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*Work supported by the U. S. Department of Energy.
Work is being submitted to the 9th Conf. on Atomic Collisions in Solids, Lyon, France, July 6-10, 1981.

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Introduction

Radiation-induced segregation (RIS) of alloy components toward and away from point defect sinks is common in alloys irradiated at elevated temperatures.[1] For example, the compound Ni_3Si (γ') is found at dislocations, grain boundaries, and external surfaces after electron,[2] light-ion,[3,4] self-ion[5] and fast-neutron[6] irradiations of normally stable, solid-solution Ni-Si alloys, demonstrating that Si enrichment occurs at sinks during the irradiation. A detailed understanding of the mechanisms by which RIS occurs in different alloys and of the effects of the primary recoil spectrum of the irradiation have not yet evolved. Quantitative information on the kinetics of RIS is an important step toward such an understanding.

We have measured composition changes near the irradiated surfaces of binary Ni-based alloys during He and Kr irradiations using high-resolution Rutherford Backscattering Spectrometry (RBS). For the He irradiation, backscattered ions from the beam that was employed for the production of defects were used for simultaneous RBS analysis of the near-surface composition. These in-situ measurements of composition changes during

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irradiation at elevated temperature provide quantitative information on the kinetics of RIS. In this paper we demonstrate the use of the in-situ RBS technique to measure RIS in different alloys and show examples of the type of kinetic information that can be obtained. The versatility of the technique is demonstrated by presenting results on alloys for which the solute atomic mass is greater than (Ni-Ge), less than (Ni-Si), and nearly the same as (Cu-Ni) that of the host atoms. We also compare RIS results obtained for Kr and He irradiations of Ni-Si to illustrate the effect of the different primary recoil spectra on the kinetics of RIS.

Technique

The application of Rutherford backscattering to study the depth distribution of alloy components near a surface is described in detail in Ref. 7. The technique, as applied in the present investigations, is based on differences between RBS spectra acquired during successive irradiations and the spectrum obtained from the as-prepared alloy. The changes in alloy composition during irradiation as a function of depth and time appear as changes in backscattering yields at different energies. To illustrate the technique, computer simulations of difference spectra which represent segregation effects in Ni-Si, Ni-Ge, and Cu-Ni are shown in Fig. 1. The spectra were calculated from an assumed concentration distribution by a computer program similar to that described by Ziegler et al.[8] A difference spectrum is obtained by subtracting an RBS spectrum for the unirradiated, homogeneous alloy from a spectrum for a specimen with segregation. Figs. 1a and 1c show difference spectra for Ni_3Si and Ni_3Ge layers of three thicknesses on the surfaces of a Ni-10 at. % Si and Ni-10 at. % Ge alloy, respectively.

Fig. 1b shows difference spectra for Ni-enriched layers containing 60 at. % Ni on the surface of a Cu-40 at. % Ni alloy.

There is a large difference in the masses of Ni and Si. When the Ni_3Si layer thickness becomes larger than the experimental resolution, two clearly separated steps appear in the difference spectra representing the decreased Ni and increased Si concentrations at the surface (fig. 1a). As the layer thickness increases still further, the width of each step increases. Overlap of the steps begins to occur when the layer thickness reaches ~ 100 nm. For 2 MeV He ions, this overlap can be delayed up to a maximum thickness of ~ 300 nm by adjusting the backscattering geometry.(7) In Ni-Ge the mass difference is less, and overlap of the Ni and Ge signals occurs at about the same thickness that the steps become fully developed. For thicker layers, the Ge-signal from the back of the layer superimposes on the Ni-signal from the front of the layer (bottom of fig. 1c). In Cu-Ni the mass difference is quite small. Here, the difference plots show a narrow dip at the front which corresponds to depletion of the heavier Cu atoms at the surface, followed by a narrow peak which corresponds to Ni enrichment at the surface. As the layer thickness increases, the back-portion of the "Cu-deficit" signal nearly compensates the front-portion of the "Ni-excess" signal because of the nearly equal scattering cross sections of Cu and Ni. The narrow peak corresponds to the "Ni-excess" signal originating from the back-portion of the layer. Hence the peak shifts toward lower energies as the film grows. The dip, which corresponds to the "Cu-deficit" signal from the front-edge of the layer, remains fixed. Thus, layer thicknesses can be determined from the energy difference between dip and peak in the RBS difference spectra even in alloys containing neighboring elements of the periodic table.

