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RESPONSE OF SOLUTE AND PRECIPITATION-STRENGTHENED COPPER ALLOYS AT HIGH NEUTRON EXPOSURE

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ABSTRACT

A variety of solute and precipitation strengthened copper base alloys have been irradiated to neutron-induced displacement levels of 34 to 150 dpa at 415°C and 32 dpa at 529°C in the Fast Flux Test Facility to assess their potential for high heat flux applications in fusion reactors. Several MZC-type alloys appear to offer the most promise for further study. For low fluence applications CuBeNi and spinodally strengthened CuNiTi alloys may also be suitable. Although Cu-2Be resists swelling, it is not recommended for fusion reactor applications because of its low conductivity.

1. Introduction

Copper-based alloys have been suggested as candidates for fusion applications as first wall, limiter and diverter components, with the latter application of most current interest [1]. The attractiveness of copper arises primarily from its very high thermal conductivity compared to stainless steel, allowing it to serve in high heat flux applications with reduced levels of thermal fatigue. Until recently, however, there have been little data available on the response of copper alloys to radiation at levels greater than 1 dpa. This paper outlines the major conclusions of a series of studies conducted at 411-430°C to doses as large as 150 dpa and at 539°C to 32 dpa.

These studies were conducted in the Fast Flux Test Facility (FFTF) employing controlled temperature (±5°C) irradiation in the Materials Open Test Assembly (MOTA). The experimental program involved three generations of irradiations, with the third generation currently in reactor. The first generation experiment (Generation 1) was exploratory in nature and was completed after reaching 1.6 x 10^{27} n m^{-2}, which corresponds to ~98 dpa for pure copper in FFTF.

Earlier publications described the results of this experiment at damage levels of 16, 47, 63 and 98 dpa [2-6]. The results of this experiment led to the initiation of the Generation 2 experiment where various copper alloys were irradiated to 34, 50, 104, and 150 dpa at 411-430°C. Generation 2 also included specimens of some alloys irradiated to 32 dpa at 529°C. These experiments focused on the alloy classes that exhibited promise in the Generation 1 experiment. This paper describes the results at the two higher fluence levels for all alloys except the oxide dispersion strengthened alloys, which are presented in a companion paper [7]. Data for the lower fluence two levels were presented in earlier papers [8-10] and are also included in this paper.

2. Experimental Details

Table 1 lists the compositions and heat treatments for the various classes of alloys examined in this study. Alloys in the first class are referred to as MZC alloys containing additions of Cr, Zr, and in some cases, Mg. Additions of Cr and Zr form precipitating phases that strengthen the matrix while magnesium acts as an oxygen scavenger to protect the zirconium additions [11]. The AMAX MZC alloy was produced by AMAX Base Metals Research and Development, Inc.

TABLE 1 Description of Generation 1.5 and 2.0 Copper Alloys

ALLOY	Composition (wt%)	Condition
MZC alloys		
AMAX HTA[a]	Cu-0.9Cr-0.1Zr-0.05Mg	90% CW[b], A[b]: 475°C/0.5 hr/AC[b]
AMAX HTB[a]	Cu-0.9Cr-0.1Zr-0.05Mg	90% CW, A: 500°C/1 hr/AC
MIT #2	Cu-0.6Cr-0.13Zr-0.05Mg	75% CW, A: 500°C/1 hr/AC
MIT #3	Cu-0.5Cr-0.5Zr-0.05Mg	SA[b]: 950°C/1 hr/WQ[b], A: 500°C/1 hr/AC
JRC	Cu-0.65Cr-0.08Zr	SA: 1000°C, 44% CW, A: 460°C
Be-containing alloys		
CuBe HTA	Cu-1.96Be	SA: 765°C/1 hr/WQ, 20% CW, A: 320°C/3 hrs/AC
CuBe HTB	Cu-1.96Be	SA: 765°C/1 hr/WQ, A: 320°C/3 hrs/AC
CuNiBe HTA	Cu-1.8Ni-0.3Be	SA: 900°C/1 hr/WQ, 20% CW, A: 482°C/3 hr/AC
CuNiBe HTB	Cu-1.8Ni-0.3Be	SA: 955°C/30 min/WQ, A: 482°C/3 hr/AC
CuNiBe HTC[a]	Cu-1.8Ni-0.3Be	SA: 900°C/1 hr/AC, 20% CW
Spinodal CuNiTi alloys		
MIT	Cu-5.0Ni-2.1Ti + 0.8% TiO_2 + 0.22% Zr	SA 950°C/20 min/WQ, A: 500°C/1 hr/AC
AMAX	Cu-5.0Ni-2.5Ti	SA 900°C/1 hr/WQ, A: 525°C/1 hr/AC
Reference Material		
MARZ Cu	99.999% pure Cu	Annealed: 450°C/15 min/AC

