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CALCULATION OF TRANSMUTATION IN COPPER AND COMPARISON WITH MEASURED ELECTRICAL PROPERTIES

REFERENCE: Greenwood, L. R., Garner, F. A., and Edwards, D. J. , "Calculation of Transmutation in Copper and Comparison with Measured Electrical Properties," Eighth ASTM-Euratom Symposium on Reactor Dosimetry, ASTM-STP 1228, Harry Farrar IV, E. Parvin Lippincott, and John G. Williams, Eds., American Society for Testing and Materials, Philadelphia, 1994.

ABSTRACT: Calculations of the transmutation of pure copper have been performed for the Fast Flux Test Facility/Materials Open Test Assembly (FFTF/MOTA) and for the STARFIRE first-wall fusion reactor. The principal transmutation products in decreasing order of importance are nickel, zinc, and cobalt. Contrary to previously published calculations, nickel and zinc are produced at nearly equal rates in FFTF, but cobalt is insignificant. The fusion reactor case shows much higher transmutation rates and produces about twice as much nickel as zinc. Transmutation rates for FFTF were determined using adjusted neutron energy spectra based on dosimetry measurements at various positions in the MOTA. The predicted transmutation rates were compared directly with nickel concentrations measured by Energy Dispersive X-Ray Spectrometry (EDS) microchemistry and with measurements of the electrical conductivity of copper and two copper alloys irradiated in the MOTA. Measurements and calculations agree within ±15%.

KEYWORDS: transmutation, copper, electrical conductivity

In a previous series of calculations using the REAC computer code [1-3], it was shown that pure copper irradiated in the Fast Flux Test Facility (FFTF) would develop a significant amount of nickel and zinc during a typical irradiation in the Materials Open Test Assembly (MOTA). The predicted ratio of nickel/zinc was about 2/1. These reports also showed that the nickel/zinc ratio from transmutation of copper would increase substantially (about 10/1) in a typical fusion reactor (STARFIRE) spectra. These two elements significantly reduce both the electrical and thermal conductivities of copper, with nickel exerting the largest influence on a per atom basis [3]. Thus, irradiations in FFTF produce conductivity changes that are lower than that expected in fusion spectra.

The previous FFTF calculations were based on the assumption of continuous irradiation in the center of the original FFTF core operating at 400 MW. The current core configuration is different, however, and operates at 291 MW with a somewhat softer neutron spectrum [4]. These differences in neutron environment are consequences of core and reflector changes associated with the placement of the Core Demonstration Experiment (CDE) in FFTF Cycle 9 starting in September 1986. These changes influenced the fluxes and spectra of the MOTA-1E, 1F, 1G, 2A, and 2B irradiations.

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The neutron spectrum and fluxes depend on the axial position in the MOTA. While early copper irradiations were conducted at in-core locations, most current copper irradiations are being conducted at positions near or below the bottom of the core where the neutron spectrum is softer. Since MOTA 2A contained the most extensive set of dosimetry monitors employed in any of the MOTAs, the transmutation of pure copper was recalculated for this MOTA, especially for below-core positions. To evaluate the impact of the correct nickel/zinc ratio from the decay of ^{64}Cu and the various changes in neutron flux and spectra, two sets of calculations were performed.

In the first calculation, the reaction rates in MOTA-2A were determined from spectral analyses [5] using the exact run history of 300 EFPD (effective full power days) at 291 MW with two shutdown periods between the three reactor cycles of ~100 days each. Calculations were performed at three MOTA positions where spectral measurements were performed, namely, -1 cm, -49 cm, and -63 cm, all measured from core center. The -49 and -63 cm positions define the upper and lower boundaries of the MOTA below-core basket. The most important reaction rates were calculated directly by the STAY'SL computer code following spectral adjustment [6]. The weaker reaction rates were estimated using ratios of known cross-sections. Examination of one of the most important reactions, the partition of the decay products of ^{64}Cu following the $^{63}Cu(n,\gamma)$ reaction, revealed an important discrepancy with the previous work, thereby affecting the predicted ratio of nickel/zinc substantially. Whereas the original REAC calculations assumed an equal production of ^{64}Ni and ^{64}Zn from ^{64}Cu, the recommended decay scheme of ^{64}Cu predicts 62.9±0.4% ^{64}Ni and 37.1±0.4% ^{64}Zn [7].

