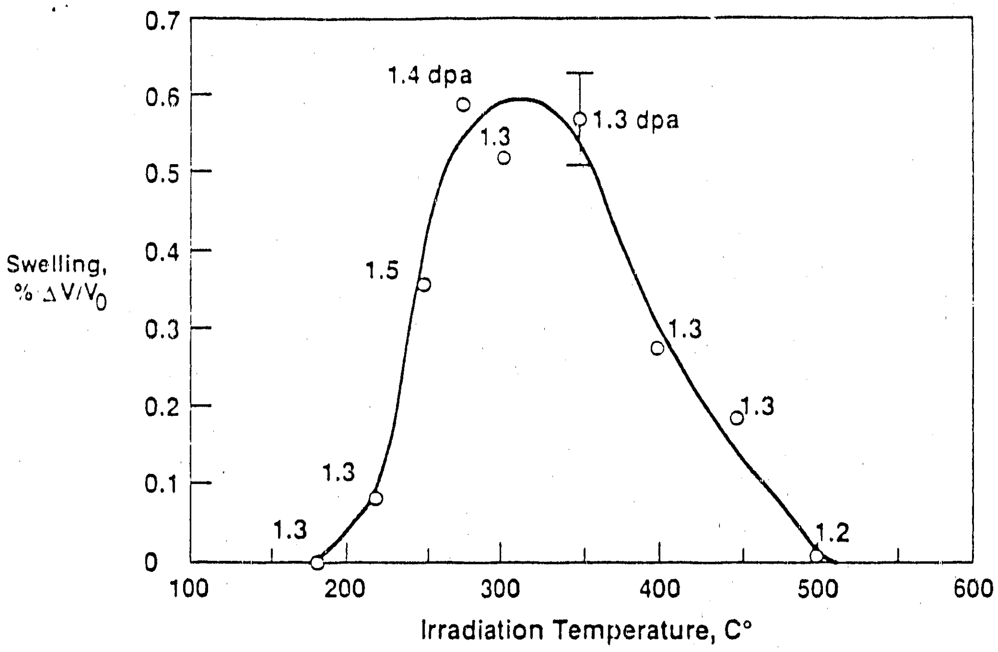


FIGURE 1. Swelling of Pure Copper in the ORR Mixed Spectrum Reactor as Determined from Density Measurements of Irradiated Microscopy Disks.[3]

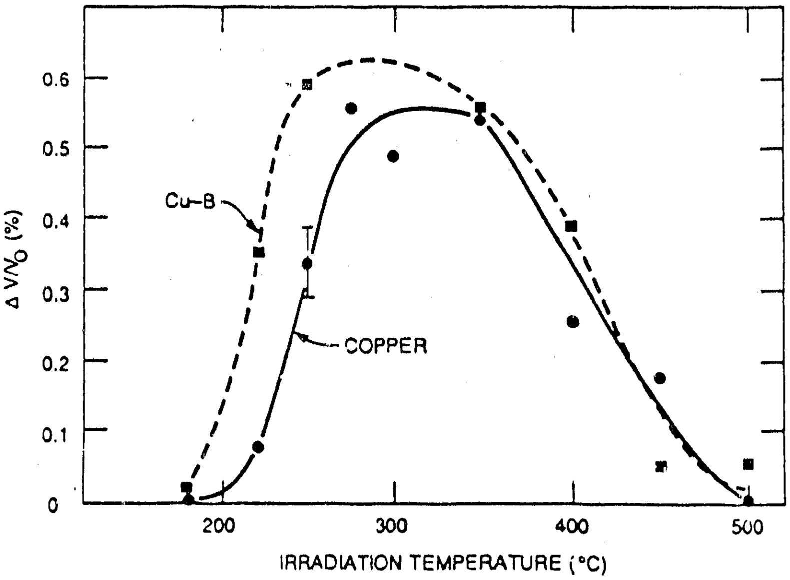


FIGURE 2. Comparison of Swelling Produced in ORR Irradiation of Pure Copper and Copper with ~100 appm of ^{10}B.[4]

dislocation loops and stacking fault tetrahedra. Figure 3 shows the enhancement of cavity formation (voids and bubbles) observed in the copper-boron alloy.

Irradiation in the Fast Flux Test Facility (FFTF)

The irradiation program conducted in this sodium-cooled fast reactor consisted of several generations of irradiation experiments with active temperature control to ± 5°C. An overview of these experiments has been presented elsewhere.[5] The first generation experiment was exploratory in nature and was completed after reaching 1.6×10^{23} n cm^{-2} ($E > 0.1$ MeV), which for pure copper in the FFTF spectrum corresponds to ~98 dpa. Earlier publications have described the results of this experiment at damage levels of 16, 47, 63 and 98 dpa.[6-9]

Figure 4 shows those alloys exhibiting the largest amounts of swelling in the first generation experiment. Pure zone refined copper reaches 56% at 98 dpa, exhibiting a very small incubation period for swelling and no indication of saturation of swellings. Cu-0.1 wt% Ag initially swells at a rate of ~1%/dpa but then decreases to the 0.5% dpa exhibited by pure copper and Cu-5 wt% Ni. Cu-5 wt% Al appears to swell in a manner very much like Cu-0.1 wt% Ag.

