ELSEVIER

Journal of Nuclear Materials 258–263 (1998) 1015–1021

journal of nuclear materials

The effect of neutron dose, irradiation and testing temperature on mechanical properties of copper alloys

S.A. Fabritsiev [a,*], A.S. Pokrovsky [b], D.J. Edwards [c], S.J. Zinkle [d]

[a] *D.V. Efremov Scientific Research Institute, 189631 St.Petersburg, Russian Federation*

[b] *Scientific Research Institute of Atomic Reactors, 433510 Dimitrovgrad, Russian Federation*

[c] *Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, USA*

[d] *Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6376, USA*

Abstract

The paper presents the results of comparative investigations of radiation embrittlement of UHS–PH copper alloys of Cu–Ni–Be, Cu–Cr–Ni–Si type and the base Cu–Cr–Zr alloy after irradiation to 0.2 dpa at temperatures of 150°C and 300°C. The investigations undertaken and the analysis of changes in the mechanical properties of high-strength alloys of Cu–Ni–Be and Cu–Cr–Ni–Si irradiated to 0.2 dpa at 150°C and 300°C allowed for the conclusion that at low irradiation and testing temperatures alloys are prone to low-temperature embrittlement, which shows up in these alloys in the same way as in ITER base alloy. At elevated irradiation and testing temperatures the high-strength Cu–Ni–Be and Cu–Cr–Ni–Si alloys embrittle, and what is more, demonstrate, when irradiated, a low level of fracture stress (about twice as low as the initial material).

1. Introduction

Intensive studies pursued in the last 15 years made it possible to understand quantitatively the most important radiation effects observed in copper alloys to be used for the ITER divertor and first wall [1–4]. Investigations into the effect of neutron irradiation to doses of 10 dpa on the mechanical properties of precipitation hardened (PH) and dispersion strengthened (DS) copper alloys revealed two main factors, which will limit the materials lifetime in the operation temperature range of 100–350°C. These are low temperature embrittlement (LTE) [5–8] at relatively low irradiation temperatures of 100–150°C and softening (particularly pronounced for PH alloys) and He embrittlement at increased temperatures [9–12]

The neutron spectrum was also shown to considerably affect radiation resistance of copper alloys [10–13]. The available data on copper alloy radiation resistance were obtained mainly for representatives of two classes of materials; these are Cu–Cr–Zr for PH alloys and GlidCop™ Al 25 for DS alloys. But some ITER components require that the copper alloys have an extremely high level of strength, i.e. 400–500 MPa at 200°C. ITER base alloys cannot provide this level of strength properties. In this connection the ultrahigh-strength PH copper alloys (UHS–PH) of Cu–Ni–Be [7,14–17], Cu–Cr–Ni–Si [18], Cu-Be [19] type have been investigated in the last few years with the aim of their application in the ITER high-heat flux components.

The present paper presents the results of comparative investigations of radiation embrittlement of UHS–PH copper alloys of Cu–Ni–Be, Cu–Cr–Ni–Si type and the base Cu–Cr–Zr alloy after irradiation to 0.2 dpa at temperatures of 150°C and 300°C.

2. Experimental procedure

The Brush-Wellman Hycon Cu–2% Ni–0.4% Be alloy were investigated in the AT (solution annealed and aged) and HT (solution annealed and cold worked and aged) conditions, which produced an extremely high level of strength properties (σ_y – 500 MPa at 250°C). Cu–0.58% Cr–2.46% Ni–0.64% Si alloy was investigated in the

* Corresponding author. Tel.: +7-812 464 4463; fax: +7-812 464 4623; e-mail: fabr@niiefa.spb.su.