In the second set of calculations, the original set of calculations using REAC [1-3] were repeated using the correct partition for the decay of ^{64}Cu (12.7 h) following the $^{63}Cu(n,\gamma)$ reaction for both the original FFTF core center and the STARFIRE first-wall fusion reactor spectra.

The principal reactions and decays considered in both sets of calculations are listed in Table 1, including the (n, γ), (n,p), (n,2n), and (n,α) reactions for the two copper isotopes (^{63}Cu, ^{65}Cu) and (n, γ) reactions for other isotopes as they were produced from copper. The calculations were performed by numerically integrating the differential equations for each atomic species, starting with pure, natural copper. The principal other atomic species considered were ^{64}Cu, ^{66}Cu, ^{60}Ni, ^{62}Ni, ^{63}Ni, ^{64}Ni, ^{64}Zn, ^{65}Zn, ^{66}Zn, and ^{60}Co. (Note that REAC considers all possible atomic species.) This carried the calculations to the second generation, which was clearly sufficient judging by the small production of many of the species. In the case of FFTF, the (n,γ) reactions produced most of the transmutation. For STARFIRE, the (n,2n) reactions with the 14 MeV neutrons were the most important.

Four of the transmutants are radioactive with half-lives sufficiently short that they decayed substantially during the MOTA 2A experiment. They were allowed in the calculation to decay both during and after irradiation. Copper-64 decays very quickly (12.7 h) to ^{64}Zn and ^{64}Ni in the ratio of nickel/zinc = 1.7, and ^{66}Cu decays rapidly (5.1 min) to ^{66}Zn. Zinc-65 (243.8 days) decays back to ^{65}Cu and ^{60}Co (5.27 years) decays at a slower rate to ^{60}Ni. Nickel-63 is also radioactive and decays back to ^{63}Cu, but its decay is minimal since its half-life is 100 years.

RESULTS AND DISCUSSION

The results based on the STAY'SL calculations are shown in Figure 1. Although calculations were performed for each day of operation, summaries are plotted only for intervals of 20 days for a total of 700