For simple cases, e. g. Fig. 1a bottom, the layer thickness can be determined directly from the energies of the front and back edges of the layer. For layer thicknesses less than the resolution of the system (~ 5 nm for our experimental conditions) the energy corresponding to the back edge of the layer is not clearly defined. In this case the area in the difference spectrum can be related to the thickness. For more complex cases, e.g. when the atomic masses of the alloy components are close (see Fig. 1b) or when a layer with a depth dependent composition is formed, the computer simulation program can be employed to fit the difference spectrum and the composition profile can be obtained iteratively.

In order to study the growth kinetics of surface layers resulting from radiation-induced segregation using the in-situ RBS technique, it is necessary (1) that the bombarding ions have a lighter mass than at least one of the alloying components, i.e., that the ions do indeed backscatter, and (2) that statistically significant RBS spectra can be acquired using doses for which the segregation effects are small. We have successfully employed MeV He and Li irradiations. For example, with 2.0 MeV He, an incident angle of 150^{o}, an exit angle of 75^{o}, a 1.0 mm beam diameter, and a solid angle of 2.5×10^{-4} steradians for the detector, ~ 4×10^{4} counts are acquired per nm and displacement per atom (dpa) in Ni based alloys. Thus a suitable spectrum requires only ~ 0.1 dpa of irradiation.

Examples

Fig. 2a shows typical RBS difference spectra obtained during 2.0 MeV He irradiation of a Ni-12.7 at. % Si alloy at 556^{o}C. The decrease in Ni yield

and the increase in Si yield in the surface region relative to the initially homogeneous alloy are readily apparent. The change in yields is consistent with the formation of Ni_3Si. Also apparent is the increase of the layer thickness with increasing time (dose). The increase in Ni yield which can be seen just below the Ni depleted surface layer in Fig. 2a shows that mass is conserved during segregation. This Ni-enriched subsurface region was not included in the computer-generated spectra of Fig. 1. Difference spectra for 2.0 MeV He irradiation of Ni-10 at. % Ge and Cu-40 at. % Ni are shown in Fig. 2b and 2c, respectively.

The experimental difference spectra shown in Fig. 2 give clear evidence that Si and Ge segregate to the irradiated surface in binary Ni alloys and that Ni segregates to the surface in irradiated Cu-40 % Ni. Analysis of these data reveals that the layer thickness in the Ni-Si specimen at the end of the irradiation is ~ 35 nm. In Cu-40 % Ni, the Ni enriches to about 60% and the enriched layer extends to ~ 12 nm. The enriched Ni layer however does not have a constant composition over the entire enriched layer and a computer simulation using a concentration gradient was necessary to determine the actual composition vs. depth profile. The results on the Ni-10 at. % Ge alloy are consistent with the growth of a Ni_3Ge layer on top of a Ge-depleted subsurface layer. Further details regarding the growth rates and temperature dependence for these various alloys can be found elsewhere.[9]

An application of the in-situ RBS technique for quantitative kinetic analysis will be given next. These experiments on the growth rates of Ni_3Si surface layers were designed to establish the relative importance of energetic displacement cascades for creating solute traps during elevated temperature

irradiation compared to their role as regions of enhanced defect recombination and clustering. Important parameters in all kinetic models of radiation effects at elevated temperature include the production rate of mobile defects and the sink concentration.[10-12] These two quantities depend upon the energy density within the initial displacement cascade. Only those defects which escape recombination or clustering within the cascade region can contribute to long-range diffusion. We have found that, on the basis of calculated[13] dpa rates, the Ni_3Si surface layers grow approximately six times faster during 2.0 MeV He irradiation than during 3.25 MeV Kr irradiation at the same temperature. The principal difference between the Kr and He irradiations is their primary recoil spectra. Irradiation with Kr produces most of the defects in energetic displacement cascades, whereas He irradiation produces most of the defects by low-energy primary recoils. For example, only ~ 10% of the defects produced by 3.25 MeV Kr result from recoils below 2 keV, whereas for 2.0 MeV He irradiation ~ 50% of the defects are produced from recoils below 2 keV.

