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Influence of composition, heat treatment and neutron irradiation on the electrical conductivity of copper alloys

M. Eldrup *, B.N. Singh

Materials Research Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

Abstract

The electrical conductivity of three different types of copper alloys, viz. CuNiBe, CuCrZr and Cu–Al_2O_3 as well as of pure copper are reported. The alloys have undergone different pre-irradiation heat treatments and have been fission-neutron irradiated up to 0.3 dpa. In some cases post-irradiation annealing has been carried out. The results are discussed with reference to equivalent Transmission Electron Microscopy results on the microstructure of the materials. The CuNiBe has the lowest conductivity ($\leqslant 55\%$ of that of pure Cu), and Cu–Al_2O_3 the highest (75–90% of pure Cu).

1. Introduction

Because of the high thermal conductivity of copper, three different copper alloys, i.e. CuNiBe, CuCrZr and the prime candidate Cu–Al_2O_3, are under consideration for their applications in the structural components of International Thermonuclear Experimental Reactor (ITER) [1,2]. The heat sink materials will have to be joined to the first wall and divertor materials at relatively high temperatures (900–1000°C). During the joining process at these high temperatures, the microstructure of the alloys may change, the degree of change depending upon the actual composition and structure [3]. The two alloys, CuNiBe and CuCrZr, have been chosen as potential back-up materials to the prime candidate Cu–Al_2O_3, and for that reason it was decided to carry out a series of experiments to simulate the effect of bonding and bakeout thermal treatments on pre- and post-irradiation microstructures, mechanical properties and electrical resistivity of CuNiBe and CuCrZr alloys. In this paper we report results of electrical conductivity measurements.

The conductivity measurements have two purposes. One is to characterize the defect properties of the alloys. This can be done because the conductivity depends on the defect configuration and concentration in the material, i.e. the distribution and concentration of impurities (alloying elements and transmutation products) as well as radiation created defects. The other purpose is to obtain direct information about the electrical conductivity as an approximate measure of thermal conductivity.

2. Materials and experimental procedure

The materials used for the investigations were oxygen-free high conductivity copper (OFHC-Cu) CuNiBe, CuCrZr and Cu–Al_2O_3 alloys. The OFHC-Cu, CuNiBe and CuCrZr alloys were supplied by Tréfimétaux (France) as 20 mm thick plates. In addition, specimens of a commercial CuNiBe (Hycon 3HP) manufactured by Brush Wellman (USA) and of a CuCrZr alloy from Outokumpu (Finland) were included in the study. Oxide dispersion strengthened copper (Cu–Al_2O_3) was supplied by SCM Metals (USA) (trade mark GlidCop CuAl-25 or CuAl-60) in the form of rods in the as-extruded condition. Another Cu–Al_2O_3 alloy, of the same composition as CuAl-25, was cross rolled to remove texture before the specimens were cut. This material is referred to as CuAl-25 IGO (ITER Grade 0). The chemical compositions of the alloys are listed in Table 1.

The specimens used for electrical conductivity measurements were the same as those used for tensile testing.

* Corresponding author. Tel.: +45-4677 5728; fax: +45-4677 5758; e-mail: morten.eldrup@risoe.dk.

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Table 1
Chemical composition of the copper and copper alloys

OFHC-Cu	Cu–10, 3, <1 and <1 ppm of Ag, Si, Fe and Mg, respectively
CuCrZr	Cu–0.8% Cr, 0.07% Zr, 0.01% Si
Outokumpu	Cu–0.78% Cr, 0.13% Zr, 0.003% Si, 0.008% Fe
CuNiBe	Cu–1.75% Ni, 0.45% Be
Hycon	Unknown, but similar to CuNiBe
CuAl-25, CuAl-25IGO	Cu–0.25% Al as oxide particles (0.46% Al_2O_3)
CuAl-60	Cu–0.60% Al as oxide particles (1.10% Al_2O_3)

They were cut from cold rolled (~80%) sheets (~0.3 mm) to a gauge length of 7 mm and a nominal width of 3 mm. The detailed geometry of the specimens is shown in [4]. Prior to irradiation, the OFHC-Cu specimens were annealed at 550°C for 2 h, while the CuCrZr and CuNiBe specimens were given different heat treatments as summarized in Table 2. All heat treatments were carried out in vacuum (~1 mPa).

