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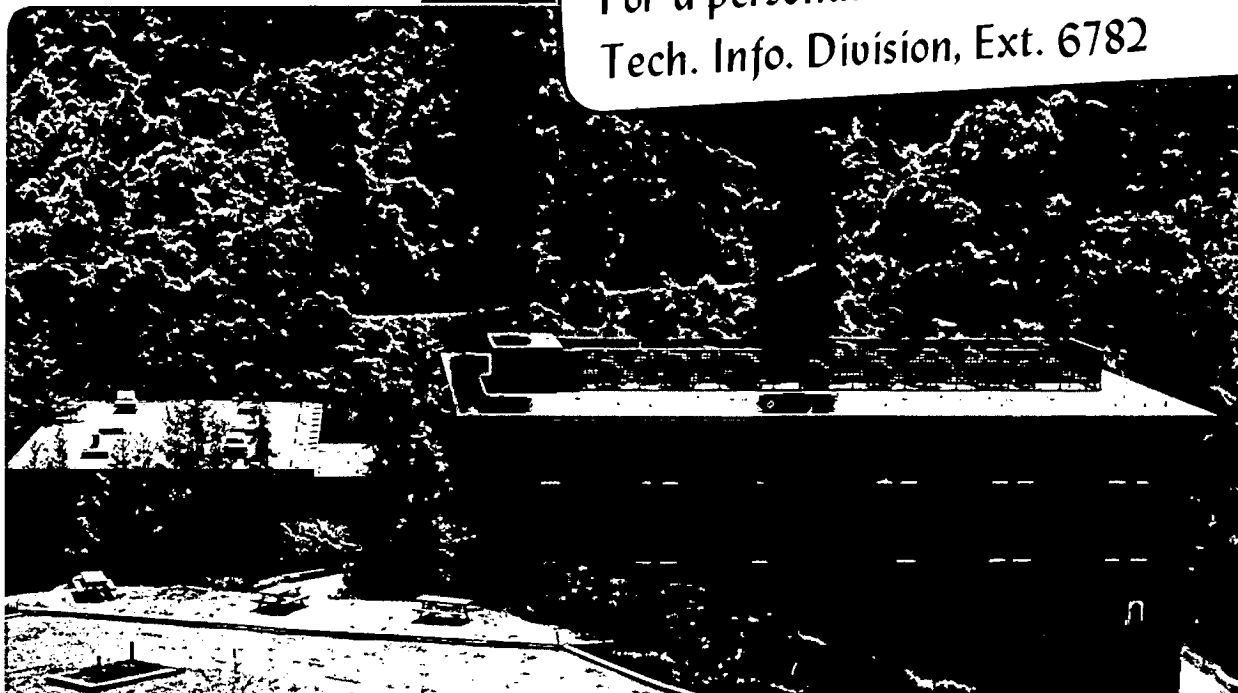
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ELECTRON IRRADIATION INDUCED CRYSTALLINE AMORPHOUS  
TRANSITIONS IN Ni-Ti ALLOYS

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A crystalline to amorphous transition is produced in shape memory NiTi alloys by in-situ electron irradiation in a high voltage electron microscope (1-2MeV). Both the low temperature and high temperature phases are so affected. This is the first time such a transition has been observed in metals. The effect is not due to ionization damage but may arise from some unusual displacement damage processes.

### Introduction

The purpose of this communication is to report a new observation concerned with in-situ electron irradiation studies using high voltage electron microscopy (1,2), as part of a program on phase stabilities in alloy systems. In this particular case a crystalline to amorphous transition is observed in both martensitic (monoclinic) and austenitic (B2 ordered) phases in the NiTi series of shape memory alloys (3,4). Although the electron radiation induced crystalline → amorphous transition is well known in ionization-sensitive materials, e.g. polymers, biological material and certain alkali halides (5-7), so far it has not been observed to occur in metallic alloys. It is interesting, however, to note that these alloys can be made amorphous by the more drastic irradiation damage produced by ion-bombardment (8), but not, so far, by conventional liquid-phase quenching (9).

### Experimental Details

The 3MeV electron microscope at Osaka University provides a wide range of working voltages under which specimens can be observed in-situ under a variety of conditions (temperature, environment, electron dose rate). A description of the microscope with its various stages and some examples of applications are given in references 1, 2. Using a heating or cooling stage (2),

phase transformations can be induced in-situ in the high voltage electron microscope (HVEM) and irradiation studies may be performed at different voltages and electron dose rates.