The difference in observed growth rates can be interpreted on the basis that defect interactions within the denser Kr-cascades decrease the number of migrating interstitials or, that defect clusters produced by the Kr-cascades act as internal sinks which compete with the surface for segregating solute. To examine the relative importance of these effects, a specimen of Ni 12.7 at. % Si was preirradiated with 3.25 MeV Kr to form a thin surface layer of Ni_3Si. The growth rate of this layer during subsequent He irradiation was determined and compared with the growth rate measured during only He irradiation. The results are shown in Fig. 3, where the thickness of the Ni_3Si film is plotted as a function of the square root of the dose. The film

growth rate, being diffusion controlled, shows the typical square root of time (dose) dependence [9]. The solid circles are film thicknesses measured at 495°C for He irradiation only. The film grown at 500°C with 3.25 MeV Kr ions to a thickness of 8 nm (intersection of lines in Fig. 3) required a calculated dose of 2.2 dpa. A beam of 2 MeV He ions was then used to continue growing the film at 495°C, and the data represented by the open squares was obtained. The slope of the line obtained after Kr irradiation is a factor of three less than the line for only He irradiation, showing that the sinks produced by the Kr irradiation significantly affect the growth kinetics. This result clearly demonstrates that the primary recoil spectrum for an irradiation can affect the alloy microstructure during irradiation even at an elevated temperature.

Conclusion

The results presented here demonstrate that in-situ, simultaneous RBS measurements can be used to obtain quantitative information about the kinetics of RIS in binary alloys. The solutes Si and Ge in Ni and Ni in Cu-40 % Ni were shown to segregate toward the surface during irradiation at elevated temperature. Ni_3Si and Ni_3Ge layers formed on the Ni-Si and Ni-Ge alloys, respectively. Finally, it was demonstrated that the type of irradiation, i.e., the primary recoil spectrum, can influence the kinetics of RIS even at elevated temperatures.

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Figure Captions

Figure 1. RBS difference spectra obtained by computer simulation. Figs. 1a and 1c show Ni_3Si and Ni_3Ge layers growing at the surface of a Ni-10 at. % Si and a Ni-10 at. % Ge alloy, respectively. Fig. 1b shows a Ni enriched layer containing ~ 60 at. % Ni growing on the surface of a Cu-40 at. % Ni alloy.

Figure 2. Experimental difference spectra for 2.0 MeV He irradiation of (a) a Ni-12.7 at. % Si, (b) a Ni-10 at. % Ge and (c) a Ni-40 at. % Cu alloy.

Figure 3. Ni_3Si layer growth during 2.0 MeV He irradiation at 495°C (filled circles) and at 495°C after preirradiation with 3.25 MeV Kr at 500°C (open squares).

