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Final Report
on Characterization of Physical and Mechanical Properties of Copper and Copper Alloys before and after Irradiation

(ITER R & D Task No. T213)

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Abstract The present report summarizes and highlights the main results of the work carried out during the last 5 – 6 years on effects of neutron irradiation on physical and mechanical properties of copper and copper alloys. The work was an European contribution to ITER Research and Development programme and was carried out by the Associations Euratom - Risø and Euratom - Tekes.

Details of the investigations carried out within the framework of the present task and the main results have been reported in various reports and journal publications. On the basis of these results some conclusions are drawn regarding the suitability of a copper alloy for its use in the first wall and divertor components of ITER. It is pointed out that the present work has managed only to identify some of the critical problems and limitations of the copper alloys for their employment in the hostile environment of 14 MeV neutrons. A considerable amount of further effort is needed to find a realistic and optimum solution.

Contents

1 Introduction

Because of their good thermal conductivity, copper alloys were chosen as heat sink materials for both first wall and divertor components of ITER (International Thermonuclear Experimental Reactor) [1,2]. Since very little was known about the effect of irradiation on physical and mechanical properties of copper alloys, at the ITER technical meeting at Garching in December 1994 it was decided to initiate investigations on the effect of irradiation on the oxide dispersion strengthened (e.g. GlidCop CuAl25) as well as precipitation hardened (e.g. CuCrZr and CuNiBe) copper alloys. Because of the thermal as well as irradiation stability [3-5] against dissolution of alumina particles, the ODS copper alloys were chosen to be the primary candidate materials for their use in the first wall and divertor components of ITER. At the same meeting it was also agreed that a backup alloy should be selected from the two well-known precipitation hardened (PH) alloys, namely CuCrZr and CuNiBe. It was, therefore, decided to carry out screening experiments to simulate the effect of bonding and bakeout thermal treatments on pre- and post-irradiation microstructures, mechanical properties and electrical resistivity of CuCrZr and CuNiBe alloys. The strategy was that on the basis of the results of these screening experiments, one of the two PH alloys should be then selected as a backup material.

This series of investigations was launched in 1995 as a part of the ITER research and development programme. The first set of results on copper and copper alloys illustrating the effect of neutron irradiation on microstructural evolution and mechanical properties was reported already in 1995 [6,7]. Since then the results of these investigations have been documented and discussed in a number of reports and journal publications (see later for specific references). By now these investigations have come to a close. The main purpose of the present report is to summarise the main results, synthesize the main conclusions and to highlight major implications. Finally, we shall endeavour to point to some perspectives for future activities in this field.

2 Scope of the Present Investigations

Prior to describing and discussing the results of the present series of investigations, it will be quite helpful to outline very briefly the general scope of the work to be summarized in this report. As indicated in the previous section, the main objective of these investigations was to establish a scientific basis for the selection of a specific copper alloy for the first wall and the divertor components of ITER. In view of the estimated operational conditions and the microstructural features of these alloys, the irradiation-induced void swelling was not considered to be an acute problem. Hence, the main focus of the present work was on the effect of neutron irradiation on the mechanical performance of these alloys. The effect of neutron irradiation on the thermal conductivity of these alloys was also considered to be important and was, therefore, investigated. In order to understand the effect of neutron irradiation on mechanical properties and thermal conductivity, it was deemed necessary to carry out a detailed microstructural characterization of the unirradiated as well as irradiated materials both before and after the specimens were subjected to mechanical deformation in uniaxial tensile tests and in fully reversible low cycle fatigue tests.

Practically all irradiation experiments were carried out using fission neutrons in the DR-3 reactor at Risø. A few experiments were done with 600 MeV protons to determine the effect of high recoil energy on the irradiation stability of alumina particles in the dispersion strengthened CuAl25 alloy. The main irradiation variables used were irradiation dose and temperature (see section 4). In addition to tensile (sections 4 and 5) and low cycle fatigue (section 6) behaviour, the effect of irradiation on fracture toughness and crack nucleation behaviour were also investigated (sections 7 and 8).

While the investigations of the effects of bonding and bakeout thermal cycles (with and without neutron irradition) were in progress, it was decided that the components will be manufactured using HIPing technique. A limited amount of effort was, therefore, devoted to the effect of HIPing and neutron irradiation on the tensile as well as fracture toughness behaviour of CuAl25 and CuCrZr alloys (section 9).

Experiments demonstrated that neutron irradiations at temperatures below 200°C lead to a drastic decrease in ductility and induce plastic instability in OFHC-copper and CuCrZr alloy. It was then decided to investigate the possibility of using post-irradiation annealing to recover the ductility and to eliminate the plastic instability. Results of these experiments are reported in Section 10.

3 Materials and Experimental Details

Even though the materials used in the present series of investigations and the details of experiments carried out have been described in a number of publications cited in this report, it is, in our view, necessary to provide a general description of the materials and experimental details in the present report. Throughout the present work, pure OFHC-copper has been used as a reference material for evaluating the effect of irradiation on microstructural evolution and mechanical properties. The OFHC-copper specimens were annealed at 550°C for 2 hours (in vacuum) prior to irradiation.

As indicated in Section 1, both dispersion strengthened (DS) and precipitation hardened (PH) copper alloys were used throughout the present work. The DS copper alloys (CuAl25, CuAl60) were supplied by OGM Americas (formerly SCM Metals Inc.) in the form of rods and in the wrought condition (i.e. without any cold work after hot extrusion). The PH copper alloys (CuCrZr and CuNiBe) were supplied by Tréfimétaux (France) in the form of 20 mm thick plates. A limited amount of work was also performed on CuCrZr alloy supplied by Outokumpu (Finland) and Hycon 3HP CuNiBe alloy manufactured by Brush Wellman Inc. (USA). The chemical composition of these alloys is given in Table 1.

