**Recent Results on the Neutron Irradiation of ITER Candidate Copper Alloys Irradiated in DR-3 at 250°C to 0.3 dpa** - DJ Edwards (PNNL), BN Singh, P. Toft and M. Eldrup (Risø National Laboratory)

OBJECTIVE

This particular experiment is one of three separate irradiations comprising the screening experiments on CuNiBe, CuCrZr and CuAl-25 aimed at helping decide which material should serve as the backup candidate to CuAl-25, the current primary candidate material.

SUMMARY

Tensile specimens of CuCrZr and CuNiBe alloys were given various heat treatments corresponding to solution anneal, prime-ageing and bonding thermal treatment with additional specimens re-aged and given a reactor bakeout treatment at 350$^0$C for 100 h. CuAl-25 was also heat treated to simulate the effects of a bonding thermal cycle on the material. A number of heat treated specimens were neutron irradiated at 250$^0$C to a dose level of ~ 0.3 dpa in the DR-3 reactor at Risø.

The main effect of the bonding thermal cycle heat treatment was a slight decrease in strength of CuCrZr and CuNiBe alloys. The strength of CuAl-25, on the other hand, remained almost unaltered. The post irradiation tests at 250$^0$C showed a severe loss of ductility in the case of the CuNiBe alloy. The irradiated CuAl-25 and CuCrZr specimens exhibited a reasonable amount of uniform elongation, with CuCrZr possessing a lower strength.

PROGRESS AND STATUS

**Introduction**

Because of their good thermal conductivity, copper alloys are being considered as heat sink materials for both first wall and divertor components of ITER (International Thermonuclear Experimental Reactor) [1,2]. The heat sink materials will have to be joined to the first wall and divertor materials at relatively high temperatures (900-1000$^0$C). During the joining process at these high temperatures, the microstructure of precipitation hardened (PH) alloys may change substantially, and consequently, these alloys may lose swelling resistance and become softer. Screening experiments were carried out at Risø to simulate the effect of bonding and bakeout thermal treatments on pre- and post-irradiation microstructures, mechanical properties and electrical resistivity of CuAl-25, CuCrZr and CuNiBe alloys. The present report describes the main results on the mechanical properties and electrical resistivity after irradiation at 250°C. A complete description of the microstructural analysis, mechanical properties and electrical resistivity measurements is in preparation [3].

**Materials and Experimental Procedure**

The materials used in the present investigations were oxygen-free high conductivity (OFHC) copper, CuCrZr, CuNiBe and CuAl-25 alloys. The OFHC-copper, CuCrZr and CuNiBe alloys were supplied by Tréfimétaux (France) in the form of 20 mm thick plates. The oxide dispersion strengthened (DS) copper (CuAl-25) was supplied by SCM Metals (USA) as GlidCop™ CuAl-25 in the form of rods in the as-wrought condition. The chemical composition of these alloys is listed in Table 1.

**Table 1: Chemical Composition**

| | |
|---|---|
| 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 |
| CuNiBe: | Cu - 1.75% Ni, 0.45% Be |
| CuAl25 | Cu - 0.25% Al as oxide particles (0.46% $Al_2O_3$) |

**Table 2: Summary of bonding and bakeout heat treatments* for CuCrZr, CuNiBe and CuAl-25 alloys**

| Type | 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 treatments A + 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. (only for CuAl-25) |
| D' | CuAl-25 in the as-wrought condition, i.e. without any heat treatment |

* - All heat treatments were done in vacuum (<$10^{-4}$ torr)

Sheet tensile specimens (gage length = 7.0 mm) were cut from cold-rolled (~80%) sheets (~0.3 mm thick) of OFHC-copper, CuCrZr and CuNiBe alloys. Prior to irradiation, sheet tensile specimens of OFHC-copper were annealed at 550°C for 2 h in vacuum. Round tensile specimens of CuAl-25 (of gauge diameter 3 mm) were machined from the as-supplied rod, which was in the as-wrought condition (i.e. without cold-work). Prior to irradiation, all of the alloys were heat treated following the list in Table 2. All heat treatments were carried out in vacuum (<1.33 MPa or $10^{-5}$ torr).