0022-3115/98/$19.00
PII: S 0 0 2 2 - 3 1 1 5 (9 8) 0 0 3 8 9 - 4

solution annealed and aged condition, with lower strength than similar Hycon condition. A previous irradiation experiment using this alloy in the solution annealed, cold worked and aged condition produced poor results on the radiation resistance, and therefore that condition was not included in this experiment [18]. Cu–0.5% Cr–0.2% Zr base alloy was investigated in the SA and aged condition (solution annealed and aged), which is recommended ITER Grade heat treatment. The STS-type sheet tensile specimens (10 mm gage dimension) were irradiated in Channel N5 of the SM-2 reactor to a dose of $\sim 3.5 \times 10^{20}$ n/cm^2 ($E > 0.1$ MeV), this being consistent with a damage of $\sim$0.2 dpa (NRT). Irradiation was performed in a loop device making it possible to control the specimens irradiation temperature to within ±5°C. Irradiated and reference specimens were tensile tested in vacuum ($\sim$1 Pa) in the temperature range of 20–500°C at a deformation rate of 1.6×10^{-3} s^{-1}. SEM investigations of the fractured surface of tested specimens were also performed. The irradiation and testing techniques are described in more detail in Refs. [20,21].

3. Results

3.1. Effect of irradiation on the mechanical properties

As follows from Fig. 1, irradiation to 0.2 dpa at $T_{irr} = 150$–170°C results in an increase in yield strength of Cu–Ni–Be alloy by about 100 MPa at $T_{test} = 20$°C. At $T_{test} = 185$°C hardening of the irradiated alloy is somewhat lower, i.e. 50 MPa, for the AT modification, and for the HT modification hardening is lacking completely. Irradiation at $T_{irr} = 300$°C results in a very weak hardening of Cu–Ni–Be alloy at $T_{test} = 20$°C and slight softening at $T_{test} = 185$°C. At $T_{test} = T_{irr} = 300$°C a dramatic drop in the strength characteristics of Cu–Ni–Be alloy is observed. In this case yield strength is only about half of the unirradiated value, and is associated with intergranular brittleness that being when the test and irradiation temperature exceed 250°C.

As follows from Fig. 2, after irradiation at $T_{irr} = 150$–170°C Cu–Ni–Be alloy has a rather low uniform elongation ($\delta_{unif} = 1.6$–2.5%) at $T_{test} = 20$°C and at higher $T_{test} = 185$°C has a lower but still different from zero uniform elongation ($\delta_{unif} = 0.5$–2.1%). After irradiation at 300°C Cu–Ni–Be alloy samples had uniform elongation close to that for unirradiated samples at $T_{test} = 20$°C ($\delta_{unif} = 10$%). But with the testing temperature increasing to 185°C the uniform and total elongation drops to a low level ($\delta_{unif} = 0.1$–2%) and at $T_{test} = 300$°C the alloy samples have zero uniform and total elongation and fail at a low level of fracture stress, i.e. 200 MPa.

Cu–Cr–Zr and Cu–Cr–Ni–Si alloys demonstrate, as is seen in Fig. 1, a typical monotonous dependence of yield strength on the testing temperature, when unirradiated. In this case Cu–Cr–Ni–Si alloy is stronger by