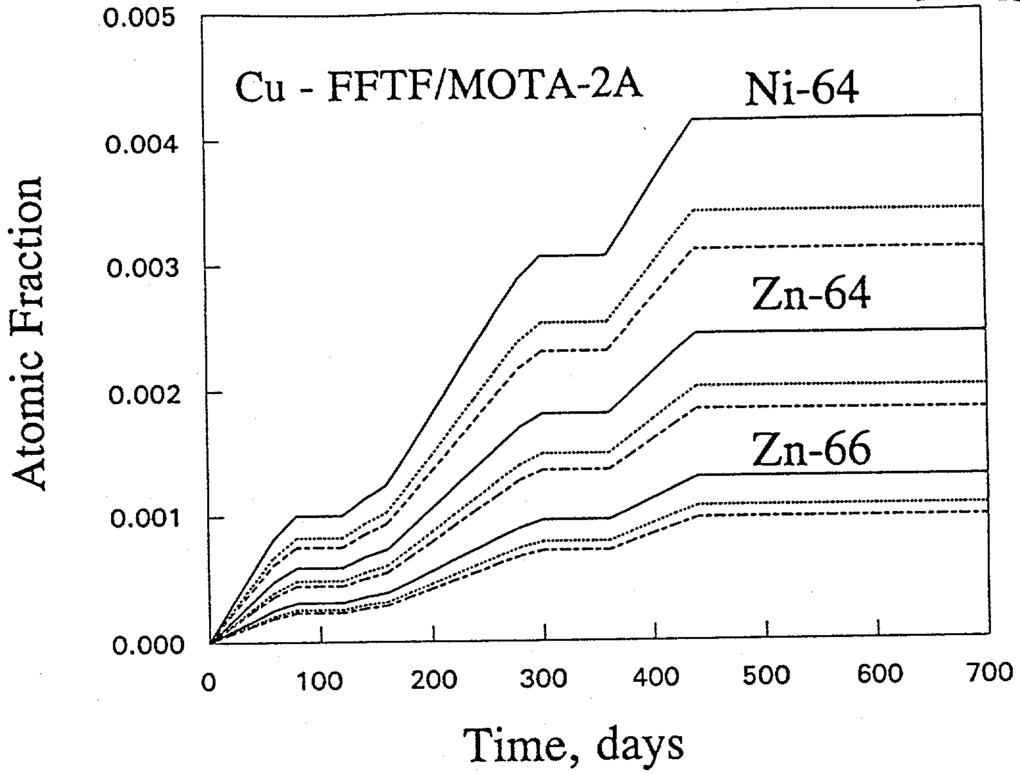

Fig. 1 - Calculation of major transmutation products in pure copper in FFTF/MOTA-2A at -1 cm (solid line), -49 cm (dotted line), and -63 cm (dashed line).

days. The apparent breaks in the curves correspond to reactor shutdowns for refueling. The MOTA-2A irradiation ended at 439 days, including the interim shutdown periods. Only ^{60}Ni, ^{60}Co, and ^{65}Zn were found to change significantly by decay during shutdown periods.

As shown in Figure 1, the STAY'SL-based results for FFTF show that the only significant species (from the standpoint of conductivity changes) are ^{64}Ni, ^{64}Zn, and ^{66}Zn, all three of which are stable isotopes. At all three positions in MOTA for which calculations were performed, slightly more nickel than zinc was produced, with the nickel/zinc ratio constant at 1.108.

This invariability of the nickel/zinc ratio with neutron spectrum is a direct consequence of the fact that both elements are produced primarily by (n,γ) reactions involving ^{63}Cu and ^{65}Cu. Both elements exhibit a very similar dependence on neutron energy. The decrease in formation rates of both elements with decreasing height in the core results primarily from the lower neutron flux at these lower levels. Since the primary reaction rates involve (n,γ) reactions, however, the transmutation rates per neutron increase toward the bottom of the core as a consequence of spectral softening. Thus, the production rates do not decrease as fast as either the fast fluence or dpa rates decrease.

Note that the nickel/zinc ratio found in the STAY'SL study is much less than the ~3/1 rates reported previously [1-3]. This difference is due primarily to the correction of the nickel/zinc ratio used for the decay of ^{64}Cu in the current calculations. The calculated individual production rates have also changed, however, reflecting the softer spectrum found in the current FFTF core. The previous 300 day REAC value for nickel production at core center (after correction for the power level difference in the two cases) is 0.359%, which is ~14% lower than the current predicted value of 0.416%. A comparable calculation for zinc yields a power-normalized REAC value of 0.120% vs. 0.373% currently predicted. Thus, the levels of nickel and zinc increase

Table 1. Principal transmutation reactions in copper

Nuclide	FFTF		STARFIRE
^{64}Ni	$^{63}Cu(n,\gamma)^{64}Cu(\varepsilon)^{64}Ni$	62.9%	$^{65}Cu(n,2n)^{64}Cu(\varepsilon)^{64}Ni$
^{64}Zn	$^{63}Cu(n,\gamma)^{64}Cu(\beta^-)^{64}Zn$	37.1%	$^{65}Cu(n,2n)^{64}Cu(\beta^-)^{64}Zn$
^{66}Zn	$^{65}Cu(n,\gamma)^{66}Cu(\beta^-)^{66}Zn$		
^{60}Co	$^{63}Cu(n,\alpha)^{60}Co$		$^{63}Cu(n,\alpha)^{60}Co$
^{62}Ni			$^{63}Cu(n,2n)^{62}Cu(\varepsilon)^{62}Ni$; $^{65}Cu(n,\alpha)^{62}Co(\beta^-)^{62}Ni$

Table 2. Revised calculations of the transmutation of pure copper in the original FFTF core using the REAC code.