[a] HTA = heat treatment A
HTB = heat treatment B
HTC = heat treatment C

[b] CW = cold work
A = age
SA = solution annealed
AC = air cooled
WQ = water quenched

The two MIT alloys were supplied by N. J. Grant of the Massachusetts Institute of Technology (MIT). The fourth MZC-type alloy, CuCrZr, was supplied by G. Piatti of the Joint Research Center (JRC) in Italy. It is included here as an MZC-type alloy although it contains no magnesium. The AMAX-MZC alloy, the MIT #2 MZC alloy, and the JRC CuCrZr alloy were processed using conventional ingot metallurgy practices. The MIT #3 MZC alloy was produced using rapid solidification powder metallurgy (RSPM) techniques that introduced a small volume fraction of ZrO_2 and Cr_2O_3 particles arising from surface oxidation of the RS particles.

The second class of alloys consists of a high strength Cu-2Be alloy and a high conductivity CuNiBe alloy. The high nickel content and lower beryllium content of the latter yield moderate electrical conductivities (50 to 60% IACS) yet allow relatively high strengths to be obtained [12].

The third class of alloys are spinodally strengthened CuNiTi alloys. These alloys are of interest because they are easily heat treated to high strengths and are not as susceptible to overaging as are most precipitation strengthened alloys[13]. The high strength and phase stability, however, are obtained at the expense of the electrical and thermal conductivity. The MIT CuNiTi alloy, also obtained from N. J. Grant, is a RSPM product incorporating Zr and a TiO_2 dispersion to provide additional strengthening, the former acting as a precipitate phase[13]. The AMAX CuNiTi alloy was provided by R. Livak of Los Alamos National Laboratory as rolled sheet.

Pure copper (MARZ grade) was included in all irradiations as a standard reference material. Changes in density, electrical conductivity and tensile properties were measured using either transmission electron microscopy (TEM) disks or miniature tensile specimens. Electrical conductivity is more easily measured than thermal conductivity on these highly radioactive specimens and can be used to estimate changes in thermal conductivity. The techniques employed in making these measurements are described in detail elsewhere [8,13]. All measurements at 411-414°C have been completed. Data acquisition and analysis are still in progress for specimens irradiated at 529°C.

3. Results

MARZ copper irradiated at 411-430°C exhibited a relatively reproducible behavior as shown in Figure 1, swelling at ~0.5%/dpa without evidence of saturation up to 150 dpa. Its electrical conductivity fell with both void swelling and transmutation, which forms nickel, zinc, and cobalt in order of decreasing formation rate [14]. Nickel formed by transmutation reaches 1.3 wt% in pure copper at 150 dpa in FFTF.

MARZ tensile specimens were included only at the 34 and 50 dpa levels in the Generation 2.0 experiment at 411°C. The tensile and fracture behavior of pure copper containing large swelling levels were found to be rather unusual and was described by Anderson and coworkers [15].

Since pure copper did not swell as much at 529°C (1.8% at 32 dpa), the decrease in conductivity was smaller than at 411-430°C, resulting primarily from transmutation. Addition of 5 wt% Ni prior to irradiation has been shown not to affect the swelling of copper during neutron irradiation, but it did substantially reduce its pre-irradiation conductivity however.