Fig. 1

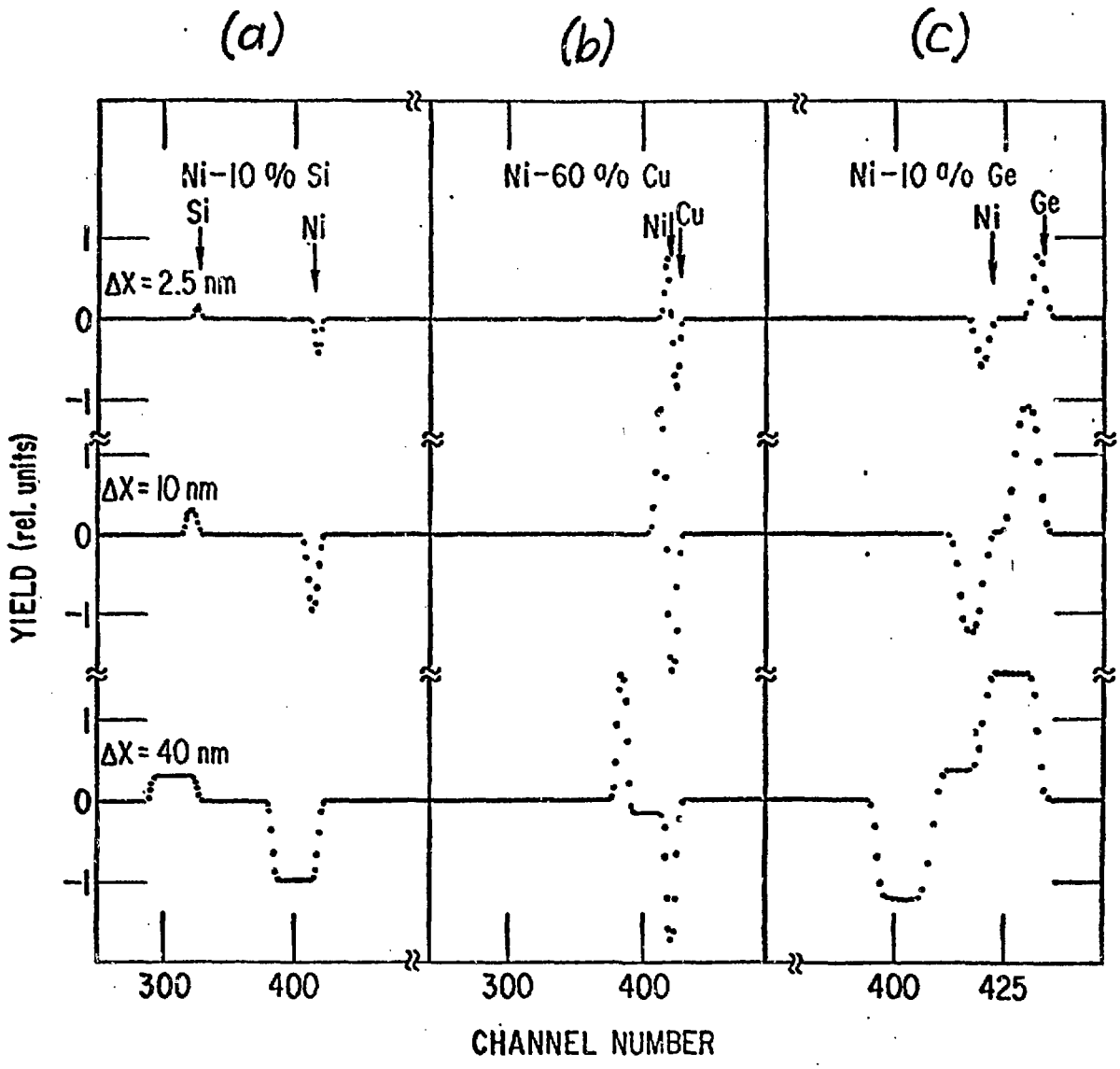
(a)
(b)
(c)
Ni-10 % Si
Si
Ni
Ni-60 % Cu
Ni
Cu
Ni-10 % Ge
Ni
Ge
ΔX = 2.5 nm
ΔX = 10 nm
ΔX = 40 nm
1
0
-1
YIELD (rel. units)
300
400
300
400
400
425
CHANNEL NUMBER