Table 1. Chemical Composition

OFHC Copper	Cu-10, 3, <1 and <1 ppm of Ag, Fe and Mg respectively
CuCrZr (Tréfimétaux)	Cu-0.8% Cr, 0.07% Zr, 0.01% Si
CuCrZr (Outokumpu)	Cu-0.78%Cr, 0.13% Zr, 0.003% Si
CuNiBe (Tréfimétaux)	Cu-1.75% Ni, 0.45% Be
CuNiBe (Hycon)	Cu-2.0% Ni, 0.35% Be
CuAl25 (Glid Cop)	Cu-0.25% Al as oxide particles (0.45% Al_2O_3)
CuAl60 (Glid Cop)	Cu-0.6% Al as oxide articles (1.1% Al_2O_3)

Generally, the PH copper alloys were prime aged (i.e. solution annealed at 950°C for 1 h, water quenched, aged at 475°C for 30 min. and finally water quenched) prior to irradiation. The DS copper alloys were used both in the as-supplied condition as well as after annealing at 950°C for 30 min.

In order to understand the effect of irradiation on the microstructural evolution and stability of the precipitates and dispersion particles, the microstructure was characterized quantitatively using transmission electron microscopy (TEM) both before and after irradiation. In most cases, electrical conductivity was also measured before and after irradiation. The microstructure of deformed specimens (i.e. after tensile and fatigue tests) was also investigated using TEM. The fracture surfaces were examined using a scanning electron microscope (SEM).

In order to characterize the effect of irradiation on mechanical performance of these alloys, tensile, low cycle fatigue, fracture toughness and crack nucleation and growth behaviour of these alloys were determined in the unirradiated and irradiated conditions. Mechanical properties were investigated at temperatures in the range of ~50 to 350°C. Generally, mechanical tests were performed at irradiation temperature. All tensile and fatigue tests at temperatures above room temperature were carried out in vacuum of ~10^{-5} torr. In most cases irradiations were carried out to a displacement dose level of ~0.3 dpa. In a limited number of cases, however, the dose dependence was also investigated.

4 Effects of Irradiation Dose and Temperature

Effects of irradiation dose and temperature on physical as well as mecha-nical properties were first investigated in pure OFHC copper and results are reported and discussed in Refs. [6,7]. The effect of irradiation dose was investigated in copper alloys at ~50°C [8] and in OFHC copper and CuCrZr alloy at 250°C [9].

The main conclusions emerging from these investigations were:

(a)   The damage accumulation at ~50°C in the form of defect clusters (interstitial loops and vacancy SFTs) in OFHC-copper, CuCrZr and CuAl25 is rather similar and the cluster density seems to reach a maximum value at doses below 0.3 dpa. A similar conclusion can be reached for the neutron irradiations at higher temperatures (e.g. 250°C [10]). In other words, results of irradiations up to a relatively low dose of 0.3 dpa should provide a reasonable indication of the effect of irradiations at higher doses. Hence, for the rest of screening experiments on these alloys, an irradiation dose of 0.3 dpa was chosen.

(b)   The Al$_2$O$_3$ particles in CuAl25 alloy seem to suffer, but only very slightly, from recoil resolution and particle size refinement [3, 9]. The precipitates in the CuNiBe alloy, on the other hand, are found to coarsen significantly already at a dose level of 0.2 dpa [8].

(c)   The most significant effect of irradiation at low temperatures (e.g. at ~50°C) is a drastic decrease in the ductility of OFHC-copper as well as copper alloys. Furthermore, the irradiated OFHC-copper and CuCrZr specimens exhibit yield drop and show the sign of plastic flow localization and instability. The CuNiBe and CuAl25 alloys, although suffer

from a severe reduction in ductility but do not show the occurrence of yield drop and plastic instability [7,8].

OFHC-copper specimens irradiated to doses of up to 0.3 dpa at 250°C do not show yield drop and plastic flow localization and show uniform elongations of greater than 30%. The CuCrZr specimens irradited at 250°C to 0.3 dpa still exhibit yield drop and plastic instability [9]. It should be noted that the CuNiBe alloy when irradiated at 250 and 350°C looses its ductility completely and suffers from intergranular failure (see later) [11,12].

(d)   The analysis of mechanical properties and microstructural evidence suggests that the increase in the initial yield stress due to irradiation may arise from the strong pinning of dislocation sources. The strong pinning occurs due to decoration of the grown-in dislocations by small and glissile interstitial loops formed in displacement cascades during neutron irradiation. Theoretical treatments have shown that the the decoration of dislocations by small loops may occur at temperature below the recovery stage V (i.e. <0.4 T_m where T_m is the melting temperature) in copper [13,14]. Based on this hypothesis, a theoretical model called "Cascade Induced Source Hardening" (CISH) has been proposed [15] and is found to be consistent with experimental results (e.g. see [16]) on the increase in the upper yield stress and the yield-drop phenomenon.

In order to understand the mechanism of dislocation decoration and the formation of rafts of loops on an atomistic level, the interaction between interstitial loops and edge dislocations has been studied using molecular dynamics (MD) technique [17,18]. Furthermore, the processes of dislocation decoration and raft formation have been recently simulated using 3D dislocation dynamics technique [19]. Finally, it should be pointed out that both of these processes have been observed experimentally in neutron irradiated metals and alloys [13, 14].

(e)   The problems of flow localization and plastic instability can be understood within the framework of the CISH model [16]. However, details of the mechanisms responsible for the initiation of the flow localization and its temporal evolution still remain unclear. The problem is being studied currently both experimentally and theoretically.

(f)   Examination of the fracture surfaces shows that even though the irradiated copper and copper alloys (except for CuNiBe) suffer from a drastic decrease in the uniform elongation, all samples irradiated at ~50°C fracture in a ductile manner.

5 Effects of Bonding and Bakeout Thermal Cycles

As indicated already in Section 1, the screening experiments were designed to simulate the effect of bonding and bakeout thermal treatments on pre- and post-irradiation microstructures, mechanical properties and electrical conductivity of CuCrZr and CuNiBe alloys. The idea was that on the basis of the results of these experiments, one of the two alloys should be then selected as a bakeup

candidate material since at that time the dispersion strengthened copper alloys were chosen to be the primary candidate materials for their use in the first wall as well as divertor components of ITER. As will be seen later, new experimental results demonstrated that the DS copper alloys have some intrinsic problems and the choice made in 1994 was not as well founded as thought at that time. The main reason for this was simply lack of sufficient experimental results.