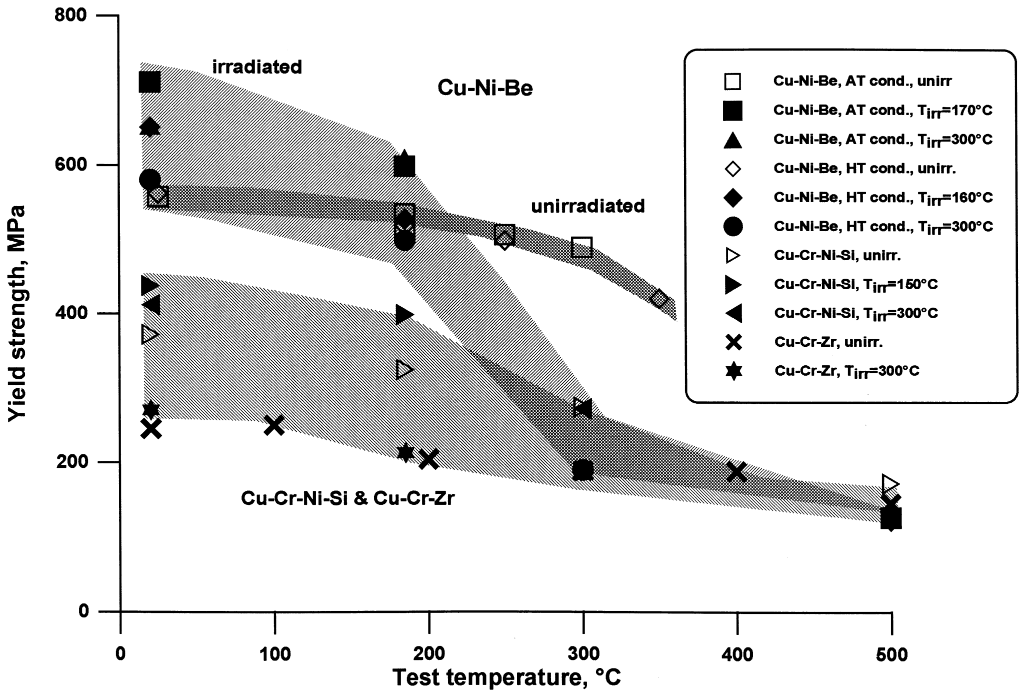

Fig. 1. Yield strength versus testing temperature of the PH copper alloy Cu–Ni–Be, AT and HT conditions, Cu–Cr–Ni–Si (SA + aged) and Cu–Cr–Zr (SA + aged), when unirradiated and after irradiation to 0.2 dpa at $T_{irr} = 150$°C and $T_{irr} = 300$°C.

about 100 MPa than Cu–Cr–Zr alloy at decreased testing temperatures. At $T_{test} = 300$–$500°C$ the difference in yield strength of these two alloys is levelled. Irradiation at 150°C results in a slight (50 MPa) hardening of Cu–Cr–Ni–Si alloy. Irradiation at 300°C does not practically affect the yield strength of Cu–Cr–Ni–Si and Cu–Cr–Zr alloys.

As follows from Fig. 2, Cu–Cr–Ni–Si and Cu–Cr–Zr alloys have markedly different temperature dependencies of uniform elongation, when unirradiated. While Cu–Cr–Zr alloy had a high uniform elongation ($\delta_{unif} = 15\%$) at all testing temperatures, Cu–Cr–Ni–Si alloy has a good ductility ($\delta_{unif} = 16\%$) only at $T_{test} = 20°C$. At increased testing temperatures uniform elongation is low and at $T_{test} = 300$–$500°C$ amounts to only 0.5–0.9%. It should be noted that the total elongation of Cu–Cr–Zr alloy is substantial throughout the testing temperature range ($\delta_{total} = 20$–40%). Yet, the total elongation of Cu–Cr–Ni–Si alloy is small and practically coincides with the value of uniform elongation. Irradiation at 150°C causes a slight decrease in the uniform elongation of Cu–Cr–Ni–Si alloy at $T_{test} = 20°C$. At $T_{test} = 185°C$ the alloy irradiated to 0.2 dpa has practically the same uniform elongation as an unirradiated material. After irradiation at 300°C Cu–Cr–Ni–Si alloy has a somewhat lower uniform elongation than an unirradiated material. Cu–Cr–Zr alloy demonstrates an increase in uniform elongation after irradiation at 300°C.

3.2. *Effect of neutron irradiation on alloy fracture character*

Cu–Ni–Be alloy. Investigations into the character of Cu–Ni–Be alloy fracture revealed that at $T_{test} = 20$–$185°C$ unirradiated alloy samples undergo transgranular fracture. At higher testing temperatures, $T_{test} = 300$–$500°C$, Cu–Ni–Be AT and HT undergo ductile intergranular fracture. After irradiation to 0.2 dpa at $T_{irr} = 300°C$ samples of Cu–Ni–Be alloy undergo ductile transgranular fracture at $T_{test} = 20°C$. As follows from SEM investigations, fracture of samples irradiated at $T_{irr} = 300°C$ and tested at $T_{test} = 20°C$ is accompanied by approximately 20% reduction in area (RA), as measured also for the unirradiated samples. At $T_{test} = 300°C$ samples irradiated at $T_{irr} = 300°C$ undergo brittle intergranular fracture. Whereas dimples 2–3 μm in diameter were observed on fracture facets of unirradiated samples tested at $T_{test} = 300°C$, facets of an irradiated samples tested under the same conditions were free from dimples.

Cu–Cr–Ni–Si and Cu–Cr–Zr alloys. Cu–Cr–Ni–Si alloy, like Cu–Ni–Be alloy, was characterised by the same tendency to ductile intergranular fracture at increased testing temperatures, when unirradiated. Irradiation at $T_{irr} = 300°C$ results in a brittle intergranular fracture at $T_{test} = 300°C$. At $T_{test} = 20°C$ irradiated samples of the alloy underwent ductile transgranular fracture.