Near equiatomic Ni-Ti alloys are well-known for their "shape memory properties", which arise from a reversible martensitic reaction. The  $M_s$  temperature is sensitive to composition, and so it is straightforward to study the behavior of both the high and low temperature phases. Alloys in the composition range 50:50 ( $M_s \sim 55^\circ\text{C}$ ) to 51.5:48.5 Ni:Ti ( $M_s \leq -100^\circ\text{C}$ ) were chosen for study, having been prepared by arc melting either under vacuum (U.S.A.) or in an argon atmosphere (Japan). The ingots were rolled into strip form, annealed at 900 or 1000°C and quenched in water at room or ice temperature (respectively). Thin foils were produced from discs by electropolishing at room temperature using a perchloric-acetic acid solution.

### Results and Discussion

Foils were irradiated at 0.5, 1, 1.5 and 2 MeV under varying dose rates from  $\sim 10^{18}$  to  $10^{20}$  electrons/cm<sup>2</sup>/sec. Images were recorded either photographically or on video-tape but it was not possible to take diffraction patterns using the latter method (owing to excessive damage to the detector). Figures 1 and 2 show typical results.

At room temperature, martensitic material is easily converted to the high temperature B2 phase, probably from beam heating effects (this can be achieved by 100kV microscopy using high current densities). One observes detwinning and disappearance of martensite plates, which occurs more rapidly with increasing dose rates. Over a period of time ( $\sim$  minutes), the irradiated area becomes amorphous, as manifested by disappearance of the bend contours in bright field images and by the gradual replacement of the diffraction spots by

a diffuse ring, typical of an amorphous material, in the diffraction pattern. As may be expected, this also occurs more rapidly with higher dose rates.

The knock-on displacement threshold for NiTi is approximately 0.5 MeV. Vitrefication does not occur at this voltage, but becomes extensive above 1 MeV. This is opposite to the voltage dependence of ionization damage of organic and inorganic crystals (5-7) which decreases with increasing electron energy. Thus it is thought that a displacement, rather than an ionization mechanism, is responsible for the present behavior.

Alloys held at  $-100^{\circ}\text{C}$ , in the martensitic state, are also vitrefied. It was not established whether the high temperature phase was produced as an intermediate step. Likewise, it has not been determined whether the alloy disorders prior to vitrefication, although the ordered B2 superlattice reflections appear to remain strong in the diffraction pattern. Both issues are important to understanding the relevant damage mechanism. On the other hand, specimens held at  $200^{\circ}\text{C}$  did not vitrefy. This might arise from immediate crystallization at this higher temperature, although there may be the possibility that the behavior is related to the  $M_s$  temperature and premartensitic instabilities (10) of the material. The observations indicated that the rate of vitrefication increased with decreasing temperature. Again, it is worth noting that this is opposite to ionization-induced vitrefication, which in some cases can be reduced dramatically at low temperature (5).

At present the influence of composition is not clear. Alloys with purportedly the same composition, but fabricated in different laboratories, show markedly different transformation rates. This may be due to different interstitial content of the alloys, particularly oxygen which is known to affect the properties of NiTi significantly.

The amorphous transition appears to be less rapid in the thinnest parts of the foils. The latter indications suggest that point defect concentrations and

mobility may be important in the transition (interstitials are expected to escape easily in thin foils).

The present results are interesting in the radiation damage field, since to our knowledge no other alloy has been made amorphous with such mild damage conditions. Specifically, neither elemental nickel or elemental titanium show this effect (11). There are important implications for the engineering applications of these alloys (ie. nitinol) in an irradiation environment such as a nuclear reactor. When made amorphous, the shape memory effect will be destroyed since it relies on the transition from one crystal structure to another. Furthermore, the mechanical properties are likely to be altered in a possibly deleterious way.

Much work remains to be done to find the conditions (composition, temperature, dose rate, electron energy, etc.) under which vitrefication occurs and its effect on bulk properties. Fundamental insight into the atomic mechanisms of the reaction is lacking in this preliminary work and will require extensive further experimentation. The structural nature of the amorphous state so created is also intriguing, especially since near equiatomic NiTi has not been made amorphous by conventional procedures (e.g. splat cooling).