The OFHC-Cu specimens were neutron irradiated in the DR3 reactor at Risø in the dose range 0.01–0.3 dpa (NRT) at 100°C and the alloys to a dose of 0.3 dpa (NRT) at temperatures of 100°C, 200°C, 250°C and 350°C. The fast neutron fluence equivalent to the 0.3 dpa is $\sim 1.4 \times 10^{24}$ nm^{-2} and the associated thermal fluence $\sim 4.2 \times 10^{24}$ nm^{-2}. Details of the irradiation procedures are given in [4–6]. A number of the specimens were annealed at 300°C for 50 h after irradiation.

All resistivity measurements were carried out at 23°C. A PC controlled module developed at Risø was used. The module applies a four point technique. It switches the current direction to eliminate the influence of thermovoltages on the resulting resistance. All measurements were carried out with two different modules to assure reproducibility.

We estimate the uncertainty on the measured electrical conductances to about ±2% (mainly due to sample dimension uncertainties).

For each set of measurements, the conductivity, σ_{Cu}, of one or two OFHC-Cu reference samples (annealed at 550°C for 2 h) was also determined. The results always agreed with the nominal value of 0.589 $(\mu\Omega\,\mathrm{cm})^{-1}$ within the uncertainty stated above. In the following, the results are presented relative to the measured reference, i.e. as "Relative Conductivity", given by σ/σ_{Cu}.

3. Results

Fig. 1 shows the results for OFHC-Cu, neutron irradiated at 100°C to different doses, both in the as-irradiated state and after annealing at 300°C for 50 h. The conductivity decreases by about 12% at the highest doses, but regains about 5% on annealing.

The results for the un-irradiated CuCrZr and CuNiBe alloys after the different heat treatments are shown in Fig. 2. Certain variations in conductivities were observed between different batches of samples with the same nominal heat treatment, while no such variation was seen between different samples for the same batch. The variations are shown by the "error bars" in Fig. 2. In the case of CuCrZr alloys, the conductivity increases from slightly less than 50% of the conductivity of pure Cu in the prime aged condition to ~60–70% after bonding treatment and finally reaches a value of ~70–

Table 2
Summary of heat treatments for CuCrZr, CuNiBe and CuAl alloys

	Heat treatment
A	Solution annealing at 950°C for 1 h followed by water quench
E	Prime ageing: Heat treatment A + ageing at 475°C for 30 min followed by water quench
B	Bonding thermal cycle: Heat treatment E + annealing at 950°C for 30 min followed by furnace cooling + re-ageing at 475°C for 30 min followed by furnace cooling
C	Bakeout thermal cycle: Heat treatment B + annealing at 350°C for 100 h followed by furnace cooling
C′	Bakeout thermal cycle: Heat treatment E + annealing at 350°C for 100 h followed by furnace cooling
D	Annealing at 950°C for 30 min followed by furnace cooling (Only CuAl)
D′	The as-wrought condition, i.e. without any heat treatment (Only CuAl)
F	Prime ageing: Annealing at 960°C for 1 h followed by water quench + ageing at 460°C for 2 h followed by water quench (Only Outukumpu)

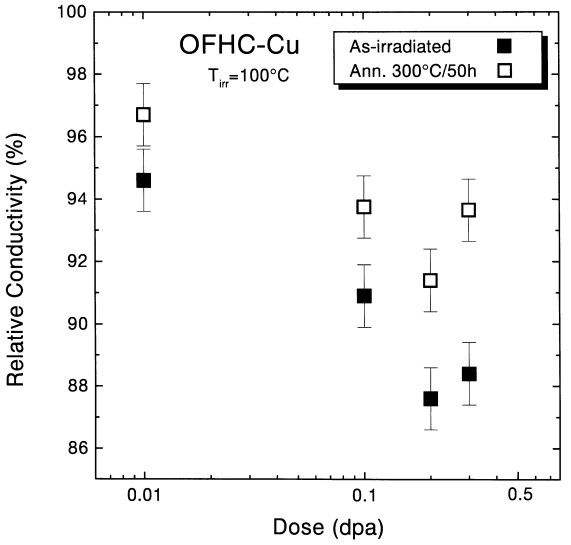

Fig. 1. Relative electrical conductivity of OFHC copper, neutron irradiated at 100°C to different doses (dpaNRT), in the as-irradiated state and after annealing at 300°C for 50 h. The error bars represent estimated uncertainties on the conductivity measurements.