The details of the screening experiments and the experimental results on effects of heat treatments and neutron irradiation on microstructural evolution, mechanical properties and electrical resistivity have been described and discussed in a number of reports and publications [12, 20-26]. For the screening experiments, the tensile specimens of CuCrZr and CuNiBe were given the following four different heat treatments (prior to irradiation): (i) solution annealing, (ii) prime ageing, (iii) bonding thermal treatment and (iv) bakeout thermal treatment. Details of these heat treatments are summarized in Table 2. The bonding thermal treatment for CuAl25 specimens consisted of annealing at 950°C for 30 min. (referred to as heat treatment D in Table 2). The bakeout treatment was not given to the CuAl25 specimens since it is well known that this temperature has little effect on the microstructure and properties of this alloy. All heat treatments were carried out in vacuum.

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 + reageing 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
D	Annealing at 950°C for 30 min. (only for CuAl-25)
D[1]	CuAl-25 in the as-wrought condition, i.e. without any heat treatment

The average grain size ranges from 16 – 22 μm in the CuNiBe alloy, whereas for the CuCrZr alloy the average grain size was found to be ~27 μm for the HTE and HTB conditions (Table 2), and 45 μm for the HTC condition. The grain structure in the CuCrZr specimens was fairly equiaxed with a narrow range of grain sizes. The CuNiBe, on the other hand, was characterized by a much broader size distribution of equiaxed grains, and many of the grains in all three conditions examined were found to have annealing twins. The CuAl25 has a grain size too small (<1 μm) to measure reliably using optical metallography. The precipitate, dislocations and defect clusters (loops and stacking fault tetrahedra (SFTs)) were characterized quantitatively using TEM both before and after neutron irradiation. All specimens used in these experiments were irradiated with fission neutrons in the DR-3 reactor at Risø to a fluence level of 1.5 x 10^{24} n/m^2 (E > 1 MeV), which corresponds to a displacement dose of 0.3 dpa (NRT). The neutron flux during irradiation was approximately 2.5 x 10^{17} n/m^{2}s

(E > 1 MeV) corresponding to a displacement damage rate of ~5 x 10^{-8} dpa/s. Irradiations were carried out 100, 250 and 350°C. Both irradiated and unirradiated specimens were tensile tested (in vacuum) at 100, 250 and 350°C (i.e. corresponding to irradiation temperature) in an INSTRON machine at a strain rate of 1.2 x 10^{-3}/s.

Details of experimental investigations and the main results on microstructure and tensile properties are described in specific publications for the irradiation and tensile tests at 100°C [23,25], 250°C [20,24] and 350°C [12,21]. The influence of alloy composition, heat treatments and neutron irradiations on the electrical conductivity of these alloys are described in Refs. [22] and [26]. In the following, therefore, only the salient features of the results and their implications will be highlighted and these are:

(a)   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 neutron irradiation at 100, 250 and 350°C to 0.3 dpa, even though the heat treatments did have noticeable effects on pre-irradiation properties. In other words, it is the neutron irradiation which determines the mechanical response of these alloys.

(b)   Like at 50°C [8], irradiation of CuCrZr alloy at 100°C to 0.3 dpa leads to a drastic decrease in ductility and induces flow localization and severe plastic instability immediately beyond the upper yield stress. Specimens with all heat treatments (i.e. HTA, HTB, HTE, HTC and HTC[1], see Table 2) exhibit this phenomenon. This phenomenon has been also observed in the prime aged CuCrZr alloy at the irradiation temperature of 250°C and at a dose level of 0.3 dpa [9].

In some other experiments, on the other hand, irradiation of CuCrZr alloy with HTB and HTE at 250°C to 0.3 dpa, has yielded an uniform elongation of about 4% and has shown no indication of plastic instability [20,24] when tested at 250°C. Anyhow, the fact that the CuCrZr alloy does have the potential of becoming plastically unstable after irradiation is a matter of serious concern from the point of view of its application in the structural components of a fusion reactor.

(c)   The dispersion strengthened copper alloy CuAl25 exhibits the greatest resistance to irradiation induced changes in microstructure, electrical resistivity and mechanical properties at the irradiation temperatures of 100, 250 and 350°C. However, both in the unirradiated and irradiated conditions the CuAl25 alloy show very low uniform elongation. It should be added that this alloy does not suffer from irradiation induced flow localization and plastic instability.

(d)   The CuNiBe alloy exhibits radiation hardening and a decrease in ductility due to irradiation at 100°C to 0.3 dpa. However, unlike CuCrZr alloy, CuNiBe does not show yield drop and plastic instability. In fact, it exhibits at least some uniform elongation (~3%). Nonetheless, the microstructure of this alloy has proven to be the least stable under neutron irradiation and at higher irradiation doses its performance may degrade even further. Ballistic dissolution and precipitation are thought to be responsible for the increase in strength and drop in electrical conductivity. Irradiations at 250° and 350°C, the radiation-induced dissolution of the existing precipitates and the precipitation of new precipitates become very marked and change the precipitate characteristic. In addition, the

radiation-induced precipitate dissolution may be responsible for promoting segregation of alloying and impurity elements in the CuNiBe alloy, particularly at and near the grain boundaries. This may be responsible for the observed grain boundary embrittlement. The severe loss of ductility in the CuNiBe alloy due to neutron irradiation at 250 and 350°C, regardless of the initial starting state or composition, poses a serious problem regarding its application in an intense flux of 14 MeV neutrons in ITER.

The electrical conductivity of the CuNiBe alloy is found to be very low both in the unirradiated and irradiated conditions varying between ~31 and 57% of the conductivity of pure copper [22,26]. The fact that the conductivity of the CuNiBe alloy is so low raises a serious question regarding the application of this alloy in the environment of a fusion reactor. In contrast, the conductivities of CuCrZr and CuAl25 vary between 50 – 80% and 75 – 90% of the conductivity of pure copper.