The Cu-1.8 wt% Ni-0.3 wt% Be alloys in the cold worked and aged, and in the annealed and aged conditions swell less than pure copper and exhibit more pronounced transient regimes of swelling. While it appears that this alloy is initially approaching the 0.5%/dpa swelling rate, there is some indication that a lower swelling rate may be developing above 47 dpa.

Two other precipitation strengthened alloys, MZC and Cu-2.0 wt% Be, are shown in Figure 5. Note that cold working before aging accelerates swelling in both CuBeNi and CuBe, due to radiation-enhanced recrystallization and solute redistribution. Radiation-induced redistribution of solutes can also lead to changes in alloy density, sometimes manifested as a densification (see annealed CuBe in Figure 5) and sometimes masquerading as void swelling. MZC is an example of the latter case and has been shown to have insufficient voidage at 16 and 63 dpa to account for the apparent swelling observed.[7]

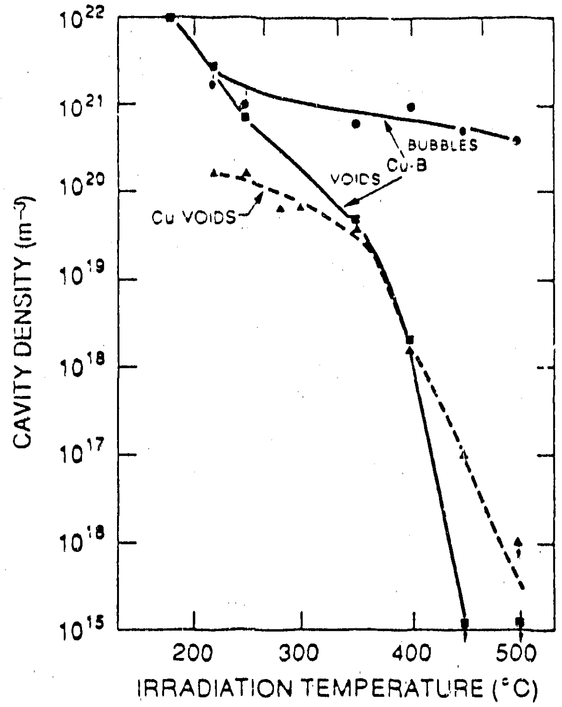


FIGURE 3. Comparison of Cavity Densities in Copper and Copper-Boron Irradiated in the ORR Reactor[4]

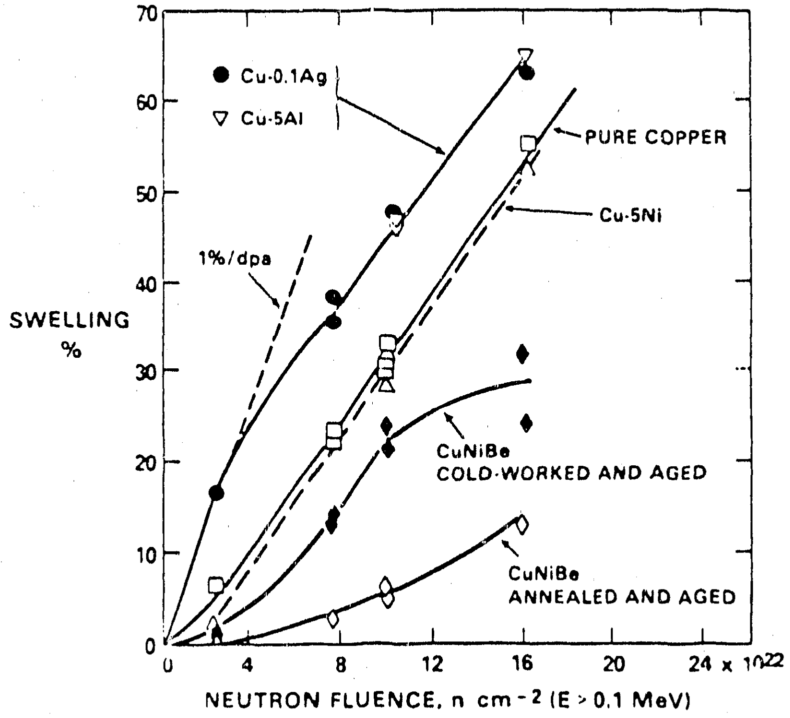


FIGURE 4. Swelling Observed in a Variety of Copper Alloys Irradiated in the FFTF Generation 1.0 Experiment at 430°C.[9] In this spectrum 1.0×10^{22} n cm^{-2} = 6.1 dpa for copper.

