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The effect of transmutation and displacement in irradiated copper for heat-sink materials

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Abstract

High-energy neutron irradiation on copper alloys will cause atomic displacements and nuclear transmutation, which will lead to degradation of thermal conductivity and mechanical properties. To study the synergistic effects, we have utilized Cu–Ni–Zn alloys to simulate the effect of transmutation. Thermal conductivity of these alloys has been derived from electrical resistivity measurements between 298 and 770 K. These alloys were also irradiated with 2.4 MeV copper self ions at room temperature and the mechanical properties were evaluated from micro-hardness measurements. The resistivity of the copper alloys depends linearly on nickel concentration. However, the effect of zinc is complex and may be less prominent than the nickel effect. It is suspected that dezincification has taken place. The change in micro-hardness shows saturation at a displacement dose of around 0.5 dpa. There is a slight influence of alloying elements, particularly zinc, on the fluence dependence of hardness change. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

High strength high conductivity copper alloys will be used for heat sink materials in high heat flux components in fusion reactors. For example, in the case of ITER, a dispersion-strengthened (DS) copper alloy like GlidCop Al25 will be used for the limiter and primary wall and a precipitation-hardening (PH) alloy like CuCrZr for the divertor [1,2]. High-energy neutron irradiation of these materials will cause atomic displacements and nuclear transmutation, which will lead to the degradation of thermal conductivity and mechanical properties of the materials. So far, the effects of displacement damage on swelling and mechanical properties have been examined, while less attention has been paid to the effect of nuclear transmutation. In both DS and PH copper alloys, the matrix is relatively free from substitutional solute before irradiation to ensure high thermal conductivity. However, even pure copper will be transformed into a Cu–Ni–Zn alloy by nuclear transmutation during fusion neutron irradiation [3]. If the heat sink materials are used for a long time, then the amount of solid nuclear transmutants will become high enough that their effects on thermal conductivity and mechanical properties cannot be ignored.

Obviously, the effect of transmutation and atomic displacement in a fusion reactor environment must be examined synergistically but it is very difficult without having an intense fusion neutron source such as IFMIF. There have been a few studies of the synergistic effect in copper with fission neutron irradiation [4–6] but in some cases, the irradiation temperatures are not fusion relevant and the experimental results are still limited. Difficult problems come from the interplay between radiation-induced defects and nuclear transmutations. It has often been assumed that property changes induced by radiation damage and nuclear transmutation are additive. Whether or not this is actually the case must be verified by experiment. In the present study, we apply ion irradiation to differentiate the effects of radiation damage and transmutation in copper. We have utilized Cu–Ni–Zn alloys to simulate the effect of transmutation.

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2. Experimental

2.1. Specimen

The amount of solid transmutation product has been calculated for various irradiation environments [3,7,8]. For the STARFIRE first wall (3.6 MW/m^2), about 5.4% Ni, 2.4% Zn and 0.3% Co are produced in pure copper after five years of operation [3]. This may be the extreme case for copper as a heat sink material. Several model alloys to simulate the nuclear transmutation effects were prepared within this concentration range. Cobalt is not added because the amount produced is small.

The alloys were prepared by double melting in an arc melting furnace with a water-cooled copper crucible in pure argon atmosphere. A high purity Cu–40%Zn mother alloy was used to introduce zinc. However, it was very difficult to control the amount of zinc because of its high vapor pressure even though the molten bath temperature was held as low as possible. The ingots were shaped and cold rolled to a thickness of 0.1 mm.

Specimens were cut from the strip, annealed at 800°C for 1 h in vacuum for specimens for electrical resistivity measurements and in an argon atmosphere for hardness measurements and then both were electropolished.

2.2. Hardness measurements

Specimens for micro-hardness measurements were either 10-mm square or 4 mm × 13 mm and 0.1-mm thick. Either a nano-indenter (Shimadzu DUH-201 type) or a dynamic micro-hardness tester (Elionix ENT-1100s) was used for hardness measurements with a method of analysis described in Ref. [9].

It has been confirmed that hardness values derived from the two kinds of equipment are consistent with each other within experimental error.

2.3. Electrical resistivity measurement

An ordinary four-point probe technique was used for electrical resistivity measurements. Specimens were in a complex shape, 1-mm wide and 0.1-mm thick with an effective length between potential leads of 73.0 mm. The error mostly coming from a geometrical shape factor was estimated to be about 5%. A Keithley Model 224 constant current source and a Keithley Model 2001 digital multimeter for low-voltage measurements were used. To eliminate stray voltage arising from contact potential and thermoelectromotive force at any junction on the circuit, the polarity of the current was reversed for each set of measurement.