Fig. 2a

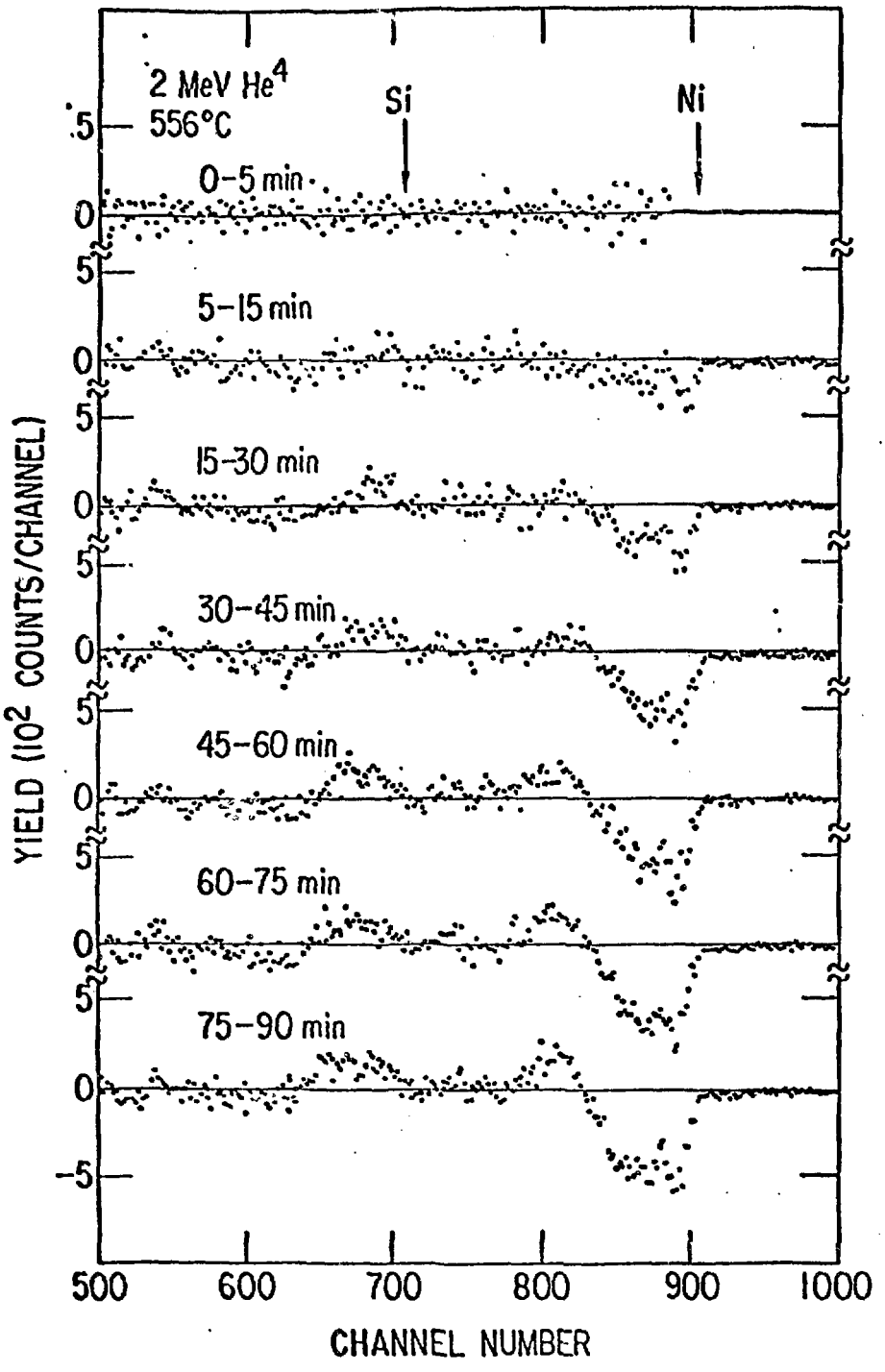
2 MeV He4
556°C
Si
Ni
0-5 min
5-15 min
15-30 min
30-45 min
45-60 min
60-75 min
75-90 min
YIELD (10² COUNTS/CHANNEL)
5
0
5
0
5
0
5
0
5
0
5
0
-5
500
600
700
800
900
1000
CHANNEL NUMBER