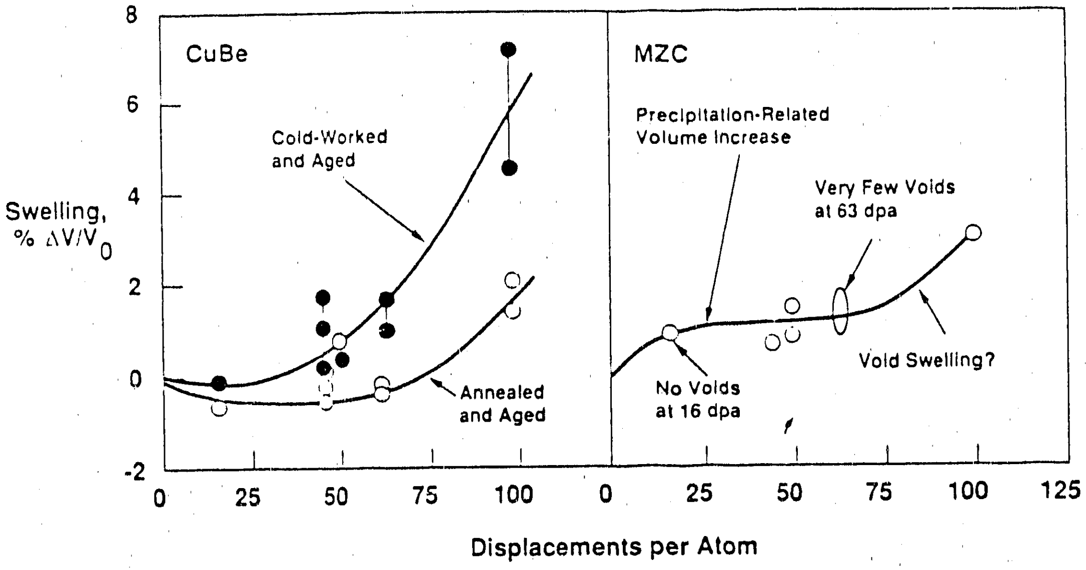


FIGURE 5. Swelling of Cu-2.0Be and MZC Irradiated at 430°C in the Generation 1.0 Experiment. Both of these alloys exhibit changes in density which result not only from void formation but also precipitation-related processes.[9]

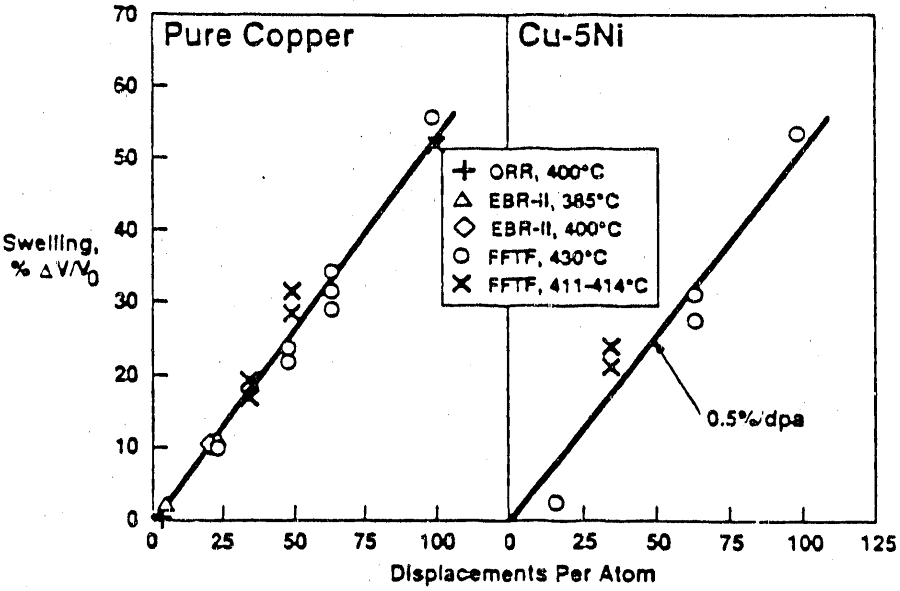


FIGURE 6. Comparison of Swelling Behavior at 385-430°C of Pure Copper and Cu-5 wt% Ni in Various Irradiation Experiments.[9] Both alloys swell at a rate of ~0.5%/dpa.

The most swelling resistant alloy in this first (Generation 1.0) experiment was the commercial dispersion strengthened Cu-Al_2O_3 alloy, known as Glidcop Al25. It was the resistance of this alloy to swelling that led to the initiation of the 1.5 and 2.0 Generation series of FFTF irradiation experiments, both of which focus on various types of dispersion strengthened alloys.[5,10]

Pure copper has been used as a standard reference material in the various generations of the FFTF copper irradiation program. For this purpose we have chosen to examine the reproducibility of its swelling and electrical conductivity in these and other irradiation experiments. Figure 6 shows a comparison of swelling observed in five separate irradiation tests conducted in three different reactors. Pure copper exhibits a relatively reproducible behavior, exhibiting a very small incubation period for swelling, followed by steady-state swelling at ~0.5%/dpa over a temperature range of at least 385-430°C.