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Figure Captions

Fig. 1. 50/50 alloy fully martensitic: (a) before irradiation; (b) 5 mins at 2MeV; dose  $\sim 10^{19}$  elec/cm<sup>2</sup>/sec transformation to austenite has occurred; (c) dose increased to  $10^{20}$  elec/cm<sup>2</sup>/sec and foil exposed further 30 mins; austenite has become amorphous in the volume irradiated. Foil orientation  $[\bar{3} \bar{5} \bar{1}]B2$ .

Fig. 2. 51/49 alloy ( $M_s \sim 100^\circ C$ ) fully austenitic (a) before irradiation SAD shows  $[1 1 1]B2$  orientation; (b) same area after 13 mins dose at  $3.5 \times 10^{18}$  elec/cm<sup>2</sup>/sec. Pattern shows two diffuse halos. Irradiated at 1MeV in cold stage at  $-80^\circ C$ .

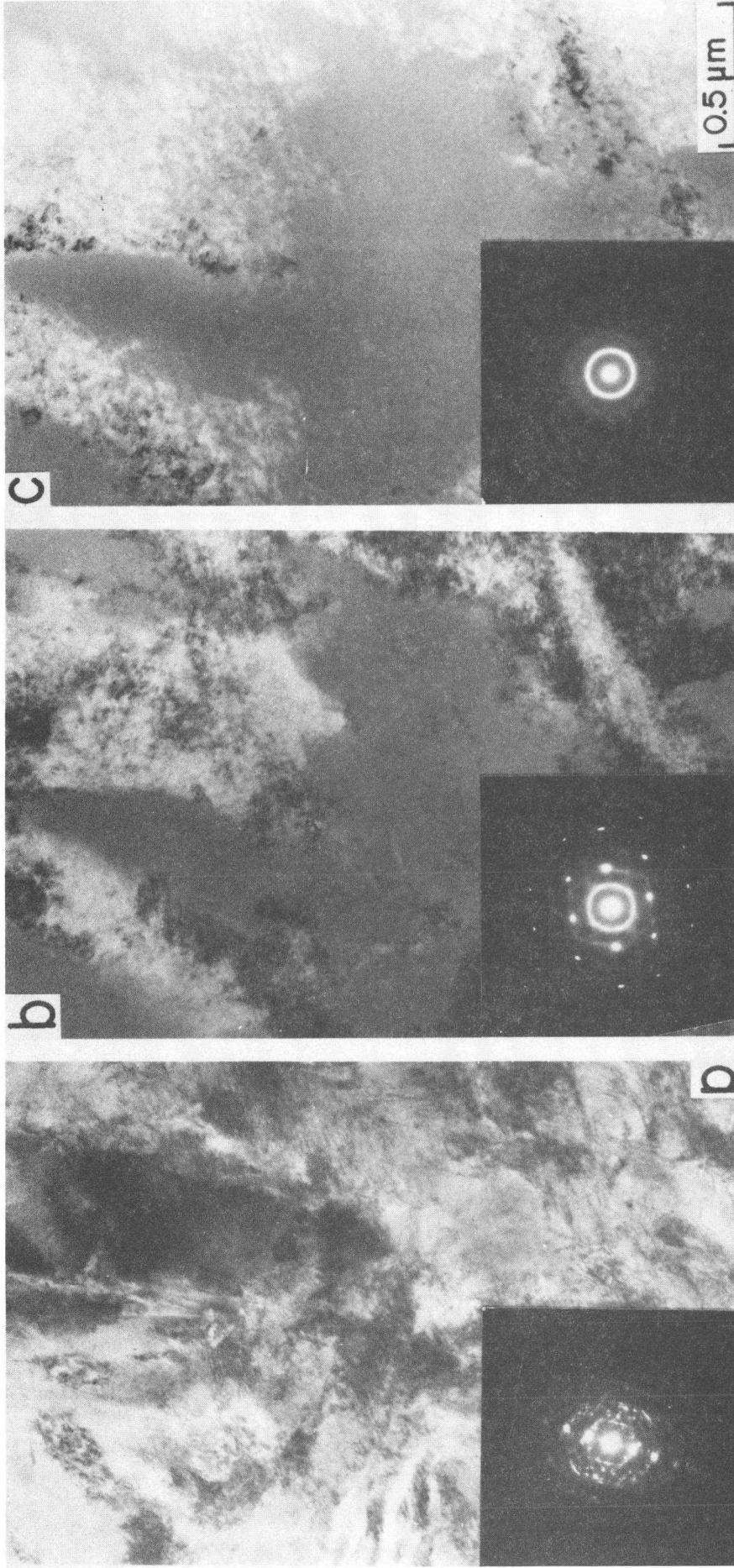
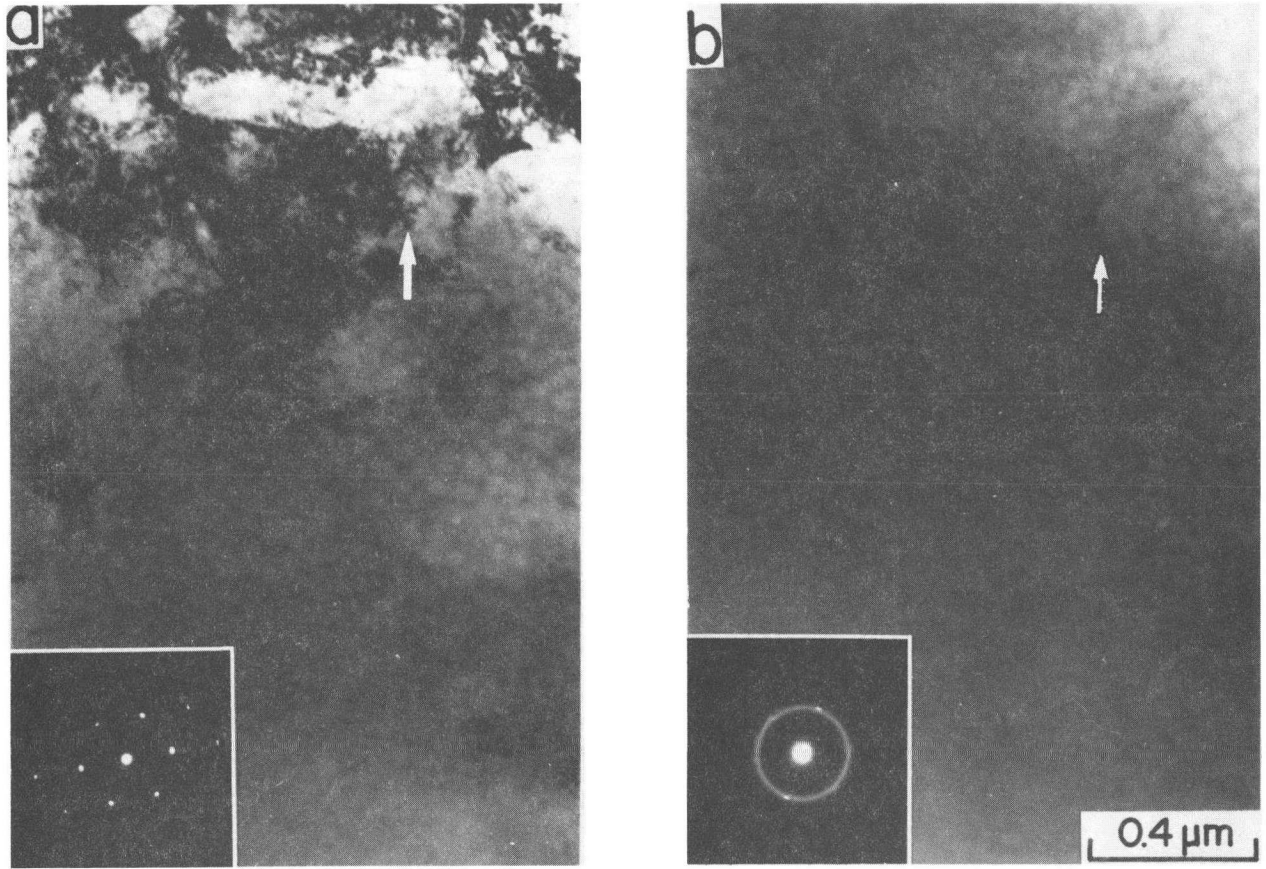


Fig. 1



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Fig. 2

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