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The effect of bonding and bakeout thermal cycles on the properties of copper alloys irradiated at 100°C

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Abstract

Tensile specimens of GildCop™ Al25, CuCrZr and CuNiBe alloys were given various heat treatments corresponding to solution anneal, prime ageing and bonding thermal treatment. Additional specimens were re-aged and given a reactor bakeout treatment at 350°C for 100 h. Specimens were neutron irradiated at 100°C to a dose level of ~0.3 dpa in the DR-3 reactor, and post-irradiation tensile tests, electrical resistivity, and microstructural examination were performed. The main effect of the bonding thermal cycle heat treatment was a slight decrease in strength of the CuCrZr and CuNiBe alloys, while strength of the Al25 remained almost unaltered. The post-irradiation tests at 100°C revealed the greatest loss of ductility occurred in the CuCrZr alloy. Irradiation caused a significant reduction in the electrical resistivity of the CuNiBe and a noticeable increase in the case of the CuCrZr, with only a minor change in the Al25 alloy.

1. Introduction

Precipitation and dispersion strengthened copper alloys (CuCrZr, CuNiBe, and GlidCop™ Al25) are being considered as heat sink materials for the first wall and divertor assemblies of ITER (International Thermonuclear Experimental Reactor) because of their high thermal conductivity and high strength [1,2]. Current designs utilise these materials at relatively low temperatures (<150°C), with possible thermal excursions due to plasma disruptions that may lead to higher temperatures for short periods of time. Several irradiation experiments [3–11] have shown that each of the current alloys will impose severe restrictions upon the designers due to their susceptibility to radiation hardening and concomitant loss of ductility, work hardening, and toughness. More recently it has been recognised that the joining procedures used to fabricate the structures will also effect the performance of the materials during irradiation since the optimal processing needed to achieve the desired thermal conductivity and strength may not be realised.

As part of a broad experiment to study the effects of heat treatments and subsequent irradiation on the properties of the various candidate alloys, a series of heat treatments were given to tensile specimens of CuCrZr, CuNiBe, and Al25. These heat treatments were chosen in order to simulate the effect of bakeout treatments and possible joining treatments such as hot isostatic pressing. These specimens were then irradiated in the DR-3 reactor at Risø National Laboratory in Denmark through a series of low dose screening experiments covering the range of 100°C, 250°C, and 350°C to a dose of 0.3 dpa. Previous reports have already presented the results of the irradiation experiments conducted at 250°C and 350°C [7–9].

The present report summarises the results of the third and final set of experiments on the same materials irradiated to 0.3 dpa, but at 100°C instead. The effect of the various heat treatments described herein on the unirradiated microstructure have already been reported previously [7,8], and will not be presented in this report in detail. Tensile properties of unirradiated and irradiated specimens with various heat treatments tested at 100°C are described. The results of electrical resistivity

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measurements at 23°C are also presented. Microstructural details are presented briefly and related to the observed changes in mechanical properties.

2. Materials and experimental procedure

The materials used in this experiment were CuCrZr, CuNiBe and GildCop™ Al25 alloys. The CuCrZr and CuNiBe alloys were supplied by Tréfimétaux (France) in the form of 20 mm thick plates. The Al_2O_3 dispersion strengthened copper alloy GildCop™ Al25 was supplied by OGM Americas (formerly SCM Metals.) in the form of rods in the as-extruded (i.e. wrought) condition. The chemical composition of these alloys is listed in Table 1. The heat treatments given to the different alloys are listed in Table 2.

Details regarding the geometry and size of the tensile specimens have been reported previously [7,8]. Tensile specimens were irradiated together in the DR-3 reactor at Risø in the High Temperature Rig at 100°C to a fluence level of 1.5×10^{24} n/m^2 (E > 1 MeV), which corresponds to a displacement dose level of ~0.3 dpa (NRT). During irradiation, temperature was measured, controlled (±2°C) and recorded continuously.

Both unirradiated and irradiated tensile specimens (2 specimens from each condition) were tested in an Instron machine at a strain rate of 1.2×10^{-3} s^{-1}. Tensile tests were carried out at 100°C in vacuum (<10^{-4} Torr). The test temperature of 100°C was reached within 30 min. All resistivity measurements were made at room temperature (23°C), using a 4-point probe module developed by the Electronics Department at Risø. The total uncertainty on each measurement was estimated to be less than 3%. The resistivity was normalised to that of pure copper and converted to electrical conductivity to demonstrate the effect of irradiation more effectively.