The major transmutation product in copper is nickel and its production rate is very dependent on neutron spectra.[11] Figure 6 also shows, however, that Cu-5% wt Ni swells in a manner not very different from that of pure copper, so transmutation to nickel is not expected to affect the bulk swelling behavior of copper very much, although it may affect some details of the microstructure. Nickel additions to copper do have a substantial impact on the electrical and thermal conductivities, however. Both nickel and the second major transmutant, zinc, strongly depress the conductivities of copper.[11,12] (In the FFTF studies only the electrical conductivity was measured.) Void swelling also decreases the conductivities.[11,12] Figure 7a shows that fast reactor irradiations of copper at 385-430°C yield electrical conductivity changes that are very consistent. Since the neutron spectra of EBR-II and FFTF are very similar, the consistency is not unexpected. Also shown in Figure 7a is electrical conductivity data derived from FFTF irradiation at 529°C. Since the swelling at this temperature is only 1.8%, most of the observed conductivity loss arises from transmutation to nickel and zinc, a process that is independent of temperature.

In pure copper it was found that the effects of transmutation and voids on electrical resistivity were directly additive in accordance with

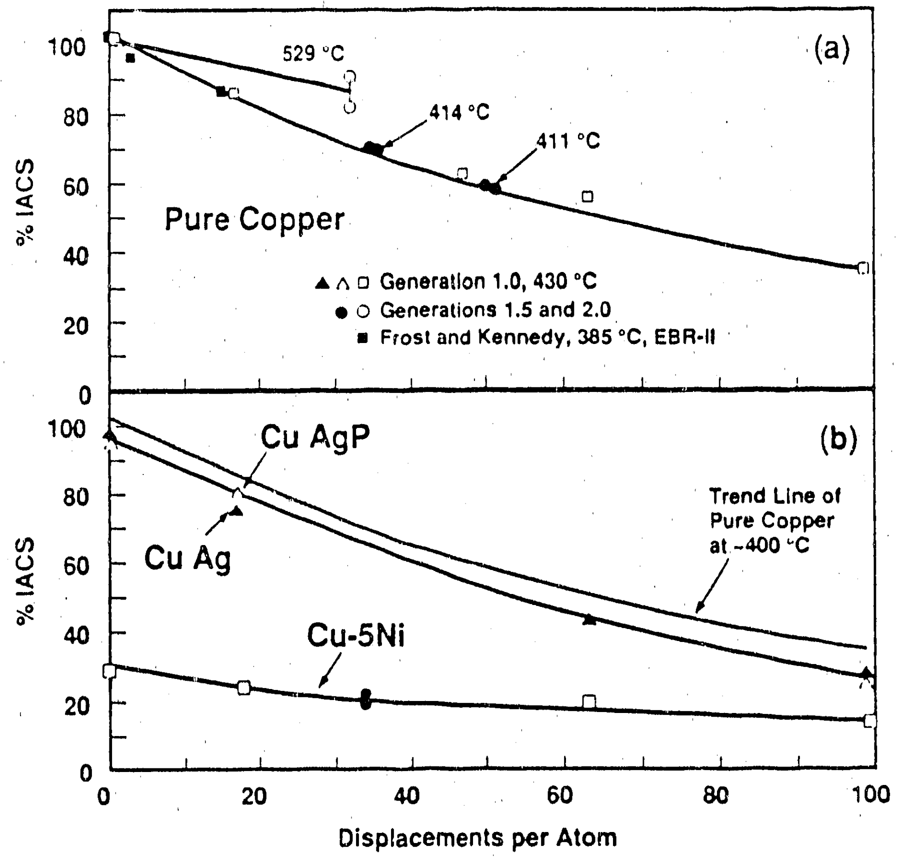


FIGURE 7. a) Neutron Induced Changes in Electrical Conductivity of Pure Copper in Various Fast Reactor Irradiation Experiments, b) Changes Observed in Cu-5Ni, CuAg and CuAgP.[9]

Matthiesson's rule, indicating that no interaction between the two processes occurred.[11,12] There are some kinds of non-additive behavior which can occur, however. There were two alloys in the first generation study involving relatively low levels of solute, CuAg and CuAgP. Note in Figure 7b that the addition of solutes in CuAg and CuAgP lowered the preirradiation conductivity from the 101% IACS of pure copper to 97 and 96% IACS, respectively. This difference in conductivity was maintained relative to that of pure copper with little change throughout the first generation experiment, indicating that these solutes probably stayed in solution. The initially low conductivity of Cu-5Ni decreases further with irradiation, as is also shown in Figure 7b.

In most solute modified alloys, radiation-induced redistribution of solutes also leads to modifications in conductivity, particularly if the solute levels are relatively large. In a previous paper it was shown that the electrical conductivity of Cu-2.0Be initially increased slightly with irradiation, but remained constant thereafter (see Figure 8).[11,13] The initial increase might be attributed to radiation-induced acceleration of precipitation and aging, but the constant conductivity thereafter was thought to be inconsistent with the continued accumulation of nickel and zinc via transmutation. It now appears that the transmutant nickel drives some of the beryllium out of solution as it forms, and the two effects compensate.[13] The strongly reduced solubility of beryllium in copper containing nickel is the principle on which the higher conducting CuBeNi (Cu-0.3Be-1.8Ni) alloy was developed to replace Cu-2.0Be. The complexity and variety of solute-related changes in conductivity for various copper alloys is also illustrated in Figure 8.