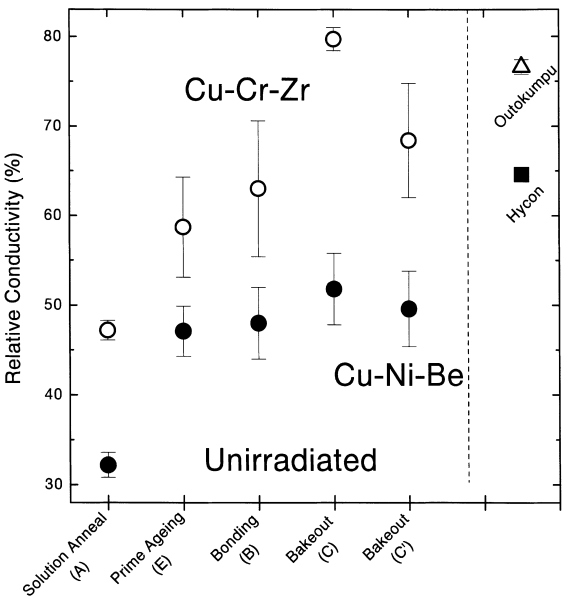

Fig. 2. Relative electrical conductivity of CuCrZr (○) and CuNiBe (●) alloys after different heat treatments in the un-irradiated state. The "error bars" represent variations in conductivities observed between different batches of samples with the same nominal heat treatment. Hycon is a commercial CuNiBe alloy and Outokumpu the CuCrZr alloy from this company after heat treatment F.

80% after bakeout treatment. The conductivities of the CuNiBe alloys, on the other hand, do not increase much beyond ~50% (except for the Hycon).

Figs. 3 and 4 show the effects of neutron irradiation on the two alloys in Fig. 2. The results are presented as the changes in relative conductivity due to irradiation to 0.3 dpa at different temperatures, i.e. $(\sigma_{irr} - \sigma_{un\text{-}irr})/\sigma_{Cu}$, where σ_{irr} and $\sigma_{un\text{-}irr}$ are the relative conductivity for the irradiated and the un-irradiated sample with the same heat treatment, respectively. As mentioned above, variations in conductivity were observed for the un-irradiated samples between batches with nominally the same heat treatment. Therefore, to make a comparison of σ_{irr} and $\sigma_{un\text{-}irr}$ meaningful, the changes plotted in Figs. 3 and 4 are all samples belonging to the same batches. The figures also display data for post-irradiation annealing of samples. For CuCrZr (Fig. 3), the A, E and B samples show conductivity increases by about 10% on irradiation which is only moderately dependent on irradiation temperature, while the Outokumpu alloy shows only little sensitivity to irradiation. Only the C sample shows a strong decrease on irradiation. On annealing (300°C/50 h), the conductivity increases in all cases, but by different amounts.

The CuNiBe alloys show a different behaviour (Fig. 4). On irradiation at 100°C, 200°C and 250°C the conductivity decreases (or is unchanged in one case), while it increases on irradiation at 350°C, the amount of change depending upon the heat treatment. Annealing increases the conductivity also for this alloy.

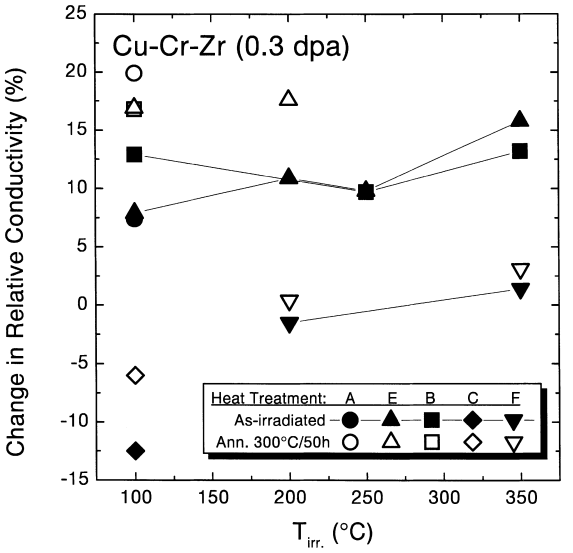

Fig. 3. The change in relative conductivity for CuCrZr resulting from neutron irradiation to 0.3 dpa at different temperatures (closed symbols) and from post-irradiation annealing (300°C/50 h) (open symbols).