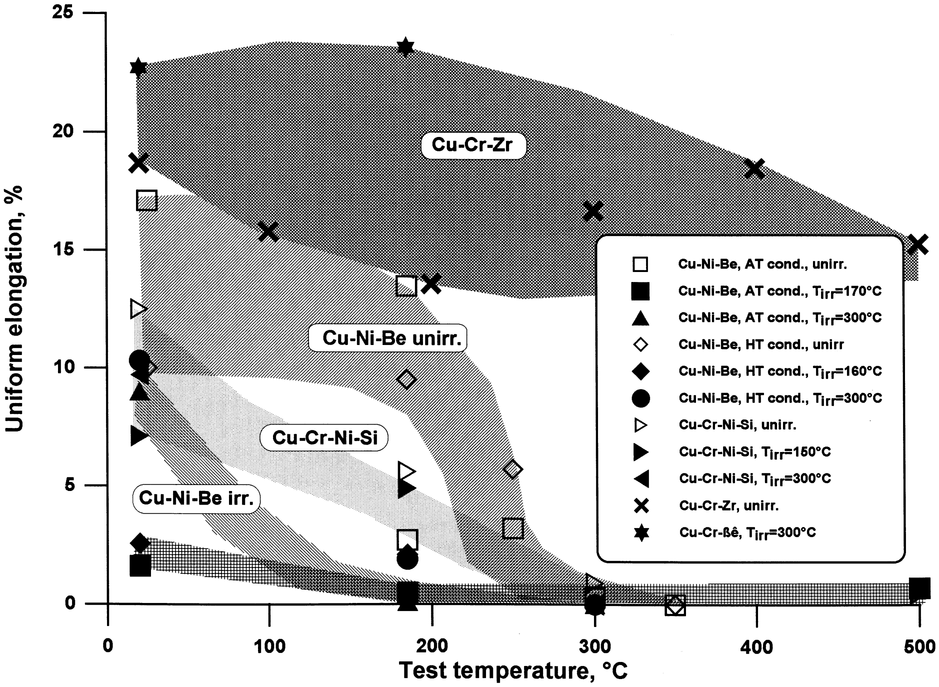

Fig. 2. Uniform elongation versus testing temperature of the PH copper alloy Cu–Ni–Be, AT and HT conditions, Cu–Cr–Ni–Si (SA + aged) and Cu–Cr–Zr (SA + aged), when unirradiated and after irradiation to 0.2 dpa at $T_{irr} = 150°C$ and $T_{irr} = 300°C$.

Cu–Cr–Zr alloy demonstrated ductile transgranular fracture at $T_{test} = 20–300°C$ both in the initial and irradiated state. Unlike Cu–Ni–Be and Cu–Cr–Ni–Si alloys, this alloy fractured at increased testing temperatures only after quite a considerable local deformation and necking (RA-80–90%). What is important, this ability for a high local deformation survives for this alloy both when irradiated to 0.2 dpa at $T_{irr} = 300°C$.

4. Discussion

The investigations revealed that even at small irradiation doses for high-strength copper alloys (UHS-PH) serious problems arise associated with a decrease in ductility (uniform elongation and reduction in area) and work hardening.

4.1. Low-temperature radiation embrittlement

At $T_{irr} = 180°C$ and $T_{test} = 20–185°C$ high-strength Cu–Ni–Be and Cu–Cr–Ni–Si alloys exhibit a decrease in their strain hardening capacity and noticeable reduction in uniform elongation, which shows up in both pure copper and other alloys (Cu–Cr–Zr, Cu–Al_2O_3, etc.) [5–8]. The high strength CuNiBe alloys also exhibit the same behaviour but to lesser extent. Irradiation to higher doses may lead to even further decrease in the ductility and strain hardening capacity of these materials. Note that all of these alloys still exhibit a ductile failure mode when irradiated and tested at temperatures below 200°C in the sense that the fracture surface are distinguished by dimples and a large reduction in area, irrespective of the degree of uniform elongation. Testing and irradiation at higher temperature leads to changes in the deformation and failure modes of the different alloys, and the higher strength CuNiBe alloys exhibit increasingly poorer properties as the irradiation and temperature increases. Characteristic of LTE display in Cu–Ni–Be alloys is that at $T_{irr} = 150°C$ they harden but rather slightly (~100 MPa), with their uniform elongation decreased by about a factor of 15 (from 15% to 1%).