As shown in Figure 2, the beryllium-bearing alloys exhibited somewhat more complex behavior in response to solute redistribution as well as transmutation and void swelling. The conductivity of the CuNiBe alloys in Generation 1 initially increased in response to overaging and radiationinduced solute redistribution at 400°C, and then declined with continuing transmutation and swelling [10]. Although the early response depended somewhat on the alloy's initial thermomechanical treatment (TMT), the conductivities of the CuNiBe alloys in various TMT conditions converged at higher fluence levels. The three TMT conditions of CuNiBe irradiated to 34 dpa at 414°C in Generation 2 exhibited an increase in conductivity, in agreement with the Generation 1 results. The swelling and conductivity reached at 539°C and 32 dpa were lower than that reached at a comparable dpa levels at 411-430°C.

The conductivity of the Cu-2Be alloy appears to be independent of TMT in both the Generation 1 and 2 experiments, with a slight initial increase in conductivity probably caused by solute redistribution and overaging, followed by a plateau, as shown in Figure 2. The Cu-2Be alloy did not swell at either temperature in the Generation 2 experiment, in contrast to its behavior at 430°C in Generation 1. This difference is attributed to a progressive contamination of the Generation 1 specimens with aluminum,[3,4] which was used as a spacer material between specimens. Aluminum is known to accelerate the onset of swelling in copper [5,6]. The loss of strength shown in Figure 2 for the CuBe alloys is thought to be related primarily to overaging and was also observed in thermal aging studies [2].

Figure 3 shows the results of tests on the MZC-type alloys. While exhibiting some variability in pre-irradiation conductivity, the post-irradiation behavior of the conductivities for the various alloys was similar. The two TMTs of the AMAX MZC alloy swelled much more than the two MIT alloys or the JRC alloy. The reason for the swelling difference has not been ascertained but is thought to be related to differences in Cr content. The MIT alloys exhibited excellent strength retention up to 150 dpa, as shown in Figure 3, but unfortunately no strength data are available for the JRC alloy. It was shown previously that the yield strength of the AMAX MZC alloy in the HTA condition decreased significantly after irradiation to 16 dpa at 430°C [2].

The spinodally strengthened CuNiTi alloys also exhibited some complexity in their response to irradiation at 411-414°C [13,16], as shown in Figure 4. The conductivity initially increased for both alloys, then began to decrease after ~50 dpa. The conductivity of the AMAX alloy appeared to reach a plateau after ~100 dpa, while the conductivity of the MIT alloy continued to decline. The MIT alloy exhibited considerably less void swelling than the AMAX alloy, most likely due to the added dispersoid and the Zr precipitates in the MIT alloy. The conductivity loss appears to be less at 539°C and 32 dpa. The strength of both spinodal alloys was shown in other studies to increase during irradiation to 34 dpa at 411°C, a phenomenon not found in any of the other alloys studied [13,16].

4. Discussion

Based on the results of a companion study[7], internally oxidized, dispersion strengthened GlidCop^{TM} alloys have been recommended as leading candidate materials for high heat flux service in fusion reactors. The MIT and JRC MZC alloys, however, exhibited sufficient promise to justify their consideration as back-up candidates. The higher swelling of the AMAC MZC disqualifies it from further consideration. CuBeNi may also be applicable for low fluence applications. Although Cu-2Be exhibited the smallest property changes under irradiation, its low conductivity may preclude its use. The spinodal CuNiTi alloys, particularly the MIT alloy, may be of value because of the stability of their conductivity, and tensile properties during irradiation.

Copper and its alloys exhibit a variety of responses to neutron irradiation, depending on alloy composition, TMT, irradiation temperature, and neutron spectra. The dependence on spectra is expressed in its strong influence on the rates of formation of solid transmutants, which can directly or indirectly affect electrical and thermal conductivity. The influence of transmutation is not always reflected in all property measurements, however, as illustrated by the lack of influence of nickel on the swelling of pure copper.

The increase in nickel, zinc and cobalt due to transmutation appears to cause no degradation of electrical conductivity in Cu-2Be. This is thought to arise from the formation of (Cu,Ni,Co)Be beryllide precipitates[17]. The removal of beryllium from solution counteracts the influence of the added transmutants. In CuNiBe most of the beryllium was already out of solution prior to irradiation and the full effect of both swelling and transmutation is exerted on the conductivity.