For transmission electron microscopy (TEM), 3 mm discs were punched from the unirradiated and irradiated sheet tensile specimens and thinned mechanically to ~0.1 mm thickness. These discs were twin-jet electropolished in a solution of 25% perchloric acid, 25% ethanol and 50% water at 11 V for about 15 s at ~20°C. Specimens were examined in a JEOL 2000 FX transmission electron microscope. The techniques used to analyse the defect cluster density and precipitate characteristics are provided in earlier reports [7,8].

3. Experimental results

A brief description of the microstructure of the irradiated alloys will be given in the following section, followed by a presentation of the electrical conductivity and mechanical properties measured for both the unirradiated and irradiated specimens. The changes in the mechanical and physical properties will be discussed and related to the observed changes in microstructure.

3.1. Microstructural analysis

The microstructure of the CuCrzr specimens given the prime aged (E) and bonding thermal cycle treatments (B) contained a high density of small defect clusters and precipitates produced during irradiation. The cluster density was found to be ~5.6×10^{23} m^{-3} for the CuCrZr alloys, independent of the heat treatment given prior to irradiation. The size distributions of the

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)

stacking fault tetrahedra (SFT) were virtually the same in either heat treated specimen, yielding an average size of 2.3 nm for the clusters, similar to that reported previously [3]. The size of the precipitates measured in weak beam images ranged from 4.5–5.6 nm, roughly double that found in the unirradiated specimens. The density of the precipitates after irradiation was found to be $\sim 0.26 \times 10^{23}$ m^{-3}, somewhat lower compared to values of 0.36–0.59 $\times 10^{23}$ m^{-3} measured in the unirradiated specimens. There were many features not recognisable as either defects or precipitates, so the lower precipitate density in the irradiated specimens may be a consequence of many of the precipitates being too small to clearly define. Those that were clearly visible and easy to distinguish were predominantly the fringed precipitates reported in the 250°C and 350°C irradiation experiments. As has been reported in the 250°C and 350°C experiments, a dislocation structure also formed in the irradiated specimens consisting of a lower density of dislocation loops and line segments. No denuded zones along the grain boundaries were present in either the unirradiated or the irradiated specimens.

The microstructure of the Tréfimétaux CuNiBe alloys reveals that this class of alloys exhibited less resistance to irradiation than the CuCrZr alloys. The average precipitate size after irradiation was identical despite the initial difference in size in the unirradiated specimens. Measurements taken from centered dark field images using precipitate reflections gave an average size of 3 nm for both the prime ageing and bonding thermal cycle heat treatments. The size of the γ'' precipitates in the unirradiated specimens was found to be 3.8 nm for the prime aged specimens, and 6.6 nm for the specimens given the bonding thermal cycle treatment. The density of precipitates in both materials was found to have decreased substantially after irradiation to level of 4.0 and 5.5 $\times 10^{23}$ m^{-3} for the heat treated E and B specimens, respectively. The precipitate density in the unirradiated specimens ranged from 14 to 18 $\times 10^{23}$ m^{-3}. The smaller size and lower density of precipitates after irradiation suggests that ballistic dissolution of the beryllides is occurring, but as will be shown later there is still an increase in the strength of the irradiated alloys. Denuded zones have been reported in the earlier studies on the irradiation of these materials as a result of the intial heat treatments. After irradiation at 100°C, and in fact at 250°C and 350°C, the denuded zones are no longer completely free of precipitates. Irradiation at 100°C leads to precipitation within the pre-irradiation denuded zone and in the boundary itself. The phases appear to be the same as in the matrix, that is, γ'' precipitates. This provides further evidence that the stability of the microstructure in this particular class of alloys is altered during irradiation, and that depending on the irradiation temperature, dissolution or coarsening of the precipitates is occuring.

