THE EFFECT OF MICROSTRUCTURE IN THE MORPHOLOGY
AND KINETICS OF AMORPHIZATION INDUCED BY ION IRRADIATION

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ABSTRACT

NiTi was irradiated with Ni ions to study the rate of amorphization as a function of temperature and to determine the temperature cutoff for the crystalline-to-amorphous transition. A series of irradiations was conducted at different temperatures from ambient to 350 °C. Prior to irradiation, the specimens contained martensitic plates and austenitic (B2) regions. However, during irradiation at temperatures of 80 °C and higher, all the specimens were entirely austenitic. As expected, amorphization was delayed as the irradiation temperature was increased. The fraction of material that became amorphous after irradiation at 250 °C to a dose of 0.7 dpa was estimated to be 5 to 10%. Specimens irradiated at higher temperatures remained crystalline, even after doses as high as 4 dpa. Irrespective of the irradiation temperature, we found a non-uniform distribution of amorphous regions that exhibited a morphology closely resembling the shape of the martensitic plates that existed in the material prior to heating it to the irradiation temperature. These observations are discussed in terms of the influence of structural defects on the kinetics of amorphization.

INTRODUCTION

The high temperature phase of the intermetallic NiTi of near equiatomic composition is an ordered compound with the B2 (CsCl-type) structure (also referred to as austenite for NiTi) up to the melting point. Upon cooling, this compound may transform martensitically into a B19' structure [1] or into a phase of rhombohedral symmetry known as the R-phase [2], or both [3]. The M_s temperature is sensitive to composition [4] as well as to the thermal history of the specimen [5]. Although the type of phase transformation that occurs strongly depends upon the cooling rate, all the thermal quenching processes reported for this intermetallic compound, including rapid solidification by splat quenching, melt spinning and laser melting, have produced a crystalline ordered phase [6,7]. By contrast, irradiation with electrons [8,9], protons [10] and heavy ions [11-13] have induced a crystalline-to-amorphous transition even at room temperature, after relatively low doses. In-situ, low temperature, high voltage electron microscope observations revealed a sequence of transformations with increasing dose. The observed transition sequence, martensite → ordered B2 → bcc → amorphous [8], indicated that loss of chemical long range order (CLRO) preceded amorphization.

Different effects were reported for room temperature Ni-ion irradiated NiTi. In-situ observations during ion irradiation of martensitic NiTi films revealed that amorphization occurred without any detectable phase transformation into other crystalline phases, at a much faster rate than under electron bombardment [12]. By contrast, low dose irradiation of mostly martensitic thick specimens produced amorphous regions (~ 50%), ordered B2 and little or no martensite [13]. The morphology of the amorphized regions was also different in the two specimen types. In the thin films, small amorphous regions kept forming with increasing dose without significant increase in size until coalescence took place.[12] The irradiated thick specimens exhibited massive amorphous regions immersed in a damaged crystalline matrix. These amorphous regions had, in certain regions, a plate-like morphology resembling the pre-irradiation martensitic plates [13]. The difference in morphology was, however, not related to the specimen thickness. Other thick specimen irradiation experiments have revealed that a large number of small amorphous regions apparently increased in size but not in concentration, as the dose was increased [11].

Our room temperature Ni-ion irradiation experiments yielded a transition path partly similar to that obtained under electron bombardment. If some loss of CLRO occurred, we were unable to detect it at the later time of observation. The peculiar morphology of the amorphous regions first suggested that some martensitic plates became amorphous directly, while others transformed first to austenite. Another possibility was that the transformation to

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B2 was an intermediate step, but it proceeded very inhomogeneously throughout the sample depending on the particular plate internal microstructure. The morphology of the amorphized regions was, at any rate, a clear indication of a complex dependence of the overall amorphization rate upon the specimen microstructure. In order to gain some insight into that dependence, we performed a series of irradiations at various temperatures between 80 and 350°C, to several doses. Post-irradiation annealing experiments on a sample irradiated at 200°C added further data for analysis.