Tensile specimens of pure copper, CuCrZr, CuNiBe and CuAl-25 alloys with the different heat treatments were irradiated at 250°C in the DR-3 reactor at Risø in the High Temperature Rig. During irradiation, temperature was measured, controlled (within ± 2°C) and recorded continuously. All specimens were irradiated at the same time to a fluence level of 1.5 x $10^{24}$ n/m$^2$ (E > 1 MeV), which corresponds to a displacement dose level of ~0.3 dpa (NRT). The neutron flux during irradiation was approximately 2.5 x $10^{17}$ n/$m^2$ (E > 1 MeV) which corresponds to a displacement damage rate of ~5 x $10^{-8}$ dpa (NRT)/s.

Both unirradiated and irradiated tensile specimens were tested in an Instron machine at a strain rate of 1.2 x $10^{-3}$ $s^{-1}$. Tensile tests were carried out at 250°C in vacuum (<$10^{-4}$ torr). The test temperature of 250°C was reached within 30 minutes. The cross-head displacement was measured and used to determine the stress-strain behaviour of the specimens. The fracture surfaces of the irradiated as well as unirradiated specimens were examined in a JEOL 840 scanning electron microscope.

All resistivity measurements were made at room temperature (23° C). In order to secure good electrical contacts, specimens were etched prior to resistivity measurements. The voltage connectors were either two sharply-pointed stainless steel pins which were pressed against the specimen, or (in a new specimen holder) spring loaded voltage probes, which gave a more well-defined and reproducible contact. The average resistivity of OFHC-copper (annealed at 550°C for 2 h) was found to be 1.682μΩ cm, which is in good agreement with the nominal resistivity of copper at room temperature of 1.698μΩ cm. The relative resistivity (RR) of the alloys was calculated from the following relationship: RR = R x t x w/ ($R_{cu}$ x $t_{Cu}$ x $w_{Cu}$), where R is the electrical resistance measured for the specimen of thickness t and width w. The index Cu refers to the values for the reference OFHC-Cu sample. The total uncertainty on each measurement was estimated to be less than 3%. The relative resistivity (RR) values for the various alloys quoted in Table 3 are the average values of six measurements made on each specimen.

## Experimental Results

Results for the electrical resistivity and mechanical properties are presented in the following sections. The details of the microstructural analysis are provided in reference 3.

### *Pre- and Post-irradiation Electrical Resistivity*

For comparison, resistivity measurements were carried out on unirradiated specimens with nominally the same heat treatments, although carried out in different batches. These measurements showed small variations in resistivity as shown in Table 3. The results on the unirradiated CuNiBe show that the HTB and HTE treatments decrease the resistivity as expected (see Table 3). Note, however, that the resistivity of the Tréfimétaux CuNiBe is much higher than that of two heats of Hycon 3HP® CuNiBe supplied by Brush Wellman Inc. (USA), another producer of CuNiBe alloys. The compositions and processing of the Brush Wellman heats have been optimized to yield a lower electrical resistivity while maintaining a reasonably high level of strength, though not as high as that of the Tréfimétaux CuNiBe. The relatively high resistivity of the Tréfimétaux CuNiBe suggests that a fraction of the beryllium and/or nickel (or other impurities) may still be in solid solution, and that the composition and thermal processing have yet to be optimized. However, note that the bakeout treatment had relatively little effect on the resistivity of the Tréfimétaux CuNiBe, indicative of the relative stability of the microstructure even when annealed at 350°C for 100 hours.

The irradiation of these alloys had little effect on the electrical resistivity. However, given that the precipitate density and size exhibited considerable change after irradiation [3], it is likely that the ballistic dissolution and re-precipitation of the precipitates still leaves solute elements in solid solution.