Fig. 2b

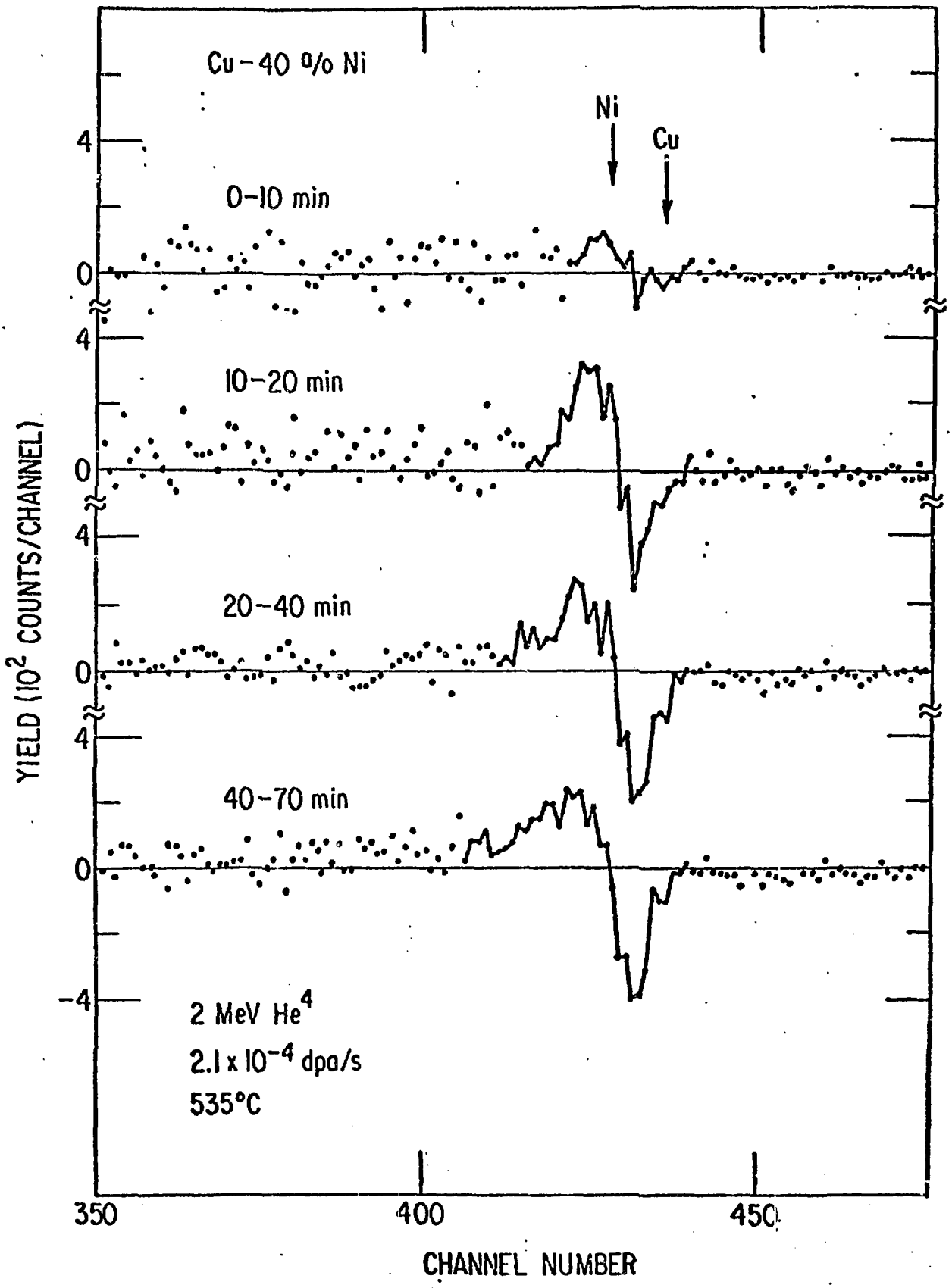
Cu – 40 % Ni
Ni
Cu
0–10 min
10–20 min
20–40 min
40–70 min
2 MeV He4
2.1 x 10-4 dpa/s
535°C
YIELD (10² COUNTS/CHANNEL)
CHANNEL NUMBER
4
0
-4
350
400
450