EXPERIMENTAL

Prior to irradiation, disc-shaped specimens of Ni-49.5 at. pct. Ti were annealed for 30 min at 850°C and air quenched (A-specimens) or at 1000°C and furnace cooled (B-specimens). The specimens were irradiated to several doses with 3MeV Ni²⁺-ions, using beam currents in the range of 50–85 nA/cm². The irradiations were conducted at nominal temperatures of 80°C (A-specimens), and 150, 200, 250 and 350°C (B-specimens). The temperature during irradiation was monitored with a thermocouple spot-welded to one specimen of a group that was irradiated at the same time. The heating time to reach the irradiation temperature varied between 30 and 180 minutes. Since martensite reverts to austenite within minutes at 80°C, all the irradiations were conducted in fully austenitic (B2) samples. The irradiated samples were observed by transmission electron microscopy. Thin foils were prepared for observation at a depth of 0.55μm, which is approximately halfway between the surface and the ion range. Phase identification was done using selected area diffraction. Amorphous and crystalline regions were also distinguished by using convergent beam electron diffraction and appropriate dark-field imaging techniques. The post-irradiation annealing experiments were conducted in-situ in a Philips CM12 analytical electron microscope, using a single-tilt heating holder with the specimen held in a 10W tantalum furnace. The temperature was increased stepwise to various temperatures. The initial increment was from room temperature to 200°C, and holding times at each temperature varied between 10 and 20 minutes. When the temperature was increased to 425°C microstructural changes became detectable, and no further temperature increase was made. Details of the irradiations and of the post-irradiation annealing are given elsewhere [14,15].

RESULTS

Selected area electron diffraction patterns revealed that both sets of specimens contained a multivariant martensitic structure after their thermal treatment. Figure 1 shows the pre-irradiation microstructure of the A- and B-specimens. The A-specimens showed a very complex, mostly martensitic microstructure with very fine platelets, while the B-specimens contained about 50% of well resolved martensitic plates and, the remainder, a mixture of B2 and R-phase. After irradiation at 80°C to a dose of 0.055 dpa, an A-specimen was partly amorphous, as can be seen in Figure 2. Although at the time of irradiation the specimen must have been austenitic, the morphology still shows a striking analogy to martensitic plates. It is difficult to relate the structure of Figure 2 with that of Figure 1a, but there seems to be a correspondence between the amorphous regions and a group of formerly existing platelets.

The amorphization kinetics was rapid at 150°C, since after a dose of 0.20 dpa the material was mostly amorphous and no crystalline traces were detected after 0.31 dpa. At 200°C the kinetics slowed significantly, since after a dose of 0.29 dpa no amorphous regions were detected, although the crystal, which remained austenitic after cooling back to room temperature, was substantially damaged as revealed by the strain contrast image shown in Figure 3. Notice that some traces of the original martensitic microstructure are still apparent in the heavily damaged sample. After 0.49 dpa at 200°C, approximately 50% of the specimen had become amorphous at the observation depth. Again in this case the plate-like morphology of the amorphous regions was quite evident, as shown in Figure 4. The crystalline-amorphous interfaces appeared well defined, and only at a high magnification could the rugged nature of the interface be noticed [14]. Selected area diffraction (SAD) patterns of large amorphous regions showed a spot pattern superimposed to the diffuse ring produced by the amorphous material, thus revealing the presence of crystalline traces. Further evidence of this crystalline debris was obtained from dark field images produced with the aperture placed on a

Fig 1. Microstructure of NiTi specimens prior to heating to the irradiation temperature.
(a) A-specimens (b) B-specimens

Fig 2. Bright field image of a NiTi A-specimen irradiated at 80°C to a dose of 0.055 dpa. Plate-like amorphous regions surrounded by a heavily damaged crystalline B2 material showing the damage in dark contrast.

Fig 3. Bright field image of a NiTi B-specimen irradiated at 200°C to a dose of 0.29 dpa. The material contains only B2 phase and is very damaged. The arrows point to some traces apparently related to the previous martensitic structure.

Fig 4. Bright field image of a B-specimen irradiated at 200°C to a dose of 0.49 dpa.

110 reflection of a SAD pattern obtained from a mostly amorphous region. Also, rings were seen superimposed on to a strong spot pattern taken in a mostly crystalline area, suggesting that many very small amorphous regions were mixed into an otherwise crystalline and damaged matrix. The crystalline portions were fully austenitic (B2).

During irradiation at 250°C, the amorphization kinetics were even slower than at 200°C, and after 0.67 dpa only a very small fraction of the material became amorphous. Figure 5 shows a part of the specimen containing an appreciable number of amorphous regions. The plate-like morphology of these amorphous regions is once more noticeable. In this case, however, no crystalline debris was observed inside the plates. This result forecloses the possibility that amorphized regions were crystallizing during irradiation.