**Table 3: Electrical resistivity measurements at room temperature for unirradiated and irradiated copper alloys given the indicated heat treatments.**

| Materials | Heat Treatment | Irradiation Dose (dpa) | Relative Resistivity† (RR) | Relative Conductivity (%) |
|---|---|---|---|---|
| OFHC-Cu | $550^0$C/2 h | 0 | 1.000 | 100 |
| CuCrZr | A | 0 | 2.09-2.16 | 46-48 |
| CuCrZr | E | 0 | 1.63-1.90 | 53-61 |
| CuCrZr | B | 0 | 1.40-1.73 | 58-71 |
| CuCrZr | C | 0 | 1.24-1.77 | 79-81 |
| CuCrZr | C' | 0 | 1.37-1.57 | 64-73 |
| CuNiBe | A | 0 | 2.96-3.23 | 31-34 |
| CuNiBe | E | 0 | 2.02-2.35 | 43-50 |
| CuNiBe | B | 0 | 2.01-2.38 | 42-50 |
| CuNiBe | C | 0 | 1.83-2.04 | 49-55 |
| CuNiBe | C' | 0 | 1.91-2.15 | 47-52 |
| Hycon 3HP | CA* | 0 | 1.55 | 65 |
| Hycon 3HP | CK* | 0 | 1.46 | 68 |
| CuAl-25 | D | 0 | 1.13 | 88 |
| CuAl-25 | D' | 0 | 1.15 | 87 |
| CuCrZr | A | 0.3 | - | - |
| CuCrZr | E | 0.3 | 1.52 | 66 |
| CuCrZr | B | 0.3 | 1.48 | 68 |
| CuNiBe | A | 0.3 | 3.22 | 31 |
| CuNiBe | E | 0.3 | 2.33 | 43 |
| CuNiBe | B | 0.3 | 2.22 | 45 |
| Hycon 3HP | CA* | 0.3 | 1.87 | 53 |

* Specimens from Oak Ridge National Laboratory, material originally from Brush Wellman Inc., Cleveland, Ohio; heat number 33667. CA and CK refer to different heat treatments that yield different starting conductivities and strengths.

† A range of values shows the measured variation in resistivity between different batches of samples with the same nominal heat treatment.

With the exception of the HTA specimens, the CuCrZr generally exhibited a lower resistivity than the CuNiBe alloys in each of the 5 heat treatments. In contrast to the CuNiBe, the bakeout treatment CuCrZr (HTC) clearly lowered the resistivity. Unlike the CuNiBe, irradiation improved the electrical resistivity of the CuCrZr alloy, but even this improvement still left the resistivity significantly higher than that of the CuAl-25 alloy. The results confirm the superior electrical resistivity of the CuAl-25 under these irradiation conditions. Transmutation effects are assumed to be minor for this low dose.

*Pre- and Post-Irradiation Mechanical Properties*

The mechanical properties of the three alloys show that irradiation can have a strong influence on the strength and ductility, with the CuNiBe showing the strongest susceptibility to irradiation effects.

The results for the individual alloys are summarized in the following sections, and the tensile data comparing the data for pure copper and the copper alloys are listed in Tables 4-6.

CuNiBe

The tensile results for the unirradiated CuNiBe specimens are provided in Figure 1 and Table 5, and show that the prime ageing treatment (HTE) yields the highest strength. The solution annealed (HTA) material possesses a higher yield strength compared to the annealed pure copper (Table 4) presumably due to the effect of solid solution strengthening. The HTB specimens exhibit a lower overall strength and higher ductility than the HTE specimens. It is significant to note that the denuded grain boundaries more prevalent in the HTB specimens [3] did not have any deleterious effect on the mechanical properties. The bakeout simulation (HTC) actually increases the strength somewhat. The effect of the bakeout simulation on specimens initially given heat treatment E is just the opposite, that is, the strength actually decreases somewhat.

Irradiation of these alloys reveals that the Tréfimétaux CuNiBe suffers a severe loss of ductility after irradiation (Figure 2, Table 6). The solution annealed (HTA) specimens exhibit a large increase in strength (178 vs. 655 MPa), but this is also accompanied by a large loss of ductility compared to the unirradiated state. The strength of the solution annealed specimens after irradiation is comparable to the specimens given the HTB and HTE treatments, indicative of the strong effect of irradiation-induced precipitation in these alloys [3]. The fracture surfaces of these alloys revealed that the failure mode changed from a completely ductile mode in the unirradiated state to a mixture of ductile intergranular and intergranular cleavage [3].