6 Low Cycle Fatigue Behaviour

The ITER design conditions require the use of high thermal conductivity materials for high heat sink applications in first wall and divertor components. Copper alloys provide the best potential to meet this requirement. The fatigue behaviour is central to materials selection since the vacuum vessel components in ITER will be subjected to thermal cycling and thus thermal-mechanical cycling loading, as a result of the cyclic plama burn operation of the system. Since very little was known about the low cycle fatigue behaviour of copper alloys selected for ITER, an experimental programme was initiated to examine the fatigue behaviour of copper and copper alloys in the unirradiated and irradiated conditions. In the present work, the low cycle fatigue behaviour of OFHC-Cu, CuCrZr (Tréfimétaux) and CuAl25 (Glid Cop) has been examined at room temperature, 100, 250 and 350°C (see Section 3 for material description). The CuCrZr was used in the prime aged condition and CuAl25 alloy was used in the wrought (as supplied) condition.

In most cases specimens were irradiated to 0.3 dpa at ~50, 100, 250 and 350°C. Fatigue tests were carried out in vacuum and at the irradiation temperature except that specimens irradiated at 50°C were tested at 22°C. Experimental details and the results of mechanical testing and microstructural investigations are described and discussed in [27-31]. It should be added that in order to facilitate a better understanding of the mechanical performance of these materials, the microstructure of the deformed specimens was investigated using TEM and the fracture surfaces were studied using SEM.

In the following only the salient features of the experimental results (reported in detail in Refs. 27-31) are briefly summarized:

(a)   First of all, it should be noted that the cyclic step tests carried out at 22°C on specimens of OFHC-copper, CuCrZr and CuAl25 alloys irradiated at ~50°C show that OFHC-copper and CuCrZr alloy suffer from a prominent yield drop whereas CuAl25 specimens do not exhibit such behaviour. This is consistent with the results of tensile tests. It is also important to note that the CuCrZr specimens irradiated at ~50°C and fatigue tested at 22°C show the evidence of the formation of "cleared channels". In other words, even under cyclic deformation the CuCrZr alloy suffers from plastic flow localization.

(b)   At all irradiation and test temperatures, the number of cycles to failure (at a given stress/strain amplitude) is found to be higher for CuAl25 than that for the CuCrZr alloy both in the unirradiated and irradiated conditions.

(c)   At the irradiation and test temperatures of 22 and 100°C, the CuAl25 exhibit a noticeable improvement in lifetime due to irradiation. At the irradiation and test temperatures of 250 and 350°C, on the other hand, the fatigue life of both alloys is reduced slightly, particularly at high strain amplitudes.

(d)   At 22 and 100°C, all unirradiated specimens deform homogeneously, whereas irradiated specimens of OFHC-copper and CuCrZr alloy deform inhomogeneously and exhibit extensive necking during fatigue experiments. The amount of necking observed in the irradiated CuAl25 specimens is very limited. This is consistent with the fact that OFHC-copper and CuCrZr alloy irradiated at these temperatures suffer from plastic instability whereas CuAl25 does not have this problem.

(e)   The observed post-fatigue microstructures indicate that the difficulty in the generation of fresh dislocations during fatigue deformation limits the scale of the fatigue damage accumulation and may be responsible for the observed improvement in the fatigue lifetime. In the case of CuAl25, the presence of alumina particles makes further contribution to this improvement by acting as strong obstacles to dislocation motion. It should be cautioned, however, that the irradiation-induced improvement in the fatigue lifetime observed in the post-irradiation tests may not occur during the service condition of ITER since the thermal/mechanical stress acting on the material may influence the damage accumulation significantly.

(f)   The fatigue life of the CuAl25 alloy shows an overwhelming dependence on the elastic response of the alloy. This is consistent with the microstructural evidence showing a lack of dislocation generation. This is why this alloy performs so well at low stress/strain amplitude and yield long lifetimes at all temperatures examined (22 – 350°C).

(g)   The fractography results suggest the surface crack nucleation. However, the crack growth follows tortuous paths through the specimens, which is likely to be controlled by the heterogeneity of the microstructure and the fine grain structure in the CuAl25 alloy. The presence of a high volume fraction of grain/subgrain boundaries and their association with alumina particles in the CuAl25 alloy is deemed to play a significant role in controlling the lifetime at 250 and 350°C.

(h)   The low cycle fatigue performance of the CuCrZr alloy appears to be controlled by its intrinsic low strength and high ductility.

(i)   All experimental results on the measured mechanical response of the CuAl25 alloy would suggest that the abundance of rather weak and unstable (mechanically as well as thermally) sub-grain boundaries present in this alloy may be an important intrinsic microstructural factor controlling the mechanical properties of this alloy. The spatial heterogeneity of the microstructure originating from the manu-facturing procedure employed in the production of this alloy is another serious factor con-

tributing to an unacceptable poor fracture behaviour of this alloy. In the case of CuAlZr alloy, on the other hand, the precipitation kinetics and the properties of the precipitates seem to determine the mechanical response of the alloy and the stability of the microstructure under neutron irradiation conditions.

7 Fracture Toughness Behaviour

The current design for ITER utilises copper alloys in the first wall and divertor structures. The function of the copper alloy in the first wall is mainly to dissipate heat produced by plasma disruptions and therefore the copper alloy is not designed to provide structural support for the first wall. However, the copper alloy for the divertor is designed for both heat dissipation and structural support of the divertor cassette. Since very little was known about the fracture toughness behaviour of copper alloys selected for ITER, an experimental programme was initiated to examine the fracture toughness of copper and copper alloys in the unirradiated and irradiated conditions. In the present work the fracture toughness behaviour of CuCrZr (Outokumpu) and CuAL25 (GlidCop) have been examined at room temperature, 200 and 350°C.

Specimens were irradiated to 0.3 dpa at 50, 200 and 350°C. Fracture toughness tests were carried out in silicon oil bath and at the irradiation temperatures except that the specimens irradiated at 50°C were tested at 22°C. Fatigue cracked single edge notched bend SEN(B) specimens were used and fracture resistance curves were determined using the displacement controlled three point bend test method with a constant displacement rate of 1.5x10^{-2} mm/min. Load, displacement and crack length were recorded during the testing. The crack length was measured using direct current potential drop DC-PD method. The fracture resistance curves were determined following the ASTM E1737-96 standard procedure. Experimental details and the results of fracture resistance testing are described and discussed in [32 - 36].