3.2. Electrical conductivity

Resistivity measurements revealed that microstructural changes induced by irradiation also lead to a measurable effect in the physical properties of the materials. Table 3 lists the electrical conductivities (normalised to OFHC-Cu) measured before and after irradiation at 100°C for all of the materials and conditions irradiated. Note that irradiation leads to an decrease in the conductivity of the pure copper due to the production of defect clusters, and that the same trend is found in the case of the Al25, though not to quite the same extent. The conductivity of the CuNiBe alloy is lower after irradiation for all three of the heat treatments listed. The conductivity of the CuCrZr specimens increases after irradiation with the specimens given the bonding thermal cycle treatment exhibiting the largest increase in conductivity. The one exception is that the CuCrZr specimens given the additional bakeout treatment (HTC) exhibited a significant decrease in conductivity, comparable to the same level observed in the case

Table 3
Electrical conductivity (% of OFHC) for copper alloys irradiated at 100°C to a dose level of 0.3 dpa

Materials	Heat treatment	Unirradiated	Irradiated
OFHC	550°C for 2 h	100	88.4
CuNiBe	A	33.7	31.0
CuNiBe	E	48.5	41.1
CuNiBe	B	49.3	37.4
CuCrZr	A	47.9	55.1
CuCrZr	E	52.2	60.8
CuCrZr	B	59.5	72.0
CuCrZr	C	78.8	66.2
Al25	D	89.5	80.4

Table 4
Tensile results for unirradiated OFHC-Cu and copper alloys with the pre-irradiation heat treatments described in Table 2 (Tests were conducted at 100°C)

Material	Heat treatment	$\sigma_{0.05}$(MPa)	$\sigma_{0.2}$(MPa)	σ_{max}(MPa)	ε_u^p(%)	ε_{total}(%)
OFHC-Cu	550°C/2 h	20	26	193	60.0	64.0
CuNiBe	A	103	108	340	55.0	58.0
CuNiBe	B	450	470	690	28.0	30.0
CuNiBe	C	530	555	760	25.5	27.5
CuNiBe	C′	600	630	860	27.0	28.0
CuNiBe	E	550	580	820	24.0	25.0
CuCrZr	A	65	70	205	43.0	44.0
CuCrZr	B	94	99	237	34.8	36.2
CuCrZr	C [a]	170	180	315	–	–
CuCrZr	C′	175	185	322	23.0	24.3
CuCrZr	E	105	110	246	34.0	35.5
Al25	D [b]	340	355	400	13.0	40.0

[a] Specimen broke prematurely.
[b] Round Specimens, 3 mm diameter gage.

Table 5
Tensile results for copper alloys irradiated at 100°C to 0.3 dpa with the pre-irradiation heat treatments described in Table 2 (Tests were conducted at 100°C)

Material	Heat treatment	$\sigma_{0.05}$ (MPa)	$\sigma_{0.2}$ (MPa)	σ_{max} (MPa)	ε_u^p(%)	ε_{total}(%)
CuNiBe	A	625	663	683	12.5	14.5
CuNiBe	B	800	880	938	3.4	5.9
CuNiBe	C′	880	960	990	3.4	5.4
CuNiBe	E	815	885	940	3.3	5.9
CuCrZr	A	365	365	370	1.1	4.0
CuCrZr	B	370	370	373	1.1	4.1
CuCrZr	C	445	450	450	1.3	4.0
CuCrZr	C′	440	440	445	1.3	4.0
CuCrZr	E	400	405	412	1.2	3.8
Al25	D [a]	540	544	546	5.5	26.0

[a] Round specimen, 3 mm diameter gage.

of OFHC copper and the Al25. Whether this is due to the same mechanism (formation of defect clusters) remains to be determined.

3.3. Mechanical properties

At the irradiation temperature of 100°C, the three alloys exhibited radiation hardening after irradiation, irrespective of the pre-irradiation heat treatment given to each material. The tensile results for the unirradiated and irradiated specimens are listed in Tables 4 and 5. The data listed in the tables and the tensile curves shown in Fig. 1 illustrate the degree of radiation hardening in the CuCrZr specimens. All four heat treated specimens are characterised by very low uniform elongations and no work hardening, and the yield stress has actually exceeded the ultimate stress in the corresponding unirradiated specimens. The result is that the materials exhibit an instability at the onset of plastic deformation. With regard to the pre-irradiation heat treatments given to the CuCrZr, the additional bakeout treatment (350°C for 100 h) produced a noticeable difference in the irradiated tensile specimens since the C and C′ specimens maintained their higher strength, though the uniform elongation is still minimal.