For comparison, specimens of a commercial CuNiBe (Hycon 3HP®) manufactured by Brush Wellman Inc. (USA) were also irradiated at 250°C to a dose level of 0.3 dpa and subsequently tested at 250°C (see Table 6 for tensile results). The material was in a fully hardened tempered condition (referred to as the HT temper in the United States), but the exact conditions are held proprietary by Brush Wellman. However, the HT temper normally involves solution annealing, cold working, and then ageing for several hours.

In the unirradiated condition the Hycon alloy has lower strength and noticeably less ductility. This changes after irradiation, however, since the irradiated CuNiBe (Hycon) exhibits somewhat lower yield strength and higher ductility than those measured in the Tréfimétaux CuNiBe (HTE). The results on CuNiBe (Hycon) reported in Table 6 are similar to those reported by Zinkle and Eatherly [4]. It should be emphasized here that it is not known how the Hycon 3HP® alloy would respond to the bonding thermal cycle (HTB), subsequent irradiation and post-irradiation mechanical testing.

**Table 4: Tensile results for OFHC-copper in the unirradiated and irradiated (at 250°C to 0.3 dpa) conditions.**

| Material | Heat Treatment | Dose (dpa) | $\sigma_{0.05}$ (MPa) | $\sigma_{0.2}$ (MPa) | $\sigma_{max}$ (MPa) | $\varepsilon^{p}_{u}$ (%) | $\varepsilon_{total}$ (%) |
|---|---|---|---|---|---|---|---|
| OFHC | 550°C/2h | 0 | 34 | 38 | 162 | 54.5 | 60.5 |
| OFHC | 550°C/2h | 0.3 | 90 | 100 | 174 | 32.0 | 34.0 |

**Table 5: Tensile results for unirradiated copper alloys with the pre-irradiation heat treatments described in Table 2. Tests were conducted at 250°C.**

| Material | Heat Treatment | $\sigma_{0.05}$ (MPa) | $\sigma_{0.2}$ (MPa) | $\sigma_{max}$ (MPa) | $\varepsilon^{P}_{u}$ (%) | $\varepsilon_{total}$ (%) |
|---|---|---|---|---|---|---|
| CuCrZr | A | 52 | 56 | 177 | 33.0 | 36.0 |
| CuCrZr | B | 94 | 100 | 219 | 27.3 | 31.3 |
| CuCrZr | C | 171 | 181 | 274 | 17.2 | 20.4 |
| CuCrZr | C' | 208 | 218 | 308 | 15.9 | 20.3 |
| CuCrZr | E | 135 | 140 | 261 | 22.6 | 25.5 |
| CuNiBe | A | 173 | 178 | 325 | 47.5 | 54.0 |
| CuNiBe | B | 455 | 480 | 665 | 24.6 | 30.5 |
| CuNiBe | C | 540 | 580 | 750 | 20.5 | 27.0 |
| CuNiBe | C' | 565 | 600 | 780 | 13.7 | 17.5 |
| CuNiBe | E | 610 | 630 | 825 | 15.0 | 19.0 |
| (Hycon)* | Similar to HTE | 575 | 620 | 690 | 3.0 | 5.3 |
| CuAl-25† | D | 306 | 315 | 326 | 1.5 | 18.5 |
| CuAl-25† | D' | 270 | 280 | 294 | 2.2 | 15.5 |