In the following only the salient features of the experimental results (reported in detail in Refs. 32 - 36) are briefly summarised:

(a)   At all irradiation and test temperatures the fracture toughness of the CuCrZr is higher than that of the CuAl25 alloy both in the unirradiated and irradiated conditions.

(b)   The fracture toughness of the unirradiated CuAl25 IG0 alloy decreases continuously with increasing temperature whereas the fracture toughness of the unirradiated CuCrZr alloy remains almost constant at temperatures up to 100°C, decreases significantly at 200°C and increases slightly at 350°C.

(c)   The CuAl25 alloy shows a marked anisotropy in fracture toughness properties. The fracture toughness along plane normal to short transverse direction is significantly lower than those along planes normal to long transverse or longitudinal directions. No such anisotropy in fracture toughness properties is observed in the CuCrZr alloy.

(d)   The fracture mode in the CuAl25 alloy changes from the ductile dimple type at ambient temperature to grain boundary type of fracture at elevated temperatures.

(e)   The fracture toughness of the CuAl25 alloy decreases markedly, by a factor of 2-3, due to neutron irradiation to the dose level of 0.3 dpa in the temperature range from 22 to 350°C. No significant effect of irradiation is observed in the fracture toughness of CuCrZr alloy at or below 200°C. However, a clear decrease in fracture toughness is observed at the irradiation and test temperature of 350°C.

8 Crack Nucleation Behaviour

Although the CuAl25 alloy was initially considered as the first candidate material for ITER the results obtained during this study clearly indicate that the loss of strain hardening capacity, the loss of uniform elongation and the marked reduction in fracture toughness are serious deficiencies in the performance of the CuAl25 alloy at elevated temperatures under neutron irradiation. Therefore fracture behaviour of CuAL25 alloy was studied in more detail by evaluating the crack nucleation and growth properties. In the present work the assessment of the crack nucleation and growth behaviour is based on the tensile test and three point bend fracture resistance test results by using notched tensile and SEN(B) specimens at room temperature and 200°C. Notched SEN(B) specimens were tested also in irradiated conditions.

Additional tests were also performed by varying the loading rate and loading mode using SEN(B) specimens in three point bend fracture resistance test. The notched tensile experiments have also been performed for CuCrZr alloy.

In the following only the salient features of the experimental results reported in detail in [37 - 40] are briefly summarised:

(a)   The effective plastic strain to fracture decrease significantly with increasing constraint ratio in tensile experiments i.e. with increasing stress state triaxiality in both CuAl25 and CuCrZr alloys.

(b)   With increasing temperature the effective plastic strain to fracture at constant constraint ratio decrease considerably in CuAl25 in contrast to CuCrZr alloy where a moderate increase is observed.

(c)   In both copper alloys fracture is ductile microvoid nucleation, growth and coalescence type of fracture although the microscopic features are prominently different.

(d)   In CuAl25 alloy the dimple size, of the order of microns, corresponding to the grain size, and the spatial distribution of the dimples are practically independent of the initial constraint level and test temperature. The primary voids nucleate along grain boundaries, pre-sumably at alumina inclusions, and only a single void population without any clear indication of microvoid sheeting is found on the fracture surface. This kind of fracture behaviour indicates that void nucleation and coalescence dominates the fracture behaviour of the CuAL25 alloy while void

growth is extremely limited due to very high density of void nuclei and subsequent coalescence even at low constraint level.

(e)   In the CuCrZr alloy primary voids nucleate at globular chromium-rich inclusions and several void populations and void sheeting are found on the fracture surface. The primary microvoids increase in size with increasing stress state triaxility i.e. constraint level in CuCrZr alloy is consistent with the ductile fracture theories where increasing stress state triaxiality enhances the void growth.

(f)   The notch sensitivity of the CuAl25 alloy is determined by crack nucleation and growth in both sharp fatigue-cracked and blunt-notched SEN(B) specimens in the unirradiated and neutron irradiated conditions. The blunt-notched specimens require higher strains prior to crack nucleation compared to the sharp fatigue-cracked specimens. Fracture surface morphology is similar in both type of specimens. These results indicate that fracture is dominated by the high density of void nuclei and their coalescence at relatively small strain values.

(g)   The strain rate sensitivity of the CuAl25 alloy is demonstrated by decreasing fracture toughness with decreasing loading rate at $200^{o}C$. The strain rate sensitivity indicate that the CuAl25 alloy is also prone to creep. Creep crack growth is indeed observed under constant load and constant displacement type of loading modes in fatigue cracked SEN(B) specimens.

(h)   Fracture toughness, notch sensitivity, strain rate sensitivity and creep crack growth behaviour of the CuAl25 alloy indicate that fracture is dominated by high density of void nuclei and their coalescence at relatively small strain values. Void growth is extremely limited and critical local strain for coalescence and subsequent crack nucleation is relatively small and readily achievable in fracture toughness and creep experiments with cracked and notched specimens.

(i)   It is suggested that the large volume fraction of grain boundaries and the presence of alumina particles on these boundaries dominate the ductile fracture behaviour of CuAl25 IG0 alloy. Ductile fracture of CuAl25 IG0 alloy is nucleation controlled where extensive void nucleation result in void coalescence at relatively low strain values. In the CuCrZr alloy, on the other hand, the ductile fracture is dominated by extensive void growth and subsequent coalescence leading to crack initiation at significantly higher strain values than that in the case of CuAl25 IG0 alloy.

9 Effect of HIPing on Tensile and Fracture Toughness Behaviour

The first wall and divertor of ITER are multilayer components consisting of austenitic stainless steel, copper alloys and plasma facing armour materials. There are several types of copper to stainless steel joints which will have to withstand the thermal and mechanical loads under neutron irradiation condition. To evaluate the structural integrity of these multilayer components, appropriate criteria are needed for the structural design and qualification of the dissimilar metal joints.