The resistivity was measured between 25°C and 500°C. In the present paper, only results obtained before irradiation will be reported.

2.4. Ion irradiation

2.4-MeV Cu^{2+} ions from a 1MV Tandetron ion accelerator at the Research Institute for Applied Mechanics, Kyushu University were irradiated at room temperature. By utilizing appropriate masking plates with a beam aperture 2 mm in diameter, 5 and 45 dpa regions were produced in the square-shaped specimens and 0.05, 0.5 and 5 dpa regions were produced in the rectangular-shaped specimens. Here, dpa values were at the peak in the damage distribution, which was calculated by the TRIM code.

3. Experimental results

3.1. Temperature dependence of electrical resistivity and thermal conductivity due to solid transmutants

Fig. 1 shows temperature dependence of electrical resistivity of pure copper, Cu–3Ni, Cu–6Ni, and Cu–6Ni–3Zn (nominal) specimens. Values for pure copper are in excellent agreement with published data [10]. The nickel dependence of resistivity is shown in Fig. 2. There is a slight temperature dependence of the nickel contribution to the resistivity. The values are 9.7 ± 1.0 nΩ m/at.% Ni at 25°C and 8.3 ± 0.8 nΩ m/at.% Ni at 500°C, being slightly smaller than the published values [11,12].

The zinc contribution to the resistivity could not be determined. Two of the zinc-containing specimens were measured, but the Cu–3Zn (nominal) specimen showed almost the same resistivity as pure copper. This is consistent with results of chemical analysis that showed that zinc was not contained in the specimen. Cu–6Ni–3Zn (nominal) specimen also showed a trace amount of zinc,

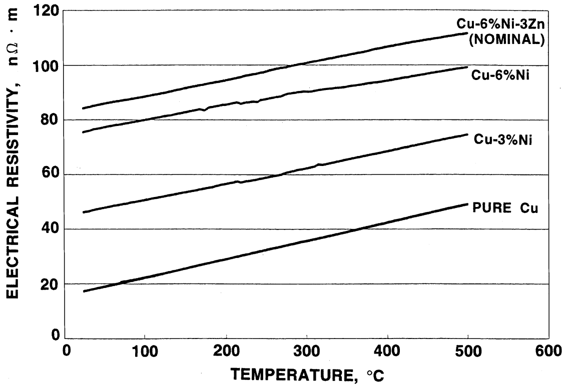

Fig. 1. Temperature dependence of electrical resistivity of pure copper, Cu–3Ni, Cu–6Ni, and Cu–6Ni–3Zn (nominal) alloys. Zn concentration determined by surface chemical analysis in Cu–6Ni–3Zn alloy was almost trace amount. The Ni contents are confirmed to be the same as aimed.

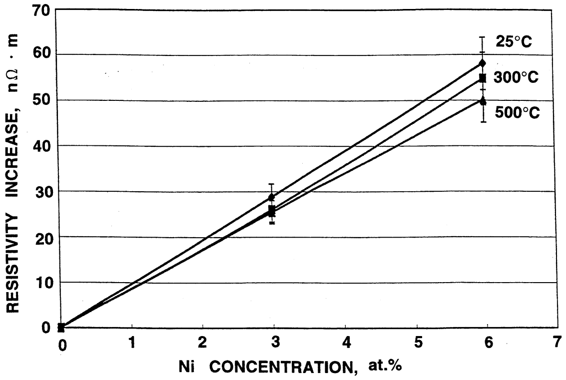

Fig. 2. Nickel concentration dependence of resistivity at different temperatures.

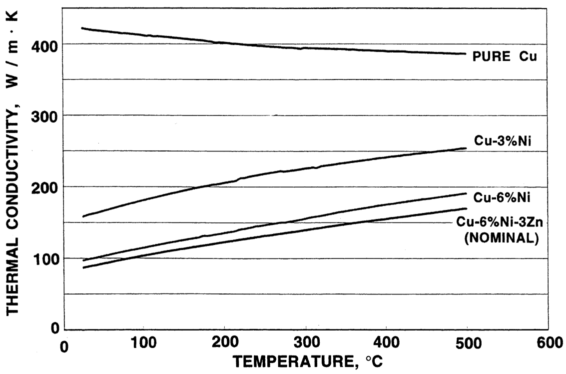

Fig. 3. Thermal conductivity of pure copper, Cu–3Ni, Cu–6Ni, and Cu–6Ni–3Zn (nominal) alloys calculated from the data of Fig. 1.

but the resistivity showed an extra contribution compared to the Cu–6Ni specimen. Because the analysis was made by X-ray micro-analysis, the value might be for the surface region of the specimen, where dezincification had occurred during vacuum annealing at 800°C. If 3 nΩ m/at.%Zn is assumed, the zinc concentration in Cu–6Ni–3Zn (nominal) is estimated to be 2.6%.