Judging from the conductivity and swelling data for the Cu-2Be alloy, the change in composition caused by transmuted nickel does not appear to alter the properties significantly, at least in the FFTF spectrum. It must be cautioned, however, that using the conductivity data from FFTF without corrections for spectrum will most likely underestimate the changes expected in a fusion environment, since nickel will form at much higher rates [14]. The production of helium from the Be(n,2α) reaction will also increase strongly in fusion spectra. These data should therefore be corrected for spectral influence, especially for conductivity, as part of the extrapolation process to a fusion environment.

The MZC class of alloys provides another example of the complex behavior that occurs in irradiated materials. In general, the conductivities of the various MZC alloys fell within a limited range, regardless of compositional and TMT differences. Although their conductivities were similar, the AMAX MZC alloy exhibited much larger swelling than either the MIT or JRC MZC alloys. The decline in conductivity for the MZC class of alloys with irradiation is attributed primarily to transmutation, since the AMAX MZC alloys have roughly the same conductivity response despite their higher void swelling.

The temperature range in which swelling occurs in pure copper at ~1 dpa was determined by Zinkle and Farrell in the Oak Ridge Research reactor (ORR) to be 180-500°C [18,19], although ~1.8% swelling was observed in the current study at 529°C and 32 dpa. If it is assumed that pure copper exhibits the greatest tendency toward swelling, then the combined results of the ORR and FFTF experiments suggest that swelling for a given alloy is possible anywhere in the range of 180-530°C and perhaps at even higher temperatures at sufficiently large displacement levels. The largest steady-state swelling rate observed in pure copper and several other alloys at high fluences in Generation 1.0 was ~0.5%/dpa. It is uncertain, however, whether this rate also applies at the peak swelling temperature of 300-350°C determined by Zinkle and Farrell, or at temperatures above 430°C, where the post-transient swelling rate has not yet been determined. Swelling appears to be only slightly sensitive to helium content below the peak swelling temperature [18,19], but the presence of relatively large amounts of oxygen may lead to a pronounced change in swelling response [7,20,21].

It is thought by the authors that if a given copper alloy survived irradiation in this study to displacement levels on the order of 100 dpa or greater at ~400°C, then it could confidently be applied at lower doses and temperatures since the rate of solute redistribution probably declines strongly with decreasing temperature. The single exception to this otherwise confident assertion lies in the possible response of fatigue properties to the higher microstructural densities that will arise at lower irradiation temperatures.

5. Conclusions

The precipitation hardened MIT and JRC MZC alloys appear to offer promise as back-up candidates for high heat flux service in fusion reactors based on their relative resistance to swelling and to changes in conductivity and tensile properties. The CuNiBe alloy may be of interest for low fluence applications, but Cu-2Be is not recommended because of its low electrical conductivity. The spinodally strengthened CuNiTi alloys merit further study based on the limited data presented in this paper.