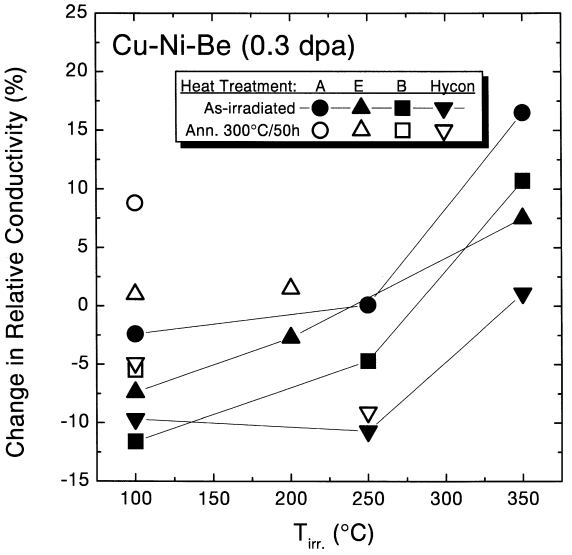

Fig. 4. The change in relative conductivity for CuNiBe resulting from neutron irradiation to 0.3 dpa at different temperatures (closed symbols) and from post-irradiation annealing (300°C/50 h) (open symbols).

Results for the Cu–Al_2O_3 alloys, both in the heat treated and the as-irradiated state and after annealing, are given in Table 3. In all cases, irradiation leads to a decrease in conductivity, while annealing has only a minor, if any, influence on the conductivity.

4. Discussion

The irradiation of pure copper (Fig. 1) clearly reduces the conductivity as a result of the creation of defects and their clusters. For irradiation at 250°C the cluster density increases with dose, tending towards saturation in the dose range 0.1–0.3 dpa [7], while for irradiation at room temperature saturation occurs at about 0.01 dpa [8]. The results in Fig. 1 ($T_{irr} = 100$°C) for the as-irradiated specimens seem to reflect a behaviour with dose more similar to the one for $T_{irr} = 250$°C than the behaviour for $T_{irr} = RT$. Annealing for 50 h at 300°C evidently does not lead to a complete, but only a partial recovery of the conductivity by about one third of its initial decrease on irradiation. In part this may be due to transmutation products (mainly Ni and Zn) [9], and in part to remaining defects and defect clusters. In a positron annihilation study of the isochronal annealing of Cu, neutron irradiated at 50°C and at 250°C, recovery started at ~250°C, but it was not complete until ~500°C [10].

As shown in Fig. 2 for the un-irradiated alloys, the conductivities for CuNiBe are clearly smaller than for CuCrZr. One reason for this probably is that the concentration of alloying elements is higher in the former than in the latter alloy (Table 1). The heat treatments E, B, C and C′ following the solution anneal (A) lead to the formation and growth of precipitates [3–6]. Therefore, as expected, the solution annealed samples have the lowest conductivities. The density of precipitates in the Tréfimétaux CuNiBe is appreciably higher and the size larger than those in CuCrZr ($13–18 \times 10^{23}$ m^{-3} and 4–7 nm compared to $0.4–0.6 \times 10^{23}$ m^{-3} and 2.3–2.9 nm [3,4]). This may be an additional reason for the conductivity of CuNiBe generally being lower than that of CuCrZr.

Some changes in the microstructure of CuNiBe take place during the bonding heat treatment (B), but less in the bakeout (C and C′) [3,4]. However, the conductivity stays almost independent of heat treatment after prime ageing, probably reflecting the fact that there is only a minor variation in the precipitate density. This is in qualitative agreement with the relatively high conductivity for the Hycon specimen, since the precipitate

Table 3
Relative electrical conductivity for Cu–Al_2O_3 alloys (0.25% and 0.6% Al). Results are for as-heat treated and for subsequently annealed specimens as well as for neutron irradiated and for subsequently annealed specimens