Internally oxidized alumina alloys exhibited the best overall performance in the Generation 1.5 and 2.0 experiments, retaining the largest fractions of their electrical conductivity (Figure 9), strength[10] and swelling resistance (Figure 10). Swelling of this class of alloys was found to be dependent on oxide content as shown in Figure 11, and possibly dependent on cold work level. These alloys are designated by their aluminum content. Al25 contains 0.25 wt% of aluminum in the form of the Al_2O_3 (~10μm in size) and Al15+B contains 0.15 wt% aluminum and ~100 appm boron. Microstructural examination of these alloys after irradiation yielded some evidence of ballistic dissolution

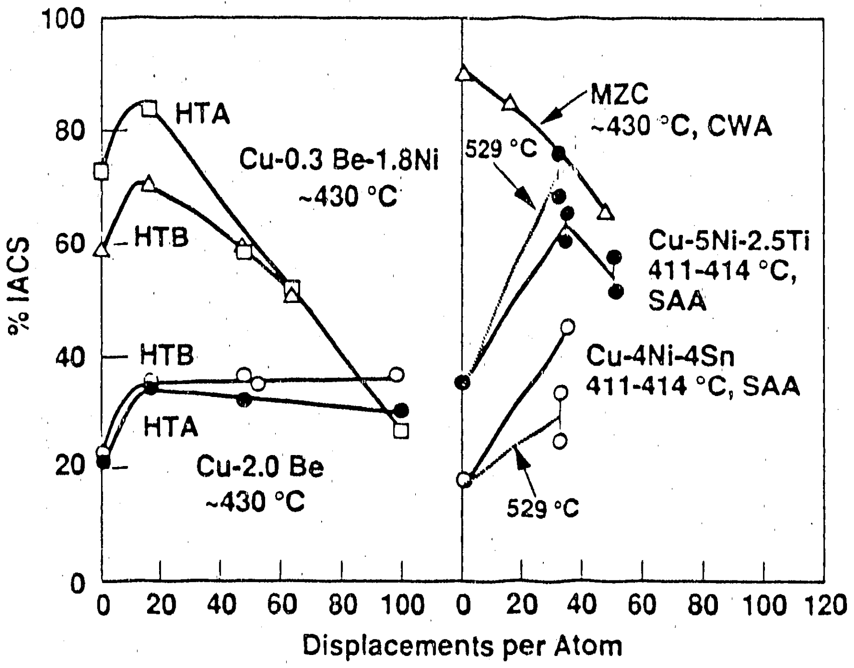


FIGURE 8. Wide Variety of Electrical Conductivity Behavior Observed in Five Alloys Irradiated in FFTF, Illustrating the Range of Interactions Between Precipitation, Solute Redistribution, Transmutation and Void Swelling.[13] HTA, HTB, SAA, CWA = cold-worked, annealed, annealed and aged, and cold worked and aged, respectively.