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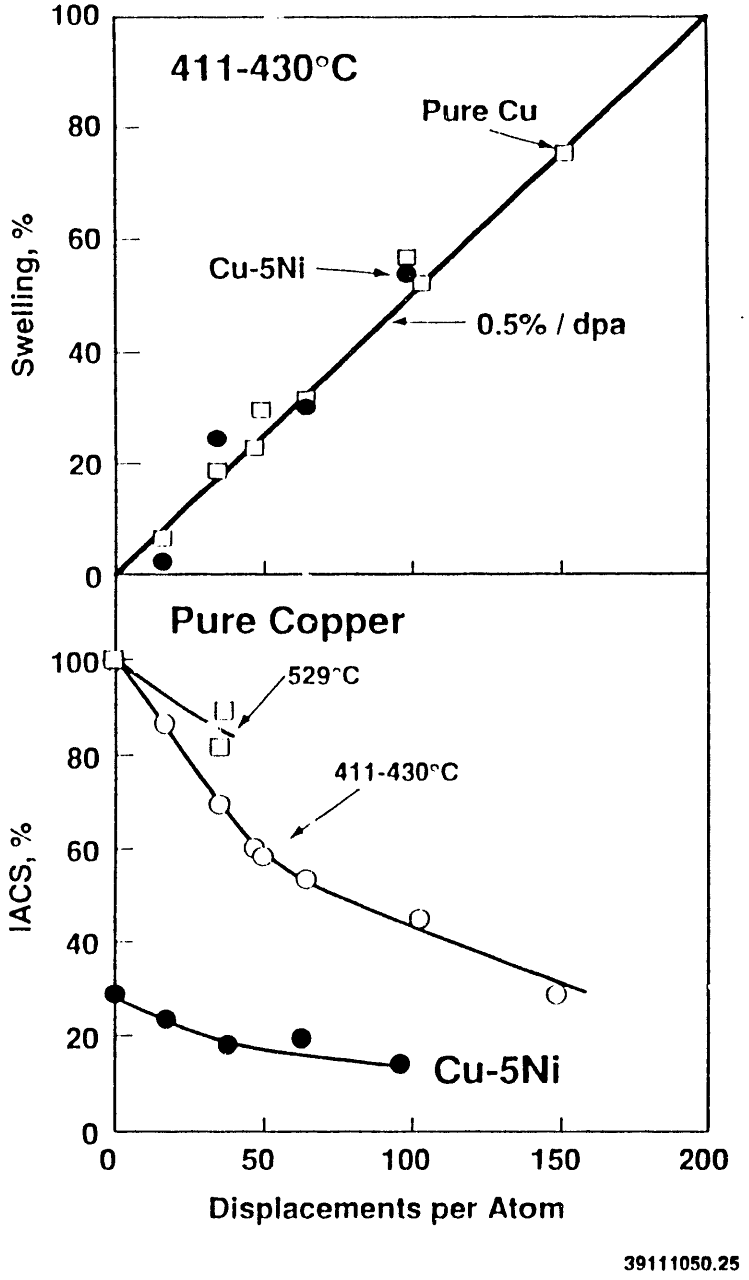

Figure 1. Swelling and conductivity changes observed in pure copper (411-430°C and 539°C) and Cu-5 wt% Ni (430°C) during irradiation in FFTF-MOTA.