The CuNiBe and Al25 also experienced a decrease in their uniform elongations and work hardening ability, but not to the same degree. Note that both the CuNiBe and Al25 still have a few percent of uniform elongation, whereas the CuCrZr is around 1%. The data listed in Tables 4 and 5 and the tensile curves for the CuNiBe (Fig. 2) show that irradiation leads to the largest

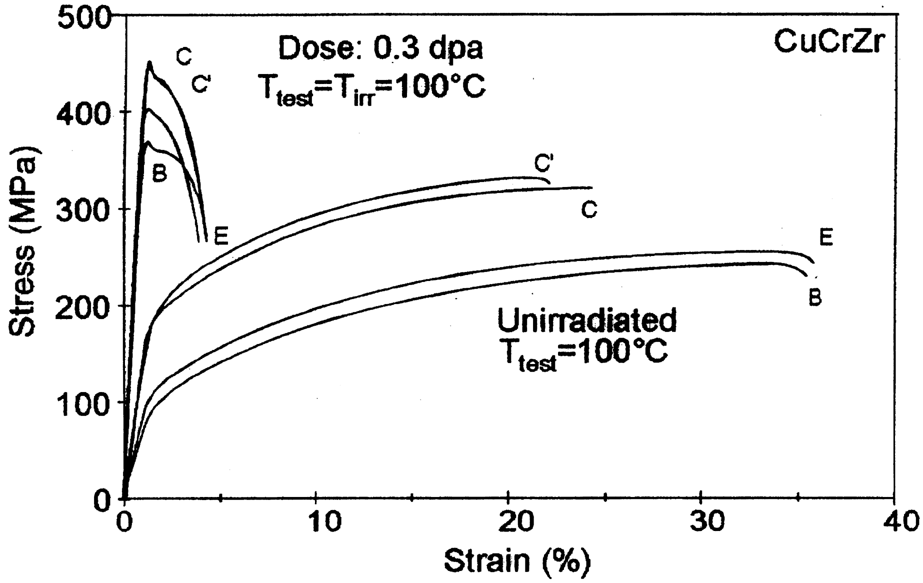

Fig. 1. The tensile properties of the various heat treated CuCrZr specimens before and after irradiation. Irradiation leads to a severe loss of uniform and total elongation, and produces an instability upon yielding. The embrittlement is not affected by the pre-irradiation heat treatment.

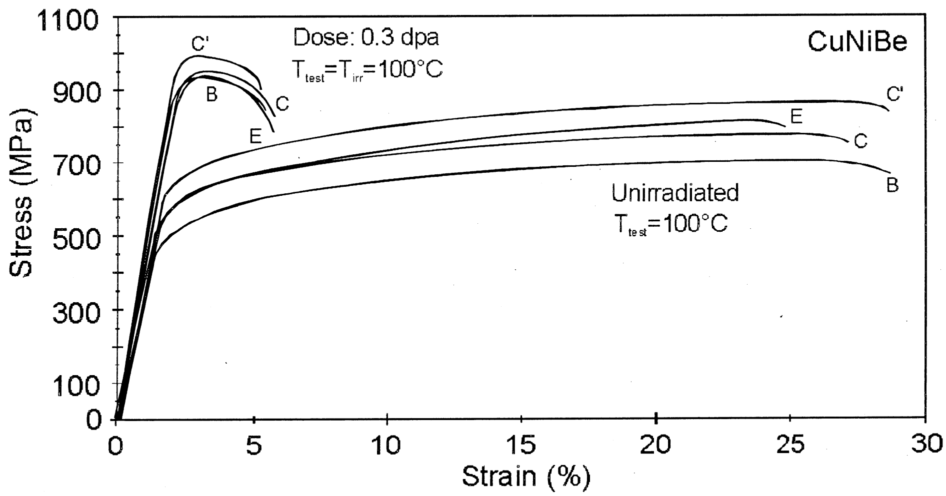

Fig. 2. The tensile properties of the various heat treated CuNiBe specimens before and after irradiation. Irradiation produces a significant increase in strength and loss of ductility, but does not lead to the instability shown for the CuCrZr alloys.

increase in strength compared to either the Al25 or the CuCrZr. A dramatic change in behavior also occurs in the solution annealed specimens of the two precipitation hardened alloys, that is, after irradiation there is as much as a factor of 5–6 increase in the yield strengths. For the CuNiBe alloys the heat treatments made little difference after irradiation.