After cooling, the partly amorphous specimens irradiated at 250°C contained B2 and R phases, and perhaps a very small amount of martensite. The specimens irradiated at 350°C remained crystalline even after doses as high as 4 dpa. After cooling to room temperature, these specimens contained, martensite in addition to the B2 and R phase and some unidentified planar defects. [14]

A specimen rendered partly amorphous by irradiation at 200°C to a dose of 0.49 dpa did not experience any microstructural changes during a sequence of step-wise post-irradiation anneals between 200 and 425°C, for a period totaling 94 min. However, after that time rapid changes began when the temperature reached 425°C. First, crystallization of the amorphous regions commenced, without involving any participation of the crystalline-amorphous interface, as can be seen in Figure 6. Next, the crystalline regions were seen to recover by annealing out the radiation-induced damage. Perhaps some recrystallization also occurred. [15]

Fig 5. Bright field image of a B-specimen irradiated at 250°C to a dose of 0.67 dpa.

Fig 6. Bright field image recorded in-situ during annealing at 425°C. The arrows point to crystals nucleated in the interior of an amorphous plate.

DISCUSSION AND CONCLUSIONS

Since ion irradiation induces displacement cascades randomly, once the process of amorphization has started one would expect that, in a microstructurally homogeneous material, the transition would proceed uniformly throughout the region that has received a uniform dose. The results presented here, however, do not conform to that expectation. Independent of the temperature, the morphological features of the transition reveal clearly that the kinetics are non-uniform. Namely, the total dose does not completely determine, at a given temperature and dose rate, the kinetics of amorphization. Our first conclusion is that microstructural inhomogeneities must be influencing the rate of amorphization locally.

An acceleration of the crystalline to amorphous transition has been observed, in single phase alloys, in the vicinity of crystalline imperfections such as dislocations [8,17].

Amorphization has also been observed at and near these imperfections while the dislocation-free regions of the material remained crystalline up to very high irradiation doses [17]. Dislocations are strong point defect sinks, and their influence on lattice stability is a strong indication of the role point defects play in the amorphization process.

In previous studies we have adopted the criterion that point defect accumulation to a critical level causes the instability of the crystalline lattice and its subsequent amorphization [18-20]. In the absence of a mechanism for interstitial retention in the lattice, at the temperatures at which vacancy mobility is poor while interstitials annihilate at sinks and control the Frenkel pair recombination, there is a much larger population of vacancies than interstitials. However, we have shown that buildup of vacancies and interstitials is not sufficient to produce the high level of point defect accumulation required to destabilize the crystal. Hence, we proposed that point defects could be retained in intermetallic compounds if, under certain conditions, instead of recombining they became coupled forming a complex. Since irradiation induces chemical disorder, the formation of that complex defect was related to the tendency of the intermetallic to be ordered, which corresponds to its lowest free energy state. The simplest model of that complex defect consists of a vacancy-interstitial pair, and assumes a trapping phenomenon. Trapping of an interstitial may occur in an atomic environment that allows the trapped species to establish a chemical short range order with this atomic environment. This trapping configuration can be stabilized by the presence of a nearby vacancy. Instability against amorphization is produced by the local buildup of vacancy-interstitial complex defects. These complexes are metastable and may undergo thermal decomposition as well as destruction from freely migrating interstitials that recombine with the vacancy trapped in a pair. This metastability of the complexes is essential to account for the temperature dependence of the amorphization rate.

Our modeling included both a mechanism of complex buildup and direct amorphization during the collapse stage of the displacement cascade. In our experiments the kinetics cannot be described by the latter process alone since the entire observation region has been uniformly irradiated to the same dose. Other authors, even though they observed a more uniform distribution of amorphous regions, arrived at the same conclusion due to the rate of increase of the amorphous fraction as a function of irradiation dose which reflected a cumulative rather than a direct impact mechanism. [11,12]. This is a highly nonlinear phenomenon due to Frenkel pair recombination and to complex destruction by freely migrating interstitials. We have shown that interstitial annihilation other than by recombination with vacancies (assumed immobile) enhances the buildup of complexes [21]. The reason is the reduction of the interstitial population available to recombine with vacancies that pertain to complexes. Therefore, the presence of interstitial sinks enhances the amorphization rate, in agreement with the previously referred observations [8,17].

In our experiments, the martensitic structure reverted to the ordered B2 phase prior to irradiation. For thermoelastic martensites, such as that occurring in NiTi, the reversion can occur either by the plate dissolving as though it were following the reverse path of its growth or by a nucleation event taking place at the midrib of double plates, or at the site where the midrib existed. The particular reversion path depends on the development stage of the plate. Figure 1b shows that both small and large, single and double plates had been present in our specimens prior to irradiation. We