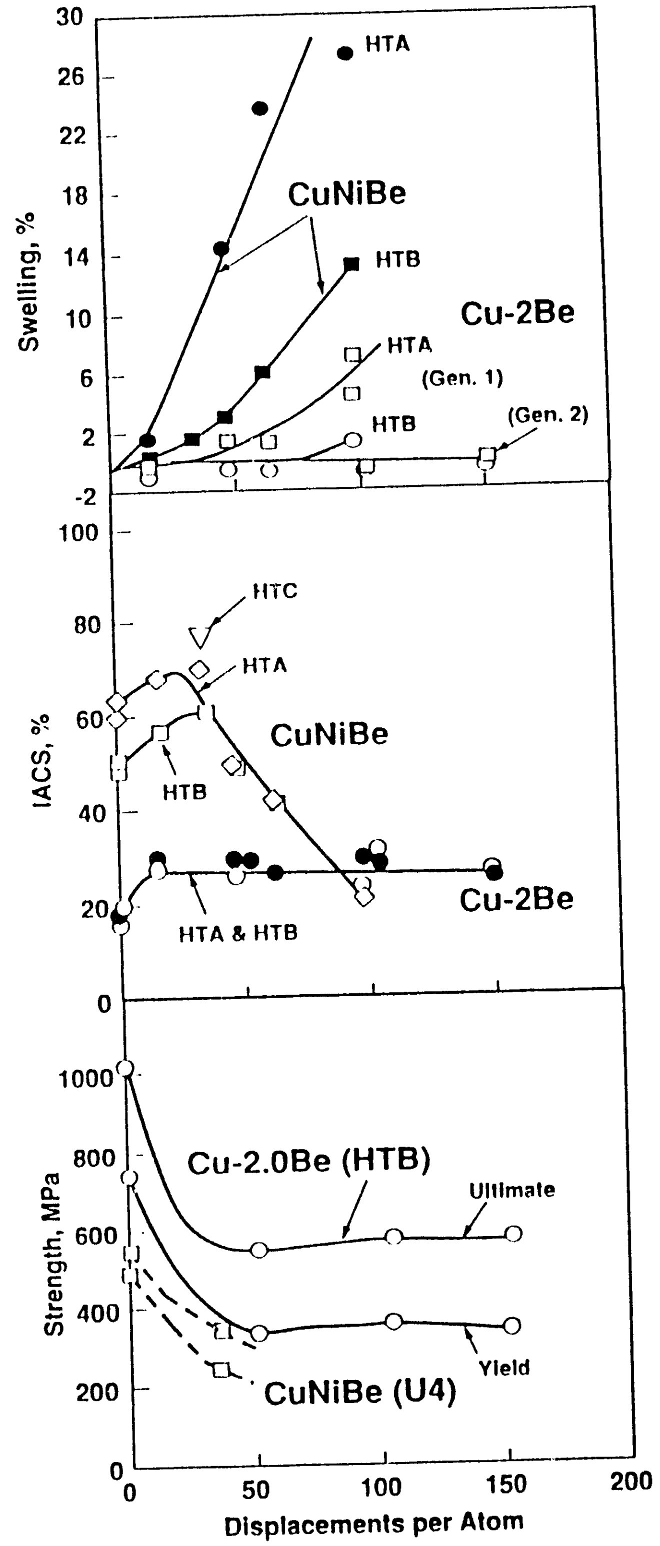

Figure 2. Swelling, conductivity and tensile strength measured in beryllium containing alloys after irradiation at 411-430°C.