The candidate method for joining the copper alloy heat sink to the stainless steel primary wall module has been chosen to be Hot Isostatic Pressing (HIP). Firstly, the joining process itself have a direct influence on the properties of the copper alloy, secondly, practically nothing is known at present about the effect of irradiation on the tensile or fracture toughness behaviour of the copper alloys joints to stainless steel. Therefore, an experimental programme was simultaneously initiated to examine the tensile and fracture toughness behaviour of HIP joints between copper alloys and stainless steel in the unirradiated and irradiated conditions. In the present work the HIP joints between CuCrZr (Outokumpu) and CuAl25 (GlidCop) alloys and 316L(N) stainless steel have been examined at room temperature, 200 and 350°C.

The joints between copper alloys and austenitic stainless steel type 316 L(N) IG0 were produced by HIP method at 960°C for 3 hours at a pressure of 120 MPa. The HIP joint specimens of CuCrZr alloy and stainless steel were additionally heat treated at 460°C for 2 hours followed by air cooling. The multiple HIP thermal cycles were simulated by carrying out repeated heat treatment without applied pressure at 960°C for 3 hours followed by slow cooling. The CuCrZr alloy to stainless steel joints were additionally aged at 460°C for 2 hours followed by air cooling.

The experimental and irradiation conditions of the HIP joint specimens were similar to those described above for copper alloys. Experimental details and the results of mechanical testing and microstructural investigations are described and discussed in [41 – 46]. In the following only the salient features concerning the behaviour of copper alloys are briefly summarized:

(a)   The strength of the prime aged CuCrZr alloy is significantly reduced due to HIP thermal cycle with slow cooling rate of ~20°Cmin^{-1} and further reduction in strength is observed after multiple HIP thermal cycles. In contrast, the applied heat treatments has no significant effects on the tensile properties of the CuAl25 IG0 alloy.

(b)   It is noteworthy that the HIP quench cycle with fast cooling rate of <100°Cmin^{-1} offers a promising method in maintaining the strength of the CuCrZr alloy during component manufacturing cycle.

(c)   The tensile and fracture toughness behaviour of both copper alloys HIP joint specimens are fully consistent with those of the base alloys both in the unirradiated and neutron irradiated conditions.

(d)   Tensile and fracture behaviour of Cu/SS joint specimens are dominated by the properties of the copper alloys, and particularly, by the strength

mismatch and mismatch in strain hardening capacities between copper alloys and stainless steel.

(e)   The test temperature, neutron irradiation and thermal cycles related to component manufacturing or operational cycles primarily affects the Cu/SS joint properties through changing the strength mismatch between the base alloys.

10 Effects of Post-irradiation Annealing

Theoretical considerations would suggest that post-irradiation annealing at temperatures above the recovery stage V ($0.4\,T_m$ where T_m is the melting temperature) may cause a recovery of the radiation hardening and may improve ductility. This raises the possibility that in-service annealing during reactor shutdowns might alleviate the problem of yield drop and flow localization and may increase the service lifetime of the respective components made of copper alloys. It was, therefore, decided to test out this possibility experimentally. For this purpose, specimens of OFHC-copper, CuCrZr, CuNiBe and CuAl25 alloys were irradiated at $100^{o}C$ and then annealed at $300^{o}C$ for 50 hours. Experimental results have been reported in Refs. [22, 47-50].

In general, post-irradiation annealing at $300^{o}C$ for 50 h reduced the yield strength, eliminated the problem of yield drop and plastic instability and reinstated enough of uniform elongation to render the materials potentially useful again. It should be noted, however, that the recovery in the yield strength and the ductility was only partial; neither the yield stress nor the uniform elongation recovered to the level observed in the unirradiated materials. The magnitude of the recovery was found to be dose dependent.

The post-irradiation annealing led to only a slight recovery in the density of stacking fault tetrahedra (SFTs) produced during irradiation at $100^{o}C$. It was, in fact, surprising that in copper specimens irradiated to doses of 0.1 dpa and higher, the total number of vacancies contained in the SFT_s after annealing at $300^{o}C$ for 50 h was almost the same as that in the as-irradiated specimens.

Since the recovery of the yield stress due to post-irradiation annealing is rather small particularly in specimens irradiated to doses higher than 0.01 dpa, it is not certain as to whether or not the problem of yield drop and plastic instability may appear again if the annealed specimens were to be irradiated again at $100^{o}C$. This possibility needs to be investigated by carrying out repeated irradiation and post-irradiation annealing experiments.

11 Comparison of Tréfimétaux and Hycon 3HP CuNiBe Alloys

The precipitation hardened CuNiBe alloys are among the three candidate alloys that have been evaluated for application in the first wall and divertor components of ITER. In the present work we have investigated the physical and mechanical properties of the Hycon 3HP[TM] alloy both before and after neutron irradiation at different temperatures and have compared its microstructure and

properties with those of the European CuNiBe candidate alloy manufactured by Tréfimétaux. The main results are reported in Ref. 51.

The experimental results led to the following conclusions:

(a)   Irradiation changes the microstructure and solute distribution in both alloys.

(b)   Irradiation increases the susceptibility to embrittlement when tested above 250°C, while the large increases in strength that occurs when irradiated and tested at 100°C suggest that irradiation-induced redistribution of the solute atoms is occurring, possibly forming very small precipitates that have not yet been observed in TEM.

(c)   The evidence provided in Ref. [51] suggests that more than one mechanisms (e.g. solute segregation to the grain boundaries and oxygen absorption) may be responsible for the embrittlement that occurs at temperatures above 200°C.

(d)   The Tréfimétaux alloy may simply require different thermo-mechanical processing to improve its overall behaviour, but at present the Hycon alloy appears to be the best one for lower temperature applications, especially considering its higher electrical conductivity and higher strength. At present, it seems unlikely that CuNiBe alloys can be recommended for applications in neutron environment where the irradiation temperature is likely to exceed 200°C. Applications at temperatures below 200°C <u>might</u> be plausible, but only after careful determination of the dose dependence of the mechanical properties including crack nucleation and fracture toughness behaviour of the alloy. The effect of a sudden temperature excursion on mechanical properties will have to be evaluated in order to establish the limits on the use of the CuNiBe alloy.

12 Concluding Remarks

First of all, it should be recognized that in spite of a considerable amount of effort made over a period of 5 – 6 years, we have managed only to identify some of the crucial problems and limitations of the copper alloys for their application in the environment of an intense flux of energetic neutrons. The solution of these problems still remains only tentative and needs a considerable amount of effort not only in the field of characterization of properties but also in the fields of materials development and thermomechanical processing technologies.