Fig. 2c

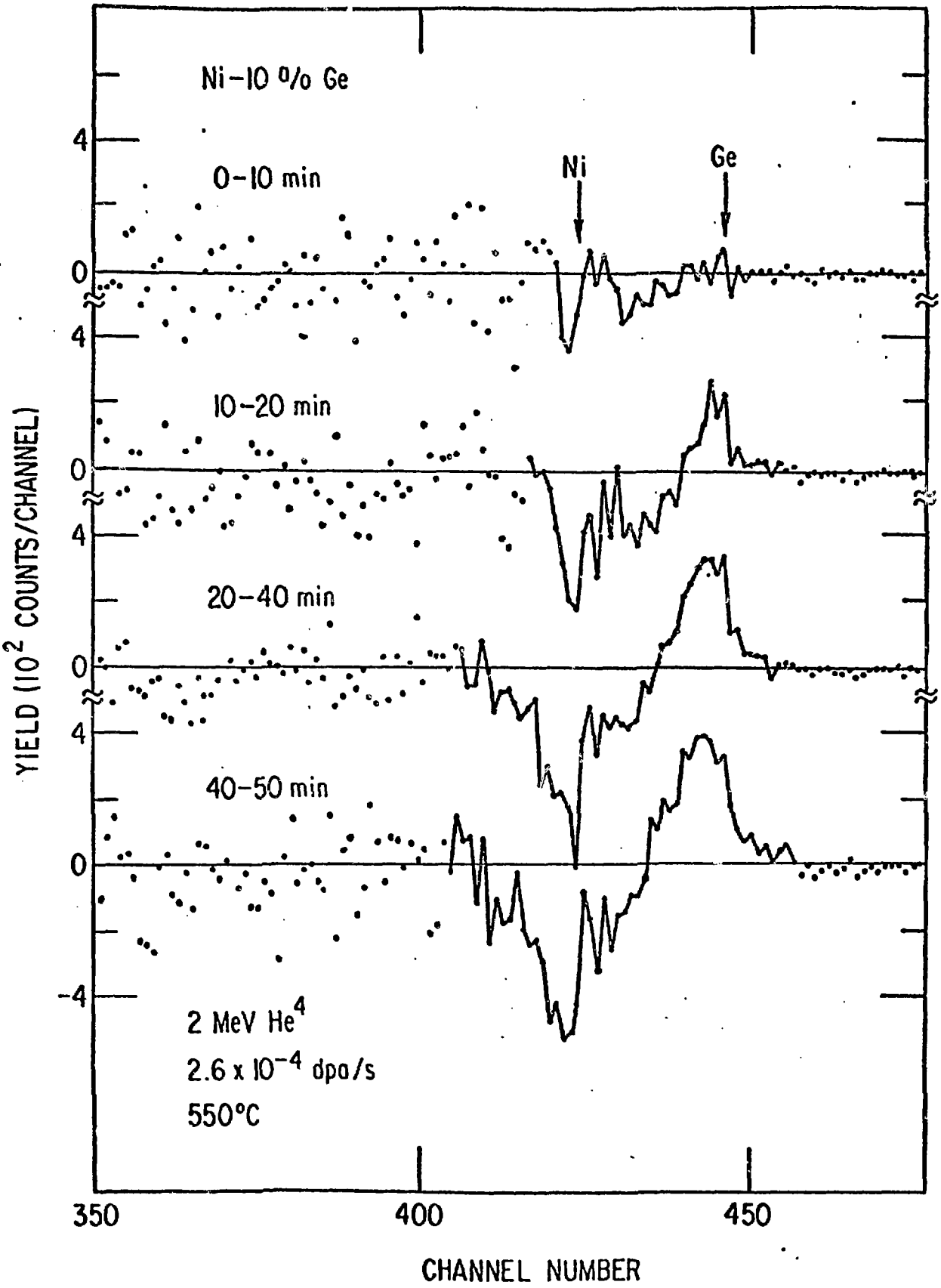
Ni-10 % Ge
0-10 min
Ni
Ge
10-20 min
20-40 min
40-50 min
2 MeV He4
2.6 x 10-4 dpa/s
550°C
YIELD (10^2 COUNTS/CHANNEL)
4
0
4
0
4
0
4
0
-4
350
400
450
CHANNEL NUMBER

Fig. 3