Heat treatment			Irradiation			Anneal (300°C/50 h)
Sample	Heat treatment	Relative conductivity (%)	Irradiation temp. (°C)	Irradiation dose (dpa)	Relative conductivity (%)	Relative conductivity (%)
CuAl-25	D′	86.9	–	–	–	–
CuAl-25	D	89.2	100	0.2	80.3	82.2
CuAl-25IGO	D	88.2	–	–		88.8
CuAl-25IGO	D	88.2	200	0.25	81.7	82.5
CuAl-25IGO	D	88.2	350	0.3	79.6	78.9
CuAl-60	D′	78.7	–	–	–	81.6
CuAl-60	D′	78.7	100	0.3	69.6	75.0
CuAl-60	D′	78.7	250	0.1	74.4	72.7
CuAl-60	D′	78.7	350	0.3	76.7	76.4

density in this material is about 5–6 times lower than that in the Tréfimétaux CuNiBe [5]. For the CuCrZr specimens, TEM shows only modest differences in precipitate densities among heat treatments E, B and C′ which is in agreement with the conductivities for these samples. In contrast to this, the C bakeout treatment results in a rather high conductivity (~80%) which suggests that a larger fraction of the alloying elements are found in the form of precipitates. Also the Outokumpu CuCrZr alloy shows a high conductivity, possibly because the prime ageing of this material took place over 2 h which would lead to a higher degree of precipitation than during the E heat treatment of Tréfimétaux CuCrZr for only 30 min.

On irradiation at 250°C and 350°C small precipitates are formed in the A specimens and the precipitates in the E and B specimens generally tend to grow in size. In CuCrZr the density increases with increasing irradiation temperature (except for B which shows a decrease at 350°C) while in CuNiBe the density decreases with increasing irradiation temperature [5]. The precipitate formation in A and the general coarsening in this and the E and B specimens may explain the increase in conductivity in CuCrZr on irradiation (Fig. 3). The post-irradiation annealing results in further segregation and thereby increases the conductivity to close to the high value observed for the pre-irradiated C sample (Fig. 2). The data for the C and Outokumpu (F) CuCrZr specimens show a decrease of conductivity due to irradiation. Both had high conductivities in the pre-irradiation state, probably resulting from the development of large precipitates. It is expected that irradiation will lead to some resolution of the alloying elements from the precipitates and thereby to a decrease in conductivity, as observed.

The conductivity decrease in the irradiated CuNiBe found at the lower irradiation temperatures (Fig. 4) may be ascribed to dissolution of precipitates. Because of the high density of precipitates there is a high probability that a displacement cascade created by a neutron may impinge directly on a precipitate, causing its dissolution. Above 250°C segregation takes place, as mentioned above, which results in the increases in conductivities observed for the irradiation temperature of 350°C.

For both CuCrZr and CuNiBe the post-irradiation annealing (300°C/50 h) lead to increases in conductivity, irrespective of the initial heat treatments. This effect is ascribed to the annealing of radiation created defects and, for the solution annealed (A) specimens for which the effect is largest, to the formation of precipitates.

The Cu–Al_2O_3 alloys show the highest conductivities of all the alloys (Table 3). On irradiation moderate decreases (<10%) are observed which depend only to a small degree on irradiation temperature. This is in accord with the rather small changes in microstructure found by TEM [3–6]. In contrast to the other two alloys, the 300°C/50 h anneal leads to only a small or no increase in conductivity, and no difference can be detected between the results for the two CuAl-25 alloys. Thus, based on the present rather low dose experiments one may confirm that, in terms of electrical conductivity, the CuAl-25 alloys are to be preferred as prime candidate material for ITER with the Outokumpu alloy coming quite close.

5. Conclusion

In spite of the fact that results of electrical conductivity measurements reflect average bulk properties of the specimens, the present work shows that at least a qualitative characterization of the precipitate microstructure in differently heat treated and irradiated Cu alloys may be obtained by such measurements.

The electrical conductivities of the investigated Cu alloys are clearly different, since un-irradiated and irradiated (0.3 dpa) CuNiBe, CuCrZr and Cu–Al_2O_3 roughly speaking fall within three ranges, viz. below 55%, 50–80% and 75–90%, respectively, of the conductivity of pure Cu (the Hycon CuNiBe material close to 65%). Within these ranges, variations in conductivities reflect heat treatment, irradiation temperature and post-irradiation annealing. The results underline the problem of cascade-induced dissolution of precipitates by cascade impingement, segregation of alloying elements and re-precipitation, and they show that in the case of pure OFHC-Cu only partial recovery of the conductivity by post-irradiation annealing at 300°C for 50 h occurs.

The low conductivities of the CuNiBe alloys make their application in the environment of a fusion reactor doubtful, while the high values for the Cu–Al_2O_3 alloys confirm their position as prime candidate.

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