From the point of view of application of copper alloys in ITER and the effect of neutron irradiation on mechanical performance of these alloys, the most serious problem turns out to be almost a complete loss of ductility and the initiation of plastic flow localization immediately beyond the upper yield stress due to neutron irradiation at temperatures below 0.4 T_m (i.e. ~270°C for copper). This phenomenon begins to dominate the deformation behaviour at irradiation doses above 0.1 dpa. It should be pointed out that the CuCrZr alloy suffers rather seriously from this problem. It should be noted, however, that this conclusion is based on the results of post-irradiation tests and may not be valid for the dynamic condition in ITER where the component will experience the stress, temperature and irradiation simultaneously. Because the irradiation produced defect

clusters and the stress-generated dislocations are likely to interact, the damage accumulation and hence the materials mechanical performance under dynamic conditions may not be the same as that observed in the post-irradiation tests.

Because of the high sink density in the copper alloys and the rather low operational temperature of ITER, the problem of void swelling is unlikely to be a major issue for the application of copper alloys.

Ballistic dissolution of precipitates and irradiation-induced segregation and precipitation at grain boundaries during irradiation with neutrons is a serious problem in the CuNiBe alloy. In fact, this is the main reason as to why this alloy is considered to be unsuitable for ITER application.

The dispersion strengthened CuAl25 is very resistant to irradiation effects and does not suffer from irradiation-induced plastic instability. However, this material has very low fracture toughness even in the unirradiated condition and is extremely susceptible to crack nucleation and growth. This may be the main reason for the lack of uniform elongation and work hardening ability observed during tensile test of the CuAl25 alloy even in the unirradiated condition. The origin of this weakness seems to lie in the initial microstructure of this alloy. The initial microstructure is extremely heterogeneous and contains a large volume fraction of rather weak and unstable (mechanically as well as thermally) sub-grain boundaries. Furthermore, the spatial distribution of the concentration of alumina particles is also very heterogeneous. The main source of these heterogeneities lies in the manufacturing process. It seems very unlikely, therefore, that this material could be improved substantially without making some radical changes in the manufacturing technology. In its present state, on the other hand, it is very difficult to see how this material (i.e. CuAl25) can be safely employed in structural components of ITER.

The low cycle fatigue life of CuAl25 and CuCrZr alloy is not affected by irradiation in any significant way at temperatures up to 250°C and particularly at low strain range values. It should be noted that these results refer to post-irradiation tests and may not necessarily represent the response of these materials in dynamic in-reactor conditions. This may be particularly relevant in the case of CuCrZr alloy where the ballistic dissolution, precipitation and radiation-induced segregation may affect dislocation mobility the degree of which may depend on the displacement dose level. These effects can be monitored only in the dynamic, in-reactor experiments.

Finally, it should be pointed out that the present series of experiments have clearly demonstrated that in order to select a material for a specific application, it is necessary to perform a variety of complimentary tests so that different facets of the materials response could be identified and understood. Only after such a combination the overall and global behaviour of the material could be reliably predicted. In the present work, for example, based only on tensile results both CuNiBe and CuAl25 alloys were found to be very promising. However, the results of other complimentary investigations led us to opposite conclusions.

Acknowledgements

References

[1]   ITER Joint Central Team, J. Nucl. Mater. <u>212</u> – <u>215</u> (1994) 3.

[2]   J.W. Davies, D.E. Driemeyer, J.R. Haines and R.T. McGrath, J. Nucl. Mater. <u>212</u> – <u>215</u> (1994) 1353.

[3]   S.J. Zinkle, A. Horsewell, B.N. Singh and W.F. Sommer, J. Nucl. Mater. <u>195</u> (1992) 11.

[4]   D.J. Edwards, F.A. Garner, J.W. Newkirk and A. Nadkarni, J. Nucl. Mater. <u>212</u> – <u>215</u> (1994) 1313.

[5]   S.J. Zinkle, E.V. Nesterova, V.R. Barabash, V.V. Rybin and A.V. Naberenkov, J. Nucl. Mater. <u>208</u> (1994) 119.

[6]   B.N. Singh, D.J. Edwards, A. Horsewell and P. Toft, Risø Report No. Risø-R-839 (EN), September (1995) pp. 34.

[7]   B.N. Singh, A. Horsewell, P. Toft and D.J. Edwards, J. Nucl. Mater. <u>224</u> (1995) 131.

[8]   B.N. Singh, D.J. Edwards and P. Toft, J. Nucl. Mater. <u>238</u> (1996) 244.

[9]   B.N. Singh, Risø-R-996 (EN), April 1998, pp. 32.

[10]   B.N. Singh and S.J. Zinkle, J. Nucl. Mater. <u>206</u> (1993) 212.

[11]   B.N. Singh, D.J. Edwards, M. Eldrup and P. Toft, Risø-R-1049 (EN), July 2000, pp. 31.

[12]   B.N. Singh, D.J. Edwards, M. Eldrup and P. Toft, J. Nucl. Mater. <u>295</u> (2001) 1.

[13]   H. Trinkaus, B.N. Singh and A.J.E. Foreman, J. Nucl. Mater. <u>249</u> (1997) 91.

[14]   H. Trinkaus, B.N. Singh and A.J.E. Foreman, J. Nucl. Mater. <u>251</u> (1997) 172.

[15]   B.N. Singh, A.J.E. Foreman and H. Trinkaus, J. Nucl. Mater. <u>249</u> (1997) 103.

[16]   N.M. Ghoniem, S.-H. Tong, B.N. Singh and L.Z. Sun, Phil. Mag. <u>A81</u> (2001) 1743.

[17]   Yu. N. Osetsky, D.J. Bacon, F. Gao, A. Serra and B.N. Singh, J. Nucl. Mater. <u>283</u> – <u>287</u> (2000) 784.

[18]   Yu. N. Osetsky, D.J. Bacon, A. Serra and B.N. Singh, MRS Symp. Proc. <u>653</u> (2001) Z3.4.