Cu–Cr–Ni–Si alloy with its considerably lower strength in the initial state ($\sigma_y \sim 325$ MPa at $T_{test} = 185°C$) does not practically demonstrate a reduction in uniform elongation at $T_{test} = 20–185°C$ after irradiation at $T_{irr} = 150°C$. When analysing the temperature dependence of uniform elongation for high-strength copper alloys Cu–Ni–Be HT&AT, Cu–2Be [22–24], Cu–Ni–Cr–Si (SA + c.w. + aged) and low-strength modifications Cu–Cr–Zr (SA + aged), Cu–Cr–Ni–Si (SA + aged), it becomes apparent that in the range of 0.2–0.3 dpa a reduction in uniform elongation of low-strength alloys is substantially less. But, when irradiated to 1 dpa, this effect is likely to be levelled.

When building up the same dependence for total elongation (Fig. 3), it becomes evident that in this

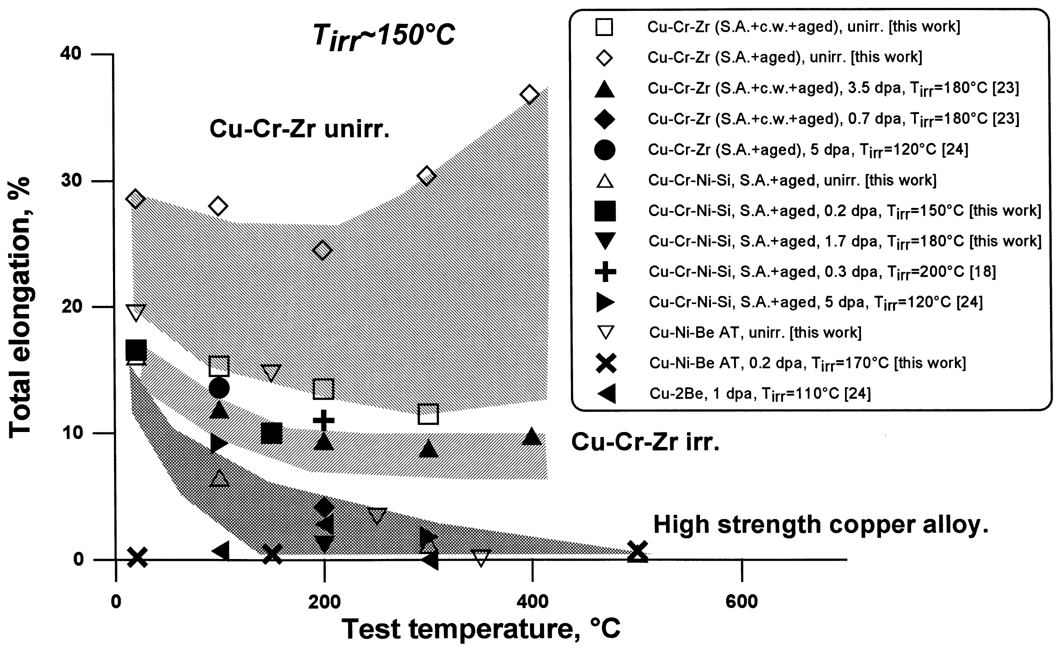

Fig. 3. Effect of low temperature irradiation ($T_{irr} \approx 150°C$) on the total elongation of PH copper alloys. Data from investigations [18,23,24] are included for the sake of comparison.

parameter Cu–Cr–Zr alloy offers advantages over high-strength Cu–Be and Cu–Cr–Ni–Si alloys. This difference is particularly marked at $T_{test} \geqslant 300°C$. Cu–Cr–Zr alloy demonstrates ability for a high local deformation both when unirradiated and after irradiation. As for high-strength Cu–Cr–Ni–Si, Cu–Ni–Be alloys, they have at increased temperatures practically zero local deformation, zero neck and fracture, when irradiated at $T_{test} = 300°C$, with the deformation close to zero.