FFTF Midplane 5.45 X 10^{15} n $cm^{-2}s^{-1}$ Atom %				
Time, days	Ni	Zn	Ni/Zn	Co
20	0.0253	0.0247	1.024	0.000067
40	0.0506	0.0494	1.024	0.000133
60	0.0759	0.0741	1.024	0.000198
80	0.1012	0.0988	1.024	0.000263
100	0.1264	0.1235	1.023	0.000327
300	0.3792	0.3705	1.023	0.000981
FFTF Top of Core 3.04 X 10^{15} n $cm^{-2}s^{-1}$				
20	0.0173	0.0167	1.036	0.000032
40	0.0346	0.0335	1.033	0.000064
60	0.0519	0.0502	1.034	0.000095
80	0.0693	0.0669	1.036	0.000126
100	0.0865	0.0836	1.035	0.000157
300	0.2600	0.2510	1.036	0.000472
FFTF Bottom of Core 3.85 X 10^{15} n $cm^{-2}s^{-1}$				
20	0.0247	0.0239	1.033	0.000036
40	0.0493	0.0477	1.034	0.000072
60	0.0739	0.0715	1.034	0.000107
80	0.0985	0.0953	1.034	0.000142
100	0.1231	0.1191	1.034	0.000177
300	0.3690	0.3570	1.034	0.000532

Table 3. Revised calculations of the transmutation of pure copper for the first wall STARFIRE spectrum, using the REAC code.

STARFIRE First Wall 1.83 X 10^{15} n $cm^{-2}s^{-1}$ Atom %				
Time, years	Ni	Zn	Ni/Zn	Co
0.5	0.517	0.234	2.209	0.030
1	1.032	0.466	2.215	0.058
2	2.118	0.952	2.225	0.133
5	5.455	2.417	2.257	0.243

significantly relative to those of the previous calculation, leading to a substantial increase (~20%, relative to the earlier calculations) in the predicted loss of electrical conductivity.

As shown in Figure 2 and Table 2, the REAC calculations were repeated, using the flux/spectrum information employed earlier for the original FFTF core loading and changing only the ^{63}Cu cross-sections for production of nickel and zinc. Note that the original 300-day core center values of 0.379% nickel and 0.165% zinc are different from the current values of 0.359% nickel and 0.373% zinc. The nickel/zinc ratio at core center is calculated to be 1.024 by REAC, and is only slightly different from that calculated by STAY'SL to be 1.108. The bottom-of-core nickel/zinc ratio increases only slightly to 1.034, still somewhat lower than that of the spectrally softer MOTA-2A value, the STAY'SL-based calculation of which does not allow spectral variations to affect the nickel/zinc ratio.

Helium production is also illustrated for the FFTF/MOTA midplane in Figure 2. However, helium production is not significant compared to the solid transmutants nickel and zinc, although helium may have some effect on void nucleation. Helium production in copper is enhanced in mixed-spectrum reactors due to the $^{63}Cu(n,\gamma)^{64}Cu(\beta^-)^{64}Zn(n,\gamma)^{65}Zn(n,\alpha)$ reactions [8]; however this effect is minimal in fast reactors such as FFTF.

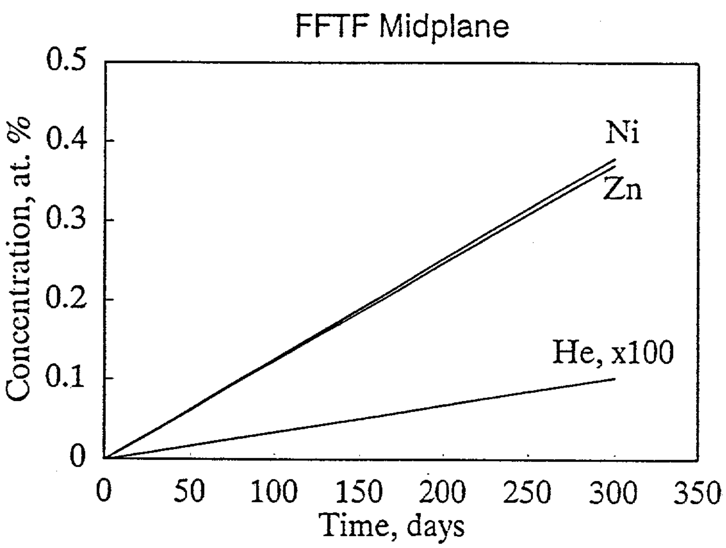

Fig. 2. Revised REAC calculations of the transmutation products of pure copper at core center of the original core of FFTF.