[19]   N.M. Ghoniem, S.H. Tong, J. Huang, B.N. Singh and M. Wen, in: Proc. ICFRM-10, Baden-Baden, October 2001, to appear in J. Nucl. Mater.

[20]   B.N. Singh, D.J. Edwards, M. Eldrup and P. Toft, Risø-R-937 (EN), January 1997, p. 55.

[21]   B.N. Singh, D.J. Edwards, M. Eldrup and P. Toft, Risø-R-971 (EN), February 1997, pp. 44.

[22]   Eldrup and B.N. Singh, Risø-R-1007 (EN), January 1998, pp. 22.

[23]   B.N. Singh, D.J. Edwards, M. Eldrup and P. Toft, Risø-R-1008 (EN), May 1998, pp. 35.

[24]   B.N. Singh, D.J. Edwards, M. Eldrup and P. Toft, J. Nucl. Mater. <u>249</u> (1997) 1.

[25]   D.J. Edwards, B.N. Singh, M. Eldrup and P. Toft, J. Nucl. Mater. <u>258</u> – <u>263</u> (1998) 978.

[26]   M. Eldrup and B.N. Singh, J. Nucl. Mater. <u>258</u> – <u>263</u> (1998) 1022.

[27]   K.D. Leady, J.F. Stubbins, B.N. Singh and F.A. Garner, J. Nucl. Mater. <u>233</u> – <u>237</u> (1996) 547.

[28]   B.N. Singh, J.F. Stubbins and P. Toft, Risø-R-991 (EN), May 1997, pp. 42.

[29]   B.N. Singh, J.F. Stubbins and P. Toft, J. Nucl. Mater. 275 (1999) 125.

[30]   B.N. Singh, J.F. Stubbins and P. Toft, Risø-R-1128 (EN), March 2000, pp. 55.

[31]   B.N. Singh, J.F. Stubbins and P. Toft, in: Proc. International Symposium on Materials Ageing and Life Management, October 3-6, 2000, Kalpakkam, India, Eds. B. Raj, K. Bhanu Sankara Rao, T. Jayakumar and P.K. Dayal, Allied Publishers Limited, New Delhi, vol. 2 (2000) 862.

[32]   S. Tähtinen, M. Pyykkönen, P. Moilanen, B.N. Singh and P. Toft, VTT Manufacturing Technology Report VALB 282, 1998, pp. 22.

[33]   S. Tähtinen, M. Pyykkönen, P. Karjalainen-Roikonen, B.N. Singh and P. Toft, J. Nucl. Mater. 258 – 263 (1998) 1010.

[34]   S. Tähtinen, M. Pyykkönen, B.N. Singh and P. Toft, in: "Effects of Radiation and Materials; 19th International Symposium", ASTM STP 1366 (2000) 1241.

[35]   S. Tähtinen and B.N. Singh, in: Proc. International Symposium on Materials Ageing and Life Management (Eds. B. Raj, K.B. Sankara Rao, T. Jayakumar and R.K. Dayal), Allied Publishers Ltd., New Delhi, vol. 3 (2000) 1080.

[36]   S. Tähtinen and A. Laukkanen, VTT Manufacturing Technology, Report VALB 369 (1999), pp. 17.

[37]   A. Laukkanen and S. Tähtinen, VTT Manufacturing Technology, Report VALB 377 (2000), pp. 19.

[38]   S. Tähtinen and A. Laukkanen, VTT Manufacturing Technology, Report VALB 433 (2000), pp. 20.

[39]   S. Tähtinen and A. Laukkanen and B.N. Singh, J. Nucl. Mater. 283 – 287 (2000) 1028.

[40]   S. Tähtinen and A. Laukkanen, VTT Manufacturing Technology, Report BVAL 64 – 001081 (2001), to be published.

[41]   M. Pyykkönen, S. Tähtinen, B.N. Singh and P. Tof, in: Proc. "20th Symposium on Fusion Technology" (Eds. B. Beaumont, P. Libeyre, B. de Gentile and G. Tonon), CEA Cadarache, Cedex, vol. 1 (1998) 173.

[42]   S. Tähtinen and B.N. Singh, VTT Manufacturing Technology Report BVAL 62 – 001030 (2000), pp. 14.

[43]   S. Tähtinen and B.N. Singh, VTT Manufacturing Technology Report BVAL 62 – 001062 (2000), pp. 12.

[44]   A. Laukkanen and S. Tähtinen, VTT Manufacturing Technology Report BVAL 64 – 011132 (2001), pp. 26.

[45]   S. Tähtinen, A. Laukkanen and B.N. Singh, Fusion Eng. Design 55 – 56 (2001) 391.

[46]   S. Tähtinen, A. Laukkanen and B.N. Singh to appear in the Proc. ICFRM-10 (Baden.-Baden, Oct, 14 - 19, 2001), J. Nucl. Maters (to be published).

[47]   B.N. Singh and P. Toft, Risø-R-1009 (EN), April 1998, pp. 20.

[48]   B.N. Singh, D.J. Edwards and P. Toft, Risø-R-1213 (EN). February 2001, pp. 30.

[49]   B.N. Singh, D.J. Edwards and P. Toft, J. Nucl. Mater. 299, (2001) 205.

[50]   D.J. Edwards, B.N. Singh, Q. Xu and P. Toft in: Proc. ICFRM-10, J. Nucl. Mater., to be published.

[51]   B.N. Singh, D.J. Edwards, M. Eldrup and P. Toft, Risø-R-1049 (EN), July 2000, pp. 31.

Abstract (max. 2000 characters)

The present report summarizes and highlights the main results of the work carried out during the last 5 – 6 years on effects of neutron irradiation on physical and mechanical properties of copper and copper alloys. The work was an European contribution to ITER Research and Development programme and was carried out by the Associations Euratom - Risø and Euratom - Tekes.

Details of the investigations carried out within the framework of the present task and the main results have been reported in various reports and journal publications. On the basis of these results some conclusions are drawn regarding the suitability of a copper alloy for its use in the first wall and divertor components of ITER. It is pointed out that the present work has managed only to identify some of the critical problems and limitations of the copper alloys for their employment in the hostile environment of 14 MeV neutrons. A considerable amount of further effort is needed to find a realistic and optimum solution.

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