For metals having high thermal conductivity like copper and copper alloys, the major part of the thermal conductivity is governed by electronic conductivity. Electronic thermal conductivity, κ_e and electronic resistivity, $\rho = \sigma^{-1}$ are related by Wiedemann–Franz law [13]. Fig. 3 is the thermal conductivity calculated from the data of Fig. 1.

3.2. Micro-hardness measurements

The hardness data before and after ion irradiation for copper and several copper alloys are shown in Fig. 4 as a function of dpa and Zn concentration. The Cu–6Ni–3Zn (nominal) alloy is from the same lot as that used for resistivity measurements described above and has hardness similar to the Cu–6Ni alloy. Again it is probable that zinc is eliminated from the surface region in this specimen. It should be noted that the damage peak for 2.4-MeV Cu ions is located 0.75 μm from the surface.

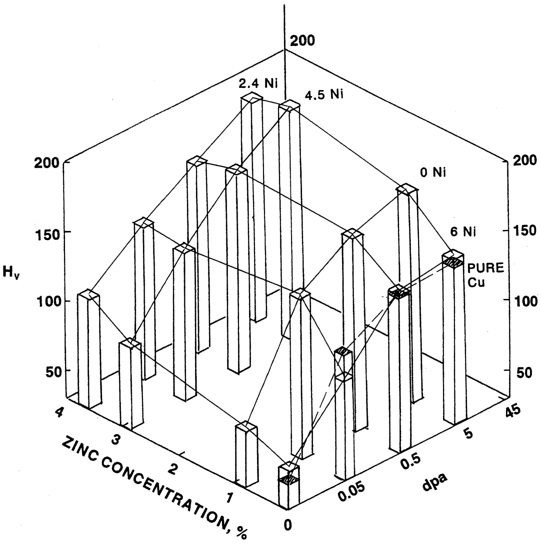

Fig. 4. The change in hardness as a function of dpa and Zn concentration. Dpa values are represented by those at the damage peak for 2.4 MeV Cu ion irradiation.

A similar plot as a function of Ni concentration does not show a systematic trend. From Fig. 4, it is shown that hardness in the unirradiated state depends clearly on zinc concentration. It is also observed that irradiation hardening almost saturates at the fluence level of 0.5 dpa for pure copper, whereas with increasing zinc concentration-hardening saturation seems to be delayed to a higher fluence.

4. Discussion

4.1. Electrical resistivity and thermal conductivity due to solid transmutants

It is interesting to see whether the effect of nuclear transmutants on resistivity change is linear or not. Since we do not have reliable chemical analysis for zinc in the electrical resistivity specimens, we cannot have a clearcut conclusion. However, as far as unirradiated conditions are concerned, the temperature dependence of resistivity obeys Matthiessen's rule, indicating that the nickel component and zinc component of resistivity are linearly dependent on their concentration.

For pure copper specimens irradiated in the SM-2 reactor at 100°C, Fabritsiev et al. [14] have reported that the radiation damage component saturates at an early stage of irradiation. The total resistivity change is expressed by the sum of the transmutant components, which increase linearly with thermal neutron fluence, and the radiation damage component, which is almost constant after the early stage of irradiation. They also have shown a steady decrease of resistivity change with increasing irradiation temperature at a fluence level of 3.5–5 dpa, eventually becoming even lower than the estimated transmutant component for irradiation temperatures above 250°C [14]. This clearly shows the presence of solute segregation at point defect sinks, as has been demonstrated by electron microscopy observations [5,15]. Non-linear effects should exist between displacement and nuclear transmutation at least at high irradiation temperatures, typically above 250°C.

4.2. Change in hardness due to solid transmutants and displacement damage

As seen in Fig. 4, the hardness before irradiation does not strongly depend on nickel concentration, whereas it clearly depends on zinc concentration. Since the atomic radius of nickel (0.125 nm) is not much different from that of copper (0.128 nm), the Cu–Ni binary system forms a solid solution over the entire concentration range. The solution hardening due to nickel addition may not be large. On the other hand, zinc is an oversized solute atom (0.137 nm) in the copper matrix. It has also been known that zinc will interact with extended dislocations by a chemical interaction known as the Suzuki effect [16]. Hence, the clear dependence of zinc concentration on hardness is expected.