* Longitudinal direction, heat number 33667, proprietary HT heat treatment

† Round tensile geometry only

<u>CuCrZr</u>

The tensile curves shown in Figure 3 and the data listed in Table 5 for CuCrZr illustrate the differences that arise due to the 5 different heat treatments. The solution annealed CuCrZr does not exhibit the same degree of solution hardening as the solution annealed CuNiBe. In fact, its yield strength is very close to that of annealed OFHC-copper, but with noticeably less ductility. The lack of cold work in the HTB and the HTE samples illustrates the difference in strengthening that can be achieved in the two PH alloys. A cold working step prior to ageing the CuNiBe alloy is not required to achieve high strength, whereas its absence in CuCrZr leads to much lower strengths than can normally be achieved. All three heat treatments for the CuCrZr result in a material that possesses a high degree of work hardening, which the CuNiBe exhibits to a lesser extent, and is almost non-existent for CuAl-25 at 250°C. In both cases the bakeout treatment (or extra ageing) resulted in a significant increase in strength over the original starting state, and with little change in ductility.

The irradiated CuCrZr results are shown in Figure 4 and listed in Table 6. Clearly the irradiation of the solution annealed specimens has produced the same effect as in the CuNiBe, that is, radiation-induced precipitation that effectively doubles the strength. Irradiation of specimens given the other two heat treatments results in a large increase in yield strength, but little change in the ultimate strength.

**Table 6: Tensile results for copper alloys irradiated at 250°C to 0.3 dpa with the pre-irradiation heat treatments described in Table 2. Tests were conducted at 250°C.**

| Material | Heat Treatment | $\sigma_{0.05}$ (MPa) | $\sigma_{0.2}$ (MPa) | $\sigma_{max}$ (MPa) | $\varepsilon^{P}_{u}$ (%) | $\varepsilon_{total}$ (%) |
|---|---|---|---|---|---|---|
| CuCrZr | A | 195 | 205 | 205 | 0.4 | 2.5 |
| CuCrZr | B | 215 | 224 | 223 | 4.0 | 5.0 |
| CuCrZr | E | 230 | 235 | 254 | 4.2 | 7.0 |
| CuNiBe | A | 590 | 655 | 670 | 0.7 | 1.9 |
| CuNiBe | B | 565 | 630 | 685 | 0.7 | 1.8 |
| CuNiBe | E | 625 | 690 | 705 | 0.3 | 1.5 |
| CuNiBe (Hycon)* | Similar to HTE | 530 | 620 | 655 | 2.1 | 3.1 |
| CuAl-25† | D | 280 | 303 | 328 | 1.8 | 15.3 |
| CuAl-25† | D' | 285 | 308 | 320 | 1.6 | 13.8 |

* Longitudinal direction, heat number 33667
† Round specimen geometry only

However, unlike the CuNiBe, this alloy still possesses a moderate amount of ductility in the HTB and HTE conditions, and retains some ability to work harden. The solution annealed condition has the lowest uniform elongation of the three irradiated conditions, and very little work hardening ability. The fracture surfaces for the CuCrZr show that before and after irradiation it still has a ductile failure mode, exhibiting a dimpled "knife edge" fracture surface due to the large reduction in area in the rectangular cross-section.

CuAl-25

The effect of annealing at 950°C for 30 min. (HTD) on the flow stress of CuAl-25 is very small (Table 5). It should be pointed out that unlike CuCrZr and CuNiBe alloys, the CuAl-25 does not seem to work harden during tensile deformation at 250°C. As in the unirradiated specimens, irradiated CuAl-25 exhibits little ability to work harden (Figure 4), which raises questions about its fracture toughness and resistance to crack growth. The fracture surfaces yield little information beyond the fact that the failure mode is ductile in nature, primarily because the grain size is too small to allow one to distinguish transgranular or intergranular failure.

**Summary of Results**

Of all the alloys, CuAl-25 proves to be the most stable in terms of the microstructure, mechanical properties and electrical resistivity. Based on these results the bonding thermal treatment should have little effect on the properties or microstructure of the DS copper alloys. However, the apparent lack of work hardening ability in CuAl-25 is a matter of concern. The case seems to be even worse in the case of irradiated CuNiBe, which loses not only its ability to work harden, but also its ability to deform plastically to any significant extent. The CuCrZr appears to be less susceptible to neutron irradiation effects at 250°C than CuNiBe, and still retains significant uniform elongation and some ability to work harden after irradiation. The poor behaviour of the CuNiBe after irradiation may be due to segregation at the grain boundaries, although there is not enough evidence to confirm this.