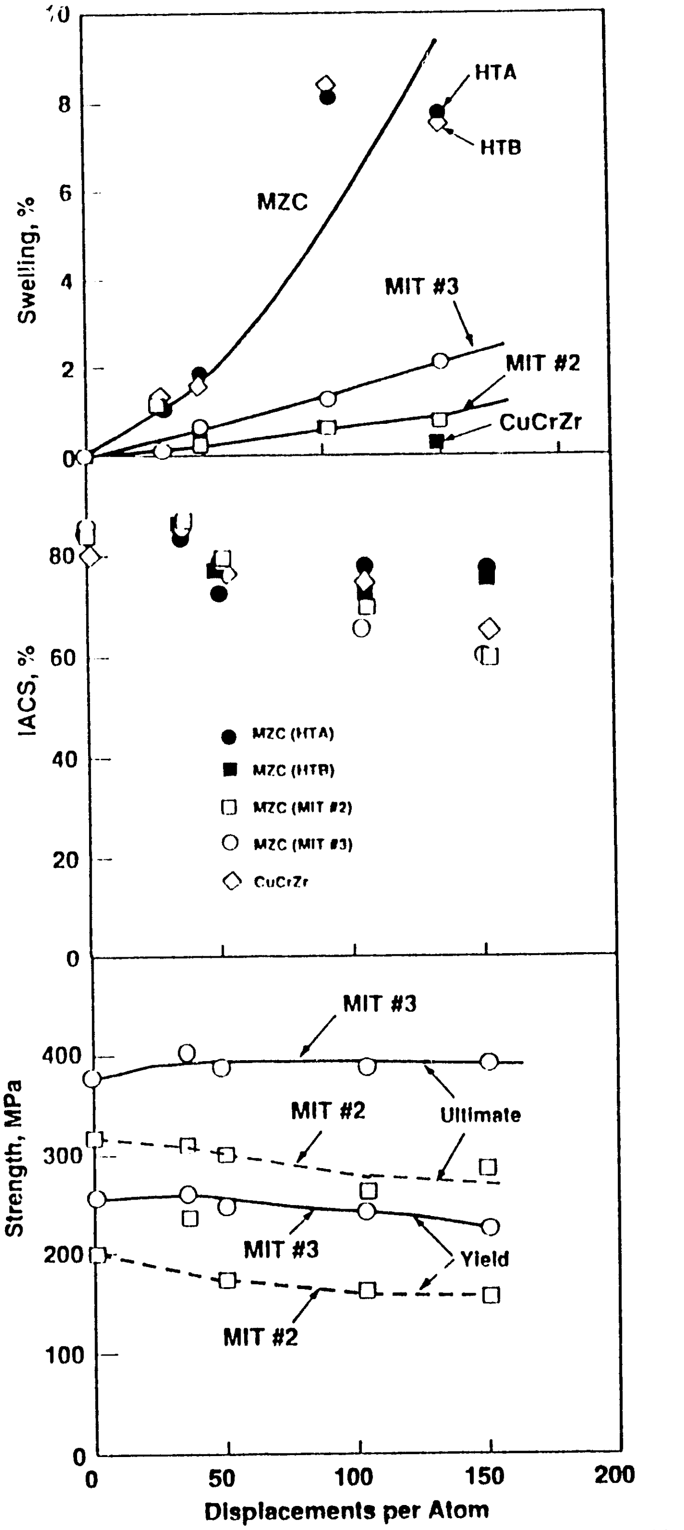

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Figure 3. Swelling, conductivity and tensile strength measured in MZC-type alloys after irradiation at 411-414°C

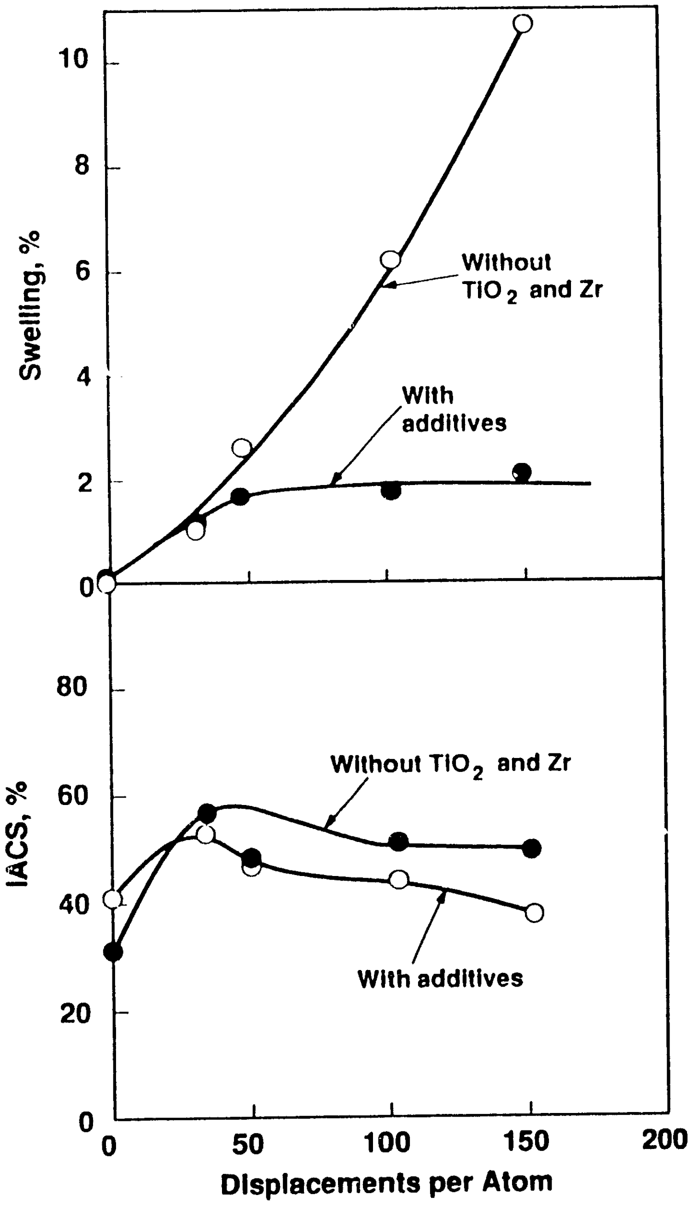

Figure 4. Swelling and conductivity changes observed in spinodally strengthened CuNiTi alloys after irradiation at

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