The change in hardness by irradiation shows additional effects of nickel and zinc. Pure copper and Cu–Ni alloys show a steeper rate of increase of hardness, which seems to saturate at a fluence level of ~0.5 dpa. On the other hand, in the specimens containing zinc, the rate of increase of hardness seems to be slower. Naberenkov and Fabritsiev [17] have reported that in copper and several copper alloys neutron irradiated at ~80°C, the increase in yield stress is larger in the specimens with lower unirradiated yield stress. Since nickel is an undersized solute in the copper matrix, it is expected that nickel forms a mixed dumbbell interstitial and migrates with the interstitial. Edwards et al. [18] have pointed out that nickel atoms form clusters which promote nucleation of interstitial loops. Muroga et al. [19] have also pointed out that in cascade-forming heavy particle irradiations, vacancy clusters are easily formed in the case of pure copper. This reduces the chance of vacancy-interstitial recombination, thus promoting interstitial loop formation.

On the other hand, since zinc atoms have a considerably larger atomic size than that of copper, a large interaction with vacancies is expected. If this is the case, vacancy mobility will be retarded and micro-structural evolution might become sluggish. Muroga et al. [19] have also shown that in Cu–3.5%Zn alloy, the swelling peak shifts to higher temperature than that in pure copper and Cu–Ni alloy. Depletion of zinc from grain boundaries during irradiation [8] also gives support to the presence of a Zn-vacancy interaction.

4.3. Some remarks on synergistic effects

Though we have not succeeded in extracting synergistic effects of displacement and transmutation, several sets of fission neutron irradiation data have suggested the presence of an interplay between transmutants and irradiation-induced defects, particularly for higher irradiation temperatures. A radiation-induced component of resistivity seems to saturate at a rather early stage of irradiation [14]. Assuming that the electrical resistivity change can be expressed by a linear combination of nickel, zinc and defect contributions, Fabritsiev et al. [14] have derived expressions for each component, the first two components being proportional to thermal fluence and the defect component being constant at about 1.2 nΩ m for both pure copper and DS copper alloy irradiated at ~100°C. This is ascribed mainly to stacking fault tetrahedra and dislocation loops [20]. In another publication, irradiation of oxygen free high conductivity copper to 0.3 dpa at 100°C resulted in a resistivity increase of about 2 nΩ m [21]. In this case, the thermal neutron fluence was $4.2 \times 10^{24}\ \mathrm{m}^{-2}$, and the transmutant contribution was estimated to be ~1.5 nΩ m. This seems to show that for relatively low dose irradiation in fission reactors, the transmutation component may not be neglected and that comprehensive studies with important variables such as neutron spectrum, fluence and irradiation temperature are required.

4.4. Some remarks on dezincification

Since the vapor pressure of zinc is very high, dezincification might occur if the copper or copper alloys are exposed to high vacuum. Preliminary experiments in some Cu–Zn alloys by gravimetry after heating at high temperatures have shown that weight loss starts to occur at about 500°C for Cu–40%Zn [22]. It may be concluded that the amount of dezincification is meager within the expected temperature range below 300°C. However, if temperature goes beyond 500°C in an off-normal transient, zinc might be released.

5. Summary and conclusions

Model copper alloys to simulate nuclear transmutation were prepared, and electrical resistivity was measured in the temperature range from 25°C to 500°C. The specimens were also irradiated with 2.4-MeV Cu^{2+} ions at room temperature to 45 dpa and micro-hardness was measured.

The results are summarized as follows:

1. In Cu–Ni binary alloys, the resistivity increase is proportional to nickel concentration. The nickel contribution to the resistivity depends slightly on temperature, being 9.7 ± 1.0 nΩ m/at.%Ni at 25°C and 8.3 ± 0.8 nΩ m/at.%Ni at 500°C.
2. Zinc was largely eliminated during preparation by arc melting. Also there is evidence that during annealing at 800°C in vacuum, zinc might have been lost from the surface region of the specimen. If this is the case, assuming published value for the resistivity contribution of ~3 nΩ m/at.%Zn [11] seems to explain both the resistivity and hardness changes.
3. Micro-hardness changes by Cu ion irradiation saturate at a relatively low fluence of about 0.5 dpa at the damage peak.
4. Before irradiation, hardness does not depend on nickel addition but it does depend on zinc concentration.
5. The rate of change of hardness is larger in copper and Cu–Ni alloys but the hardness increase is sluggish in Zn-containing alloys.
6. The presence of transmutants Ni and Zn affects changes in hardness by irradiation. Interaction of these solute elements with point defects can account for the observed changes.
7. Dezincification may not be significant except in extreme cases of temperature excursion exceeding 500°C during off-normal conditions.

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