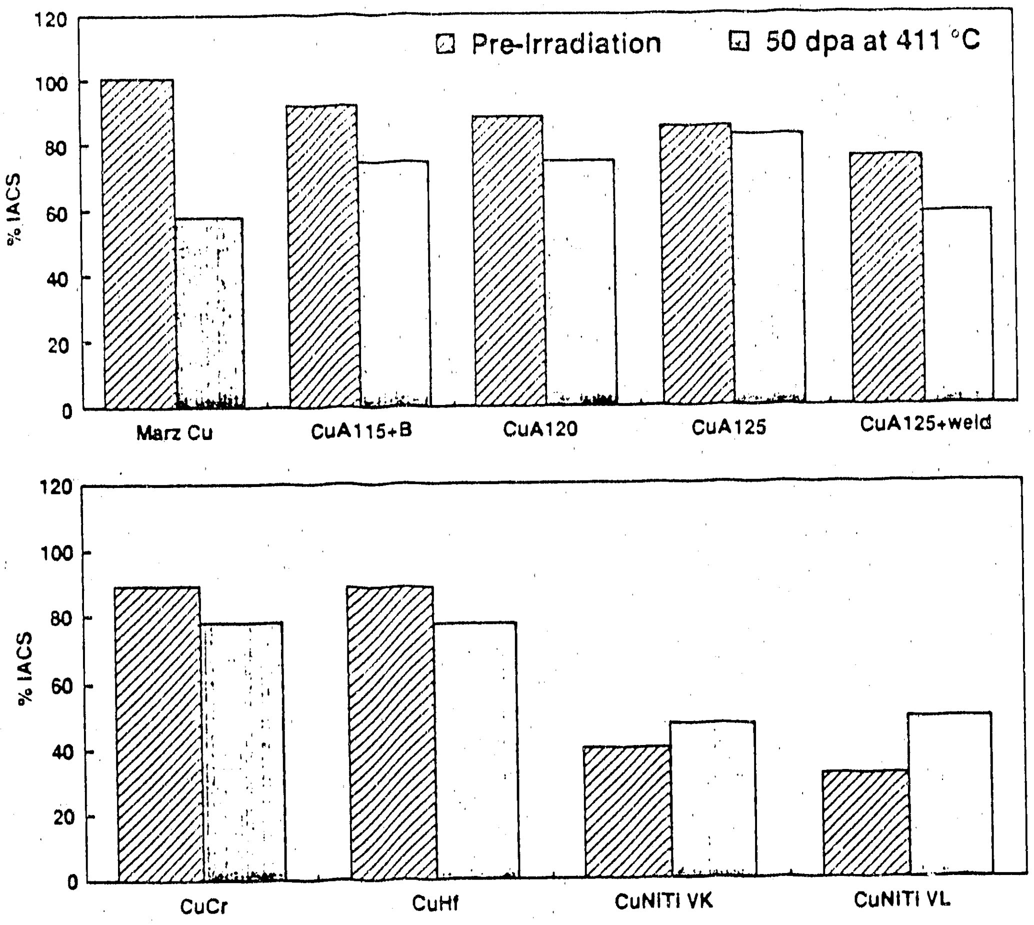


FIGURE 9. Neutron-Induced Changes in Electrical Conductivity of Various Copper Alloys Irradiated to 50 dpa at 411°C in FFTF.[13] CuCr and CuHf are copper dispersion strengthened with Cr_2O_3 and HfO_2, respectively. CuNiTi variants are spinodally-strengthened alloys.

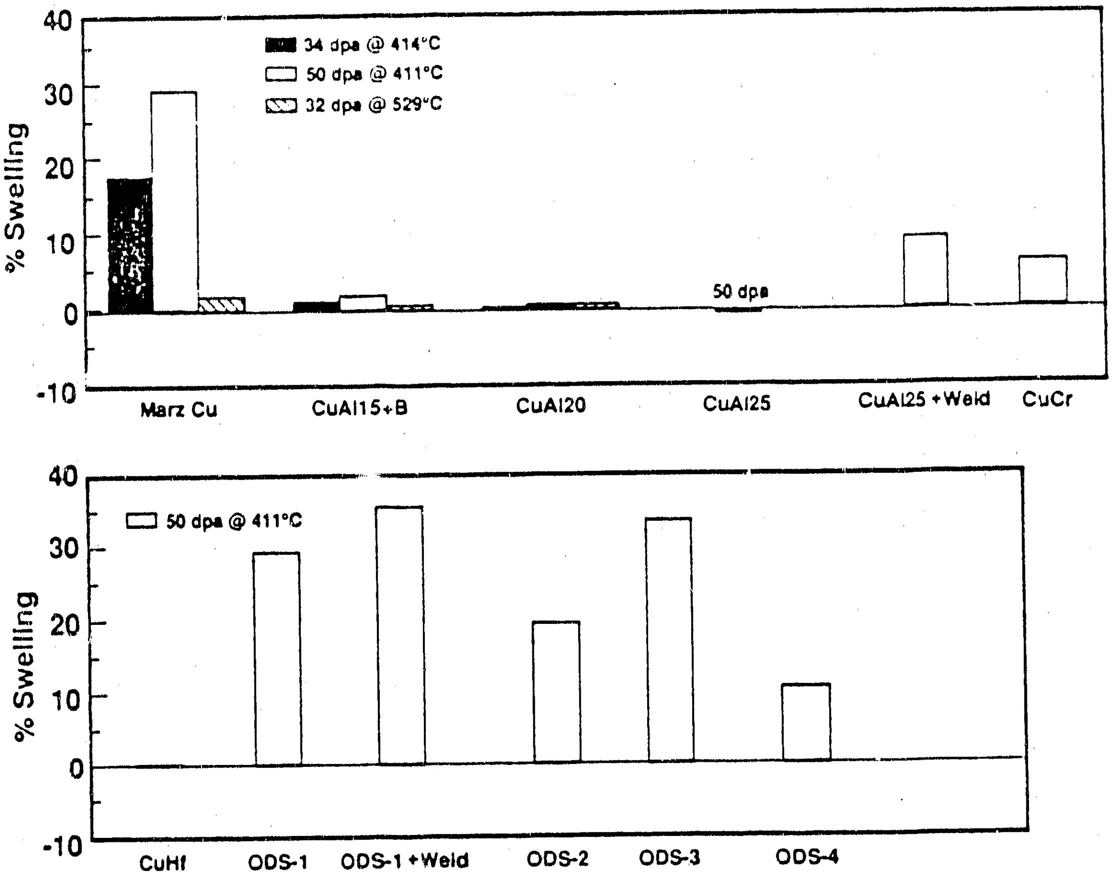


FIGURE 10. Swelling Measured by Immersion Density of Alloys Irradiated in FFTF at 411, 414 or 529°C. The ODS alloy series contained too much oxygen and exhibited very poor performance in spite of a large amount of oxide dispersion.