Irrespective of the initial state, the fracture surfaces from the CuNiBe revealed that failure occurred near or at the grain boundaries, and not within the bulk of the grains.

In both PH alloy systems (CuCrZr and CuNiBe) it is clear that the initial starting state has little effect on the final mechanical properties, even at a low dose of 0.3 dpa. The increase in yield strength observed for the HTB and HTE specimens of CuCrZr, along with the increase in conductivity, would indicate that irradiation resulted in further precipitation and coarsening that removes excess Cr and Zr from solution. Because of the different diffusion kinetics and the limited solubility of Cr in copper, the CuCrZr alloys respond differently to irradiation than the CuNiBe.

## CONCLUSIONS

On the basis of the changes measured in the mechanical properties and electrical resistivity, the following conclusions can be drawn:

- The DS copper alloy CuAl-25 exhibits the greatest resistance to radiation-induced changes in microstructure and mechanical properties.

- The different heat treatments given to the CuNiBe and CuCrZr made little difference in the mechanical properties after irradiation at 250°C to 0.3 dpa.

- Irradiation of solution annealed CuNiBe and CuCrZr leads to radiation-induced precipitation that can produce strength levels near to that of the HTB and HTE specimens.

- CuCrZr appears to offer advantages over the CuNiBe because there remains a reasonable level of ductility and work hardening even after irradiation.

- The severe loss of ductility in the CuNiBe alloy due to neutron irradiation, regardless of the initial starting state, poses a serious concern for this alloy, particularly since the actual mechanism responsible for the poor behaviour remains unclear.

## FUTURE WORK

The last irradiation experiment at 100°C on the same materials has been completed at Risø. Microstructural characterization , electrical resistivity, and mechanical testing have been completed on all of the specimens. Final analysis of the microstructural data is in progress.

## ACKNOWLEDGMENTS

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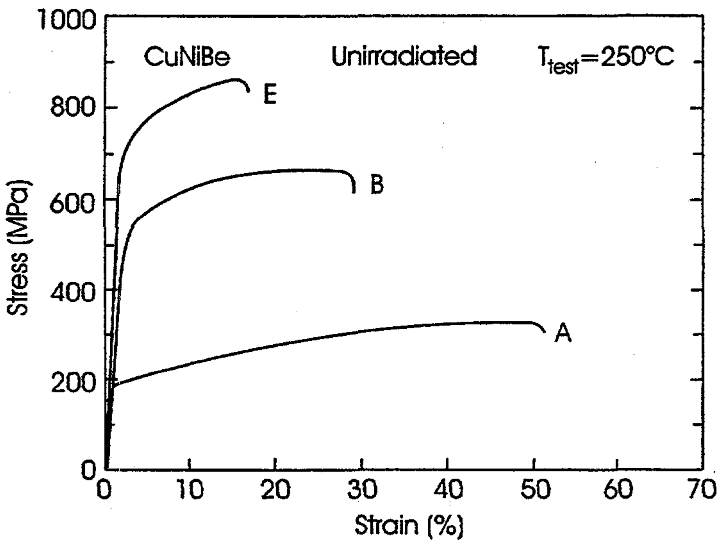


Figure 1 Tensile curves showing the influence of the different heat treatments on the deformation behavior of the CuNiBe alloy.