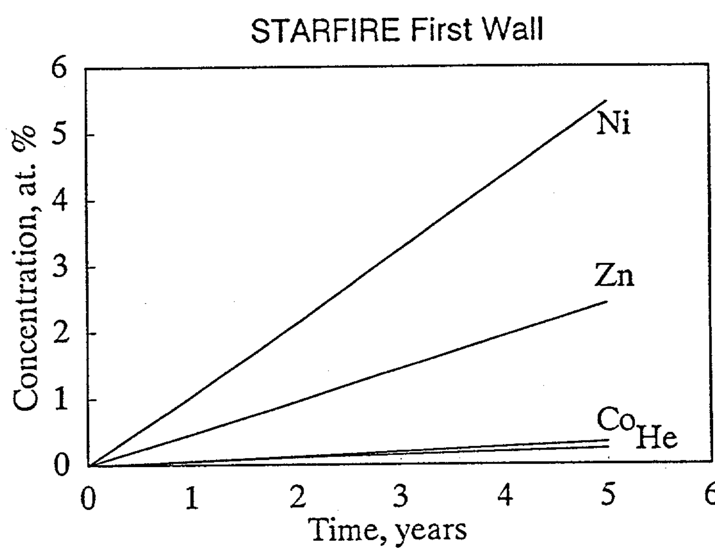

Fig. 3. Revised REAC calculations of the transmutation products of pure copper at the first wall of STARFIRE.

Fusion Reactor Calculations

Using the REAC code with re-evaluated $^{63}Cu(n,\gamma)$ reaction rates, the transmutation rates for the STARFIRE [9] first wall neutron spectrum and flux were calculated and are shown in table 3 and figure 3. The significantly increased production of nickel relative to that in FFTF is primarily a consequence of the contribution of the $^{63}Cu(n,2n)$ reaction, yielding a nickel/zinc ratio of about 2.3 after five years of continuous STARFIRE operation. In this case, the production of cobalt and helium are also found to be significant, although nickel and zinc are still the dominant transmutation products. The net nickel production in STARFIRE is shown to be about 2.5 times higher than in FFTF/MOTA at the midplane and the total production of nickel and zinc is about 1.9 times higher. This increased rate of transmutation will induce a larger loss of electrical and thermal conductivity.

Comparison with Electrical Conductivity Measurements

The validity of the revised transmutation rates calculated by REAC has been independently tested by Edwards and Garner using the measured changes in conductivity for irradiated specimens of pure copper and two commercial copper alloys, GlidCop CuAl20 and CuAl25 manufactured by SCM Metal Products [10]. The results for electrical conductivity and resistivity are illustrated in Figure 4. For the two alloys, no void swelling has been observed for CuAl25 and swelling is less than 1% for CuAl20 for irradiations in FFTF up to 150 dpa. Swelling has a strong impact on electrical and thermal conductivities. Hence, for these alloys, swelling does not complicate the interpretation of the data. It appears that the predicted transmutation rates agree within 15% of those required to produce the observed changes, slightly overpredicting the conductivity changes. This is thought to be excellent agreement considering the impact of calculational uncertainties in the adjusted neutron flux spectra, transmutation reaction rates, and local flux and spectra perturbations arising from structural and material discontinuities that cannot be included in the calculational procedure. Furthermore, small (about 5%) radial flux gradients in MOTA have not been included, and small neutron self-shielding effects have also been ignored.

For pure copper, the irradiations produced significant void swelling which leads to most of the observed conductivity loss, as shown in figure 4. As shown in figure 5, swelling proceeds at a rate of about 0.5%/dpa, even in the presence of nickel formed by transmutation or by alloying. The influence of void swelling on conductivity can be seen by comparing the conductivity loss at about 400^{o}C were swelling is strong with that at 529^{o}C where swelling does not occur [11]. Assuming that the transmutation calculations are about 15% too high (based on the GlidCop results), the conductivity and resistivity data were found to be best described by the Euken model for voidage effects on conductivity [12], as plotted in the figure. However, the models of Loeb [13] and Russell [14] also provide a reasonable fit to the data.