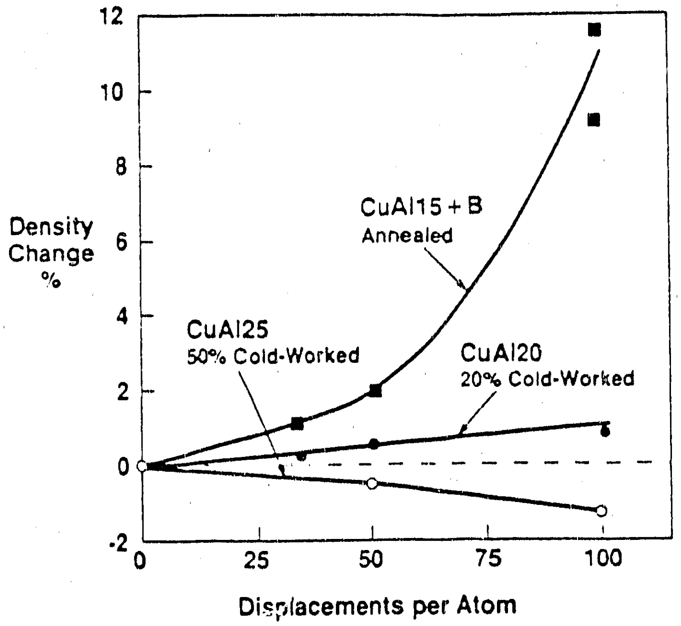


FIGURE 11. Dependence of Swelling of Internally Oxidized Alloys at 411-414°C on Al_2O_3 Content and Starting Condition[14]

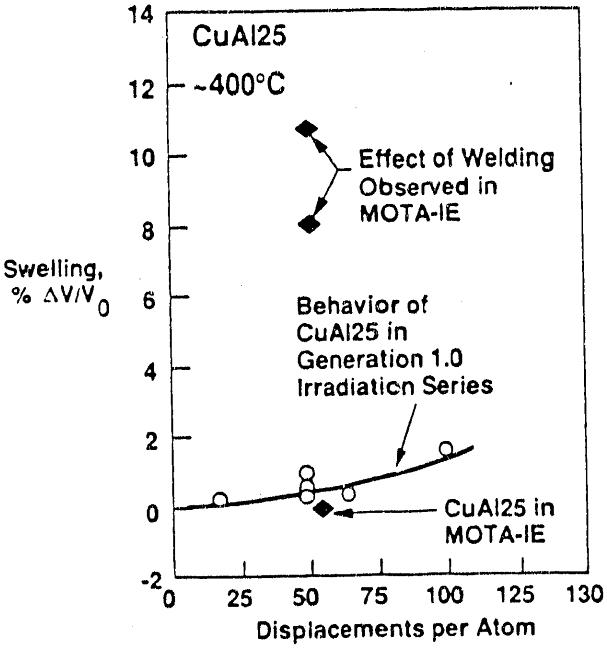
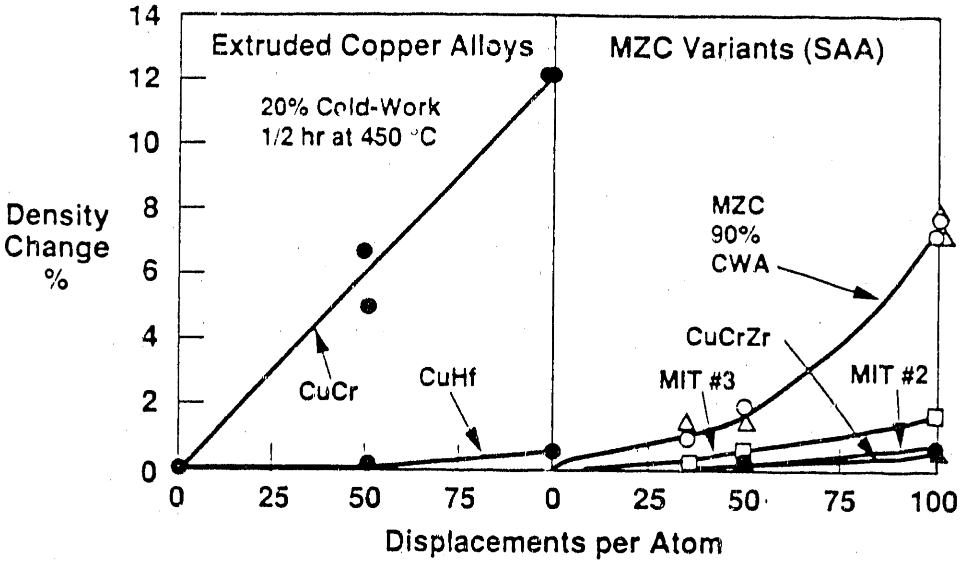


FIGURE 12. Loss of Swelling Resistance in CuAl25 Upon Laser Welding Prior to Irradiation.[5,14] MOTA-1E refers to the Generation 2.0 experiment. A later discharge of MOTA-1F showed that at ~100 dpa the welded alloy yielded swelling values that ranged from 19-43% while the unwelded alloy had densified.

of the alumina particles but this possibility requires further study. This possibility was originally thought to account for the densification of 0.3% observed in the A125 alloy at 50 dpa. At 100 dpa the densification was recently measured to be 1.1% in this same alloy, however, which led to a reevaluation of this conclusion. The densification may also result from the accumulation of nickel and zinc transmutants. There is no dependence of the electrical conductivity of these internally oxidized alloys on irradiation temperature since swelling is very low and transmutation alone accounts for the decrease.