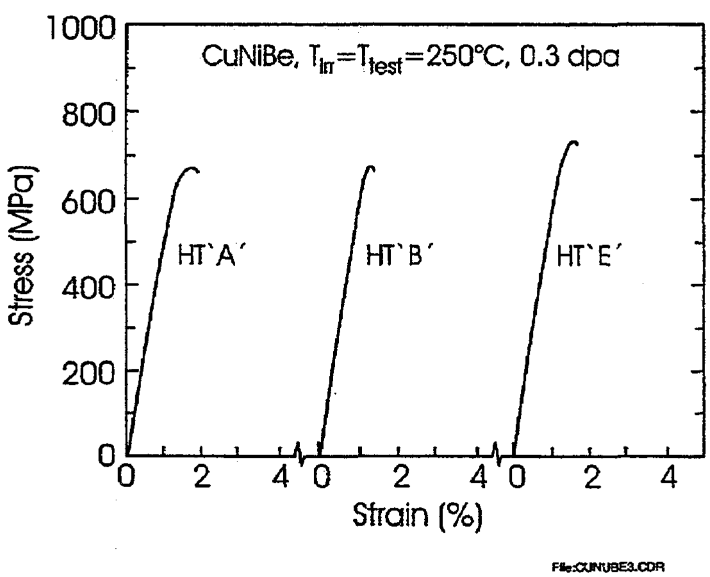


Figure 2 Tensile curves for the irradiated CuNiBe showing the severe loss of ductility after irradiation, regardless of the pre-irradiation heat treatments. Note that the post-irradiation strength is similar for all three heat treatments

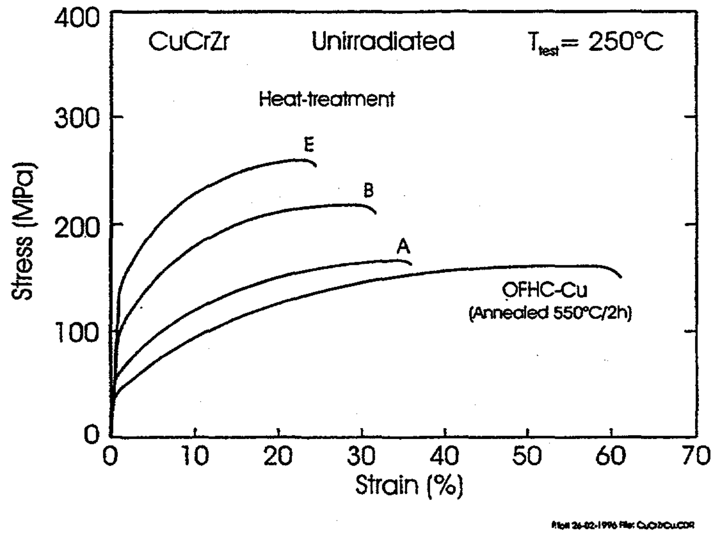


Figure 3 Tensile curves showing the influence of different heat treatments on the CuCrZr and a comparison with pure copper.

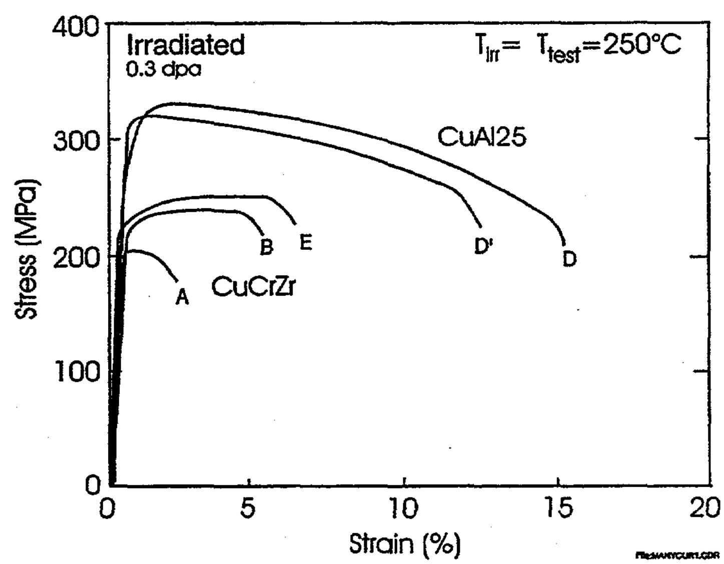


Figure 4 Comparison of the tensile behavior of CuCrZr to that of CuAl-25 after irradiation at 250°C to 0.3 dpa. Note that the CuCrZr still retains a measurable ability to work harden, whereas the CuAl-25 shows a very limited amount of work hardening.