Measurement of Nickel Transmutation

Recently, measurements were performed by Muroga and Garner [15] to determine the nickel content of a pure copper TEM (transmission electron microscope) disk irradiated in the FFTF/MOTA-2A experiment. This disk had reached 95.4 dpa at 423±5^{o}C and had swelled 45.4%. The measurements were carried out with a JEM-2000FX electron microscope equipped with an Energy-Dispersive X-ray Spectrometer (EDS) at the Pacific Northwest Laboratory. Due to the high residual activity of the specimen following thinning, the energy spectrum due to x-ray excitation alone was derived by subtracting the radiation component from the total spectrum. Results showed that transmutant nickel segregates strongly to void surfaces and the nickel concentrations in the foil averaged 0.92 at %, about 33% higher than the calculated value of 0.69 at %. However, the higher measured bulk-averaged nickel concentration reflects the disproportionate influence of the segregated nickel that lies on the bottom surface of each of the many large voids that intersect the foil surface. This leads to a "foil-averaged" composition that is somewhat larger than a true bulk-averaged composition. The x-ray excitation peak of Zn overlaps with the stronger copper peak in energy. Thus, this technique could not be used to determine the amount of zinc formed by transmutation.

Conclusions

Two new calcuations agree quite well for the nickel and zinc transmutation products from pure copper irradiated in FFTF and predicted for STARFIRE. These calculations for FFTF differ significantly from previously published transmutation calculations in that the nickel/zinc ratio is near unity in the present calculations. The calculations are in good agreement with direct EDS measurements of the nickel concentration (about 30% lower) and with measurements of the electrical conductivity of irradiated copper specimens (about 15% higher). The EDS measurements, however, are known to yield an artificially higher concentration due to nickel segregation and the foil polishing technique when applied to highly voided surfaces. This agreement helps to verify the predicted transmutation in a fusion reactor first wall spectrum using the STARFIRE reactor design. The transmutation rates are much higher in STARFIRE than in FFTF and produce a much higher ratio of nickel/zinc. These differences will lead to significantly higher conductivity losses in fusion reactor designs than measured in simulation experiments conducted in fast reactors.