Several other types of oxide-dispersion strengthened ODS alloys tested in these experiments were found to range from relatively good (CuHf) to very poor, depending on the alloy.[10] In particular, a series of "castable-weldable" ODS alloys were found to contain too much oxygen and behaved very similarly to pure copper, as also shown in Figure 10. Two mechanically alloyed coppers based on chromium or hafnium oxides exhibited low to moderate swelling and were also observed to develop redistribution and refinement of the oxide particles. The swelling behavior of these alloys is shown in Figure 13 and can be compared with the behavior of other precipitation strengthened alloys irradiated in the Generation 2.0 experiment. The strength and conductivity behavior of the other alloys shown in Figure 13 are described in references 13 and 14. The tensile and fracture behavior of pure copper are detailed in reference 16. Those of other alloys are listed in references 6, 10, and 14.

Laser welding was found to completely destroy the swelling resistance of both the Glidcop and ODS alloys, as shown in Figure 12 for A125, yielding swelling, resistivity and fracture behavior typical of pure copper.



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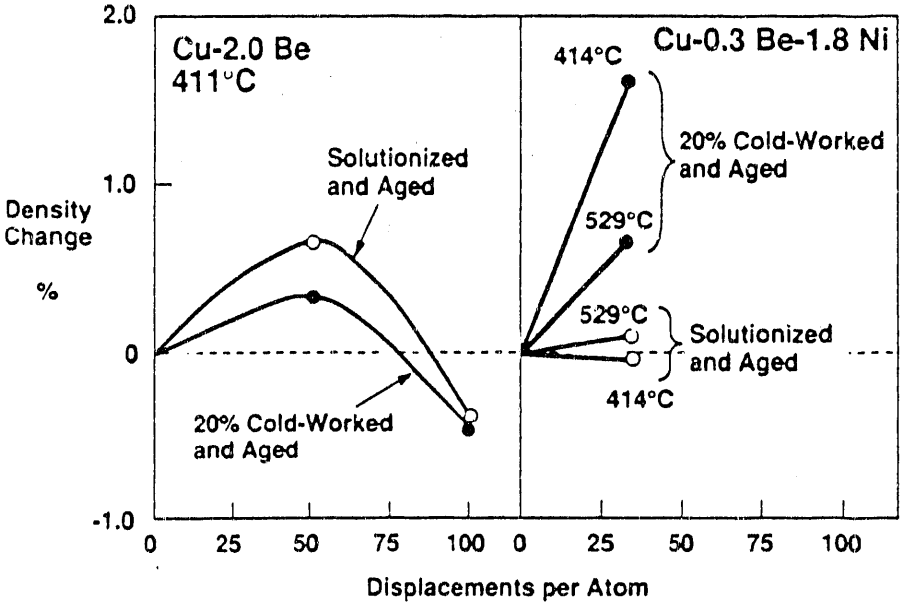

(b)

FIGURE 13. Swelling Observed in Various Copper Alloys Irradiated at 411-414°C in the Generation 1.0, 1.5 and 2.0 Experiments.[15]

CONCLUSIONS

Copper and its alloys exhibit a wide range of response to neutron irradiation that varies with alloy composition and starting state, irradiation temperature and neutron spectra. The latter is expressed primarily via its strong influence on the rates of formation of solid transmutants which can both directly or indirectly affect electrical and thermal conductivity. The influence of transmutation is not always reflected in other property measurements, however, as illustrated by nickel's lack of influence on the swelling of copper. It must be cautioned that the use of the conductivity data from FFTF will underestimate the changes expected in a fusion spectrum. These data should therefore be corrected for spectral influence before applying to a fusion device.

If we assume that pure copper exhibits the greatest tendency toward swelling, then the combined results of the ORR and FFTF experiments leads us to expect the possibility of swelling for a given alloy anywhere in the range 180-530°C and perhaps at even higher temperatures at sufficiently large displacement levels. The largest swelling rate observed at high fluence is ~0.5%/dpa but it is uncertain whether this value is valid at the peak swelling temperature of 300-350°C or at temperatures >430°C. Swelling appears to be slightly sensitive to helium content below the peak swelling temperature but the presence of relatively large amounts of oxygen may lead to a much more pronounced response.

Alloys of copper-aluminum which are strengthened by internal oxidation offer the best performance, judging by their swelling resistance, their small conductivity change and the retention of their mechanical properties. Further research is required on methods for joining these alloys that will withstand the effects of radiation.

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