4.2. Embrittlement at elevated temperatures

As follows from Figs. 1–4, irradiation of high-strength copper alloys at 300°C does not practically change their strength and ductility at $T_{test} = 20°C$. But, at increased $T_{test} = 300°C$ all investigated high-strength alloys demonstrate essentially zero uniform elongation, total lack of deformation in the neck and susceptibility to embrittlement at reduced stresses.

When building up the dependence of total elongation on testing temperature for copper alloys irradiated at 300°C, a radical difference reveals itself in the behaviour of high-strength copper alloys (Cu–Ni–Be HT&AT, Cu–2Be, Cu–Ni–Cr–Si) and base material for ITER Cu–Cr–Zr alloy (Fig. 4). Cu–Cr–Zr alloy in the SA + aged state has an extremely high total elongation both in the initial state and irradiated to 0.2 dpa state. Stronger modifications of Cu–Cr–Zr SA + c.w. + aged alloy have a somewhat lower total elongation in the initial state, but in this case ductility of the irradiated alloy decreases monotonously with a rise in the testing temperature, while remaining at the high level $\delta_{tot} = 10\%$.

High-strength Cu–Ni–Be, Cu–2Be, Cu–Cr–Ni–Si copper alloys both in the initial and irradiated state have a satisfactory ductility at $T_{test} = 20°C$. At increased testing temperatures of 300–400°C these materials demonstrate a low nearly zero level of total elongation.

4.3. Analysis of reasons for the embrittlement of high-strength copper alloys at increased temperatures

Intensive studies made to date on the structure and character of fracture of high-strength copper alloys irradiated to small doses of 0.1–0.3 dpa [14,16,18,22] reveal the main mechanisms of changes in the structure of Cu–N–Be alloys irradiated at increased temperatures of 250–350°C. By summing up the results of the studies [14,16,22] it can be seen that irradiation results in the formation of denuded zones along grain boundaries, intensification of precipitation in grain matrix and partially also on the grain boundaries.

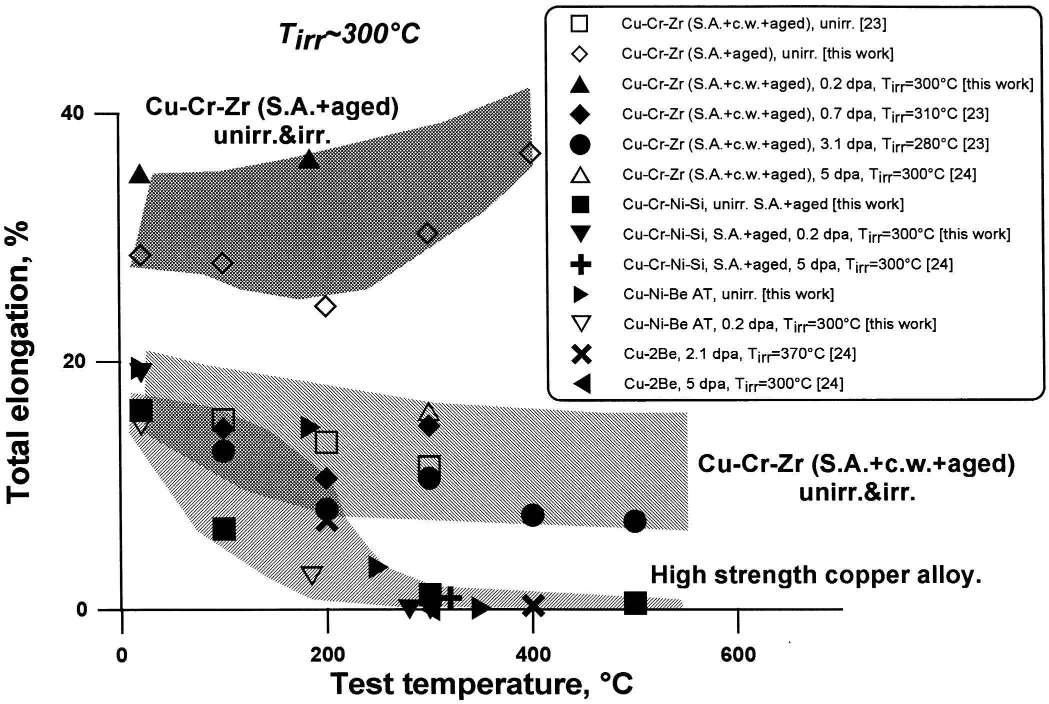

Fig. 4. Effect of elevated temperature irradiation ($T_{irr} \approx 300°C$) on the total elongation of PH copper alloys. Data from investigations [18,23,24] are included for the sake of comparison.