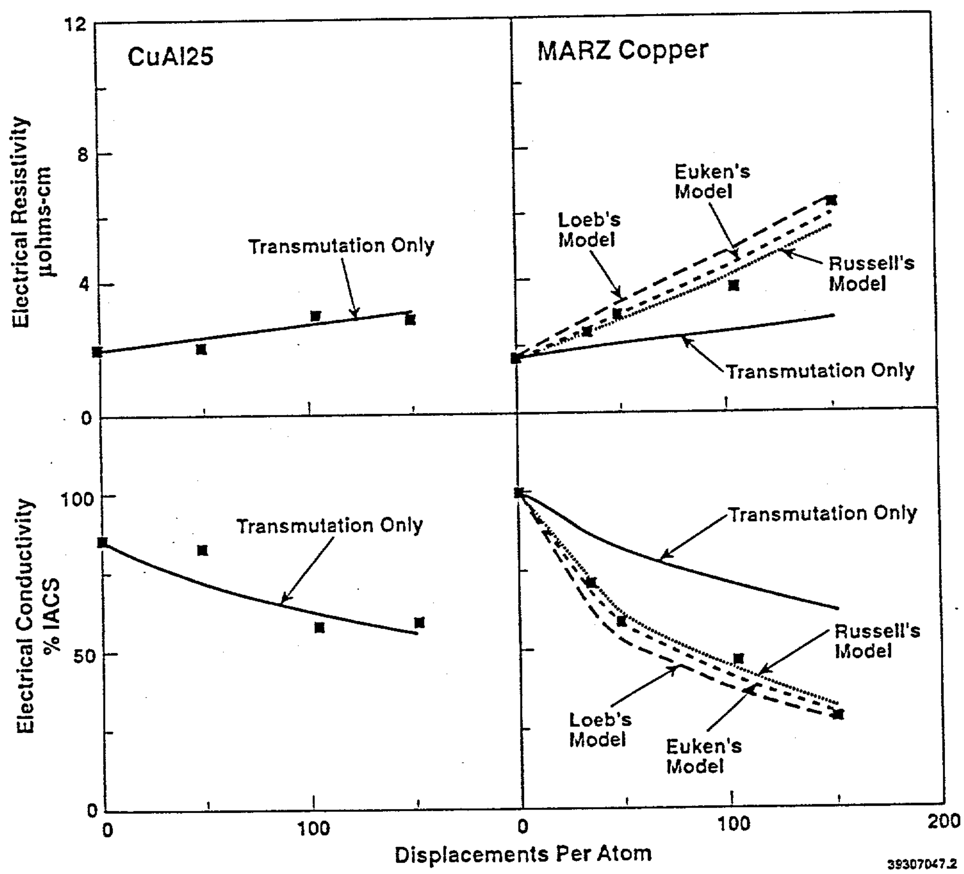

Fig. 4 Comparison of predicted and observed changes in the electrical behavior of CuAl25 and MARZ copper, assuming that the transmutation rates are 15% lower than calculated by the REAC computer code.

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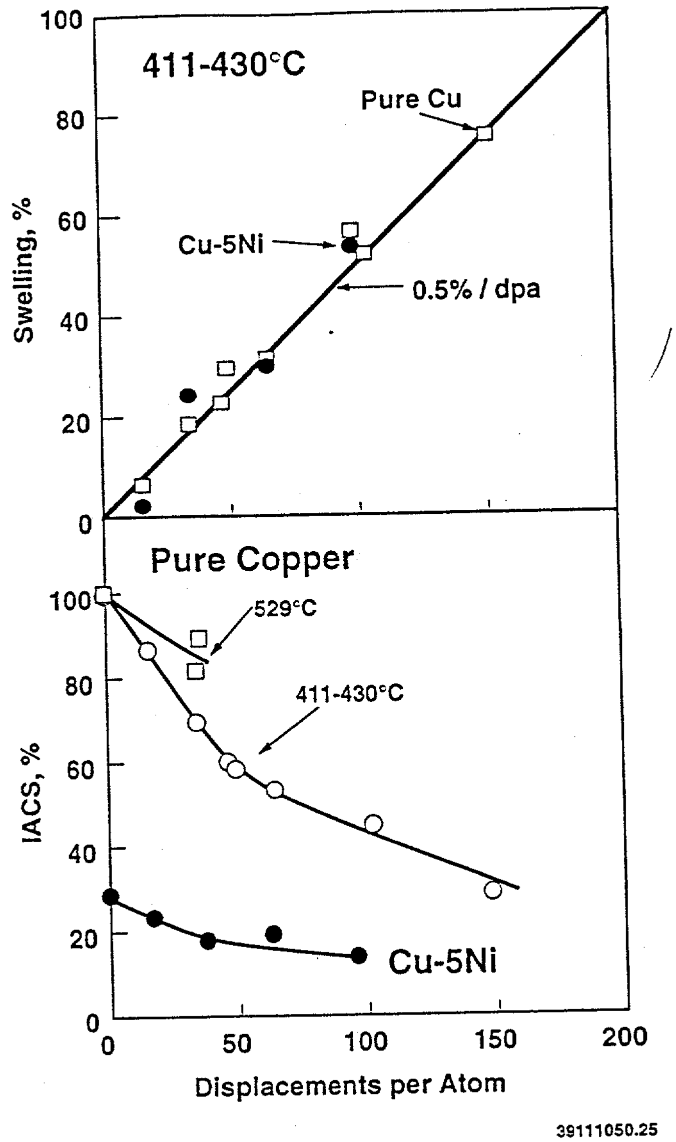

Fig. 5 Comparison of swelling and conductivity changes observed in various FFTF/MOTA irradiations of pure copper (411-430°C and 539°C) and Cu-5 wt% Ni (430°C).

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