4. Discussion

The tensile behavior of these materials indicate that they are all susceptible to radiation hardening to different degrees, and that the limited number of heat treatments used in this study to simulate the thermal treatments used in bonding or vessel bakeouts will not improve their resistance to radiation hardening. The CuNiBe and Al25 possess marginally better resistance to radiation hardening given that they still maintain a few percent uniform elongation and a finite ability to work harden. However, higher dose irradiation experiments on other versions of the same alloys have shown that they continue to lose their ductility and work hardening ability [5,10].

The CuCrZr used in this study does not compare in strength to the optimized properties available in other commercial CuCrZr properties such as the Elbrodur-G CuCrZr alloys produced by KM-Kabelmetal. However, the highest strength, highest conductivity condition is produced using a solution annealing, cold working, and ageing treatment. For the ITER first wall and possibly the divertor assemblies it is unlikely that cold working will constitute a viable step in the processing of the large panels, so the strength and potentially the conductivity of the CuCrZr will be closer to the material used in this study. One point to consider is that the CuNiBe alloys are much more responsive to ageing without cold working, so their strength can be quite high, but at the price of electrical and thermal conductivity. The different pre-irradiation heat treatments did not alleviate the poor ductility of the CuCrZr alloys after irradiation, indicating that this is a problem that has to be taken into account for fusion applications. The same can be said for all of the alloys irradiated in this study since none of them offer any significant advantage compared to each other when their response to irradiation over the temperature range of 23–350°C is considered.

Irradiation clearly changes the precipitate size and density depending on the stability of the phases present. The large increases in strength measured in the irradiated solution annealed specimens are evidence of irradiation-induced precipitation at 100°C. Of the three alloys, the γ'' precipitates in the CuNiBe alloys are the most susceptible to ballistic dissolution, but it remains unclear whether the alloying elements are reprecipitating or remain in solution. Since there is such a drastic increase in yield stress after irradiation, it would appear that irradiation may actually be producing a high density of defects and /or precipitates that have not yet been observed in the irradiated microstructure, effectively pinning the existing dislocations or dislocation sources within the material. The electrical conductivity of the CuNiBe alloys decreases after irradiation for all of the heat treatments used, but this may be a consequence of new precipitation or the Ni and Be remaining in solution, or even a combination of both. The irradiation experiments presented in earlier reports [7–9] also lead to the conclusion that these alloys are not stable under irradiation, especially at irradiation temperatures of 250°C and 350°C, where the size of the γ'' precipitates remained roughly the same but the density decreased. In the case of the CuCrZr the improvement in conductivity and larger precipitate size coupled with the slightly lower density suggests that irradiation coarsened the precipitate microstructure, and possibly removed additional Cr and Zr from solution. In effect the precipitates in these materials appear to be more stable and resistant to ballistic dissolution, as has already been shown in several studies for the Al_2O_3 particles in the GlidCop^{TM} alloys.

When considered in the light of all the studies done on these alloys to date, it is evident that radiation hardening and the subsequent effect that it has on the tensile properties, toughness, and conductivity will pose a severe limitation on their use for applications below ~200°C. Further development of these or even new alloys specifically tailored for operating in neutron environments is needed. One approach is to increase the volume fraction of oxide particles or precipitates to levels where they interfere more effectively with the movement of dislocations, that is, increasing the density of Orowan obstacles such that dislocation channelling is prevented.

5. Conclusions

Irradiation at 100°C produces a severe loss of ductility and work hardening ability in CuCrZr due to the high density of defect clusters produced during irradiation. Both the CuNiBe and the Al25 exhibit irradiation embrittlement, but to a lesser degree at this dose level. Heat treatments designed to explore the potential effects of joining processes and vessel bakeouts did not offer any improvement in the mechanical and physical properties after irradiation. This study and others have repeatedly shown that these materials can only be used if the very low uniform elongation (1% or less) can be accounted for in the design since pre-irradiation thermal processing cannot mitigate the irradiation hardening.

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