Note, that in earlier studies [14,16,22] the data on the mechanical properties of irradiated samples was presented only for the case where the tensile tests were conducted at $T_{test} = T_{irr}$. The results obtained in our study demonstrate the fundamental difference in the behaviour of the high-strength CuNiBe alloys when irradiated at $T_{irr} = 300°C$ and tested at $T_{test} = 20°C$ and $T_{test} = 300°C$. In the first case the samples undergo ductile fracture over the grain matrix after an essential deformation (10%), and when tested at an increased temperature they undergo brittle intergranular fracture.

In our experiment, in parallel with a drop in ductility of Cu–Ni–Be and Cu–Cr–Ni–Si alloys there was observed a drop in their strength down to 200 MPa at $T_{test} = T_{irr} = 300°C$. Hence, the observed effect cannot be entirely attributed to alloy matrix hardening caused by intensification of the processes of phase precipitation in the grain matrix under irradiation at $T_{irr} = 300°C$.

As of now, only some preliminary considerations are possible on mechanism of embrittlement of high-strength copper alloys at 300°C. The finite estimates require TEM and SEM investigations of irradiated materials to be performed.

Two main reasons are likely to be responsible for embrittlement. The first is matrix hardening caused by additional radiation-stimulated precipitation and complexes of radiation defects. As a result, with deformation appearing on the grain boundaries, its accommodation into the matrix, in particular in triple points, will be impeded. Considering that grain-boundary sliding is realised only at temperatures $T_{test} > 0.4–0.45\ T_{melt}$ (250–320°C), it is clear why this mechanism does not work at $T_{test} = 20–150°C$. The second reason, as we see it, is weakening of grain boundaries in an irradiated material. That this weakening really occurs is evidenced undeniably by the fact that irradiated samples of Cu–Ni–Be and Cu–Cr–Ni–Si alloys fracture prematurely at stresses of 300–200 MPa. Hence, the process of grain-boundary fracture starts in irradiated samples at nearly twice as low stresses as in unirradiated samples.

Such weakening of boundaries can be controlled by several processes. First, possible is the effect of small helium concentrations of 0.1–1 appm, which are accumulated in irradiated samples on impurities (B) and alloying elements (Be) (accumulation on copper at small irradiation doses can be neglected) [16,22].

The investigations clearly demonstrate that it is at increased testing temperatures these ultra-high-strength copper alloys have an inherent tendency to embrittlement, and irradiation enhances the embrittlement and reduces a fracture stress to 200 MPa, i.e. lower than the stipulated level. This situation requires materials engineers and designers finding an ingenious solution so as to create a high-strength and ductile copper alloy for high-heat flux components.

5. Conclusion

This investigation shows that the Cu–Ni–Be and Cu–Cr–Ni–Si alloys irradiated to 0.2 dpa at 150°C and 300°C are prone to low-temperature radiation hardening and loss of ductility, which manifests itself as an overall reduction in strain hardening capacity. At increased irradiation and testing temperatures the high-strength Cu–Ni–Be and Cu–Cr–Ni–Si alloys embrittle in a completely different manner, and exhibiting a low level of fracture stress (about half the unirradiated value). The SEM investigations confirm that this embrittlement is associated with transition at $T_{test} \geqslant 300°C$ to intergranular fracture, which, when in the irradiated state, is likely to occur by the action of helium and Be, Ni, Si segregation and is of a brittle character. Irradiated solutionized and aged Cu–Cr–Zr demonstrates a remarkable ductility and, unlike high-strength copper alloys, retains the capability for local deformation and undergoes ductile fracture after formation of a sizeable neck.

References

[1] S.J. Zinkle, S.A. Fabritsiev, Nucl. Fusion Suppl. 5 (1994) 163.
[2] H.R. Brager, H.L. Heinisch, F.A. Garner, J. Nucl. Mater. 133&134 (1985) 676.
[3] T.S. Lee, L.W. Hobbs, G. Kohse, M. Ames, O.K. Harling, N.J. Grant, J. Nucl. Mater. 141–143 (1986) 179.
[4] M. Ames, G. Kohse, T.S. Lee. N.J. Grant, O.K. Harling J. Nucl. Mater. 141–143 (1986) 174.
[5] W. Vandermeulen, V. Massaut, J. Van der Velde, W. Hendrix, in: Proceedings of the 14th Symposium on Fusion Technology, Pergamon, New York, 1986, p. 1031.
[6] P. Fenici, D.J. Boerman, G.P. Tartaglia, J.D. Elen, J. Nucl. Mater. 212–215 (1994) 399.
[7] B.N. Singh, D.J. Edwards, P. Toft, J. Nucl. Mater. 238 (1996) 244.
[8] S.A. Fabritsiev, A.S. Pokrovsky, S.J. Zinkle, D.J. Edwards, J. Nucl. Mater. 233–237 (1996) 513.
[9] S.A. Fabritsiev, V.R. Barabash, A.S. Pokrovsky, V.P. Chakin, N.I. Grechanjuk, B.A. Movchan, V.A. Osokin, Plasma Dev. Oper. 4 (1995) 1.
[10] S.A. Fabritsiev, A.S. Pokrovsky, V.R. Barabash, Yu.G. Prokofiev, Fusion Eng. Design 36 (1997) 505.
[11] S.A. Fabritsiev, V.V. Rybin, V.A. Kasakov, A.S. Pokrovsky, V.R. Barabash, J. Nucl. Mater. 195 (1992) 173.
[12] S.A. Fabritsiev, A.S. Pokrovsky, Plasma Dev. Oper. 5 (1997) 133.
[13] S.A. Fabritsiev, A.S. Pokrovsky, S.J. Zinkle, A.F. Rowcliffe, D.J. Edwards, F.A. Garner, V.A. Sandakov, B.N. Singh, V.R. Barabash, J. Nucl. Mater. 233–237 (1996) 526.
[14] S.J. Zinkle, W.S. Eatherly, in: Fusion Materials Semi-Annual Progress Report for Period Ending 30 June 1996, DOE/ER-0313/20, Oak Ridge National Laboratory, 1996, p. 207.
[15] S.J. Zinkle, W.S. Eatherly, in: Fusion Materials Semi-Annual Progress Report for Period Ending 31 December

1996, DOE/ER-0313/21, Oak Ridge National Laboratory, 1996, pp. 165–174.
[16] B.N. Singh, D.J. Edwards, M. Eldrup, P. Toft, Pre and Post-Irradiation Properties of Copper Alloys at 250°C Following Bonding and Bakeout Thermal Cycles, RISO-R-937(EN), RISO National Laboratory, Roskilde, Denmark, January 1997.
[17] K.D. Leedy, J.F. Stubbins, B.N. Singh, F.A. Garner, J. Nucl. Mater. 233–237 (1996) 547.
[18] A. Ivanov, V. Abramov, M. Rodin, J. Nucl. Mater. 233–237 (1996) 553.
[19] S.A. Fabritsiev, V.V. Rybin, V.A. Kasakov, A.S. Pokrovsky, V.R. Barabash, J. Nucl. Mater. 195 (1992) 179.
[20] S.A. Fabritsiev, A.S. Pokrovsky, H. Kawamura, these Proceedings.
[21] S.A. Fabritsiev, A.S. Pokrovsky, D.J. Edwards, S.J. Zinkle, A.F. Rowcliffe, these Proceedings.
[22] B.N. Singh, D.J. Edwards, M. Eldrup, P. Toft, Effect of Bonding and Bakeout Thermal Cycles on the Properties of Copper Alloys Irradiated at 250°C, RISO-R-971(EN), Risø National Laboratory, Roskilde, Denmark, February 1997.
[23] S.A. Fabritsiev, A.S. Pokrovksy, J. Nucl. Mater. 249 (1997) 250–258.
[24] S.A. Fabritsiev, A.S. Pokrovsky, presented at 8th Int. Conf. on Fusion Reactor Materials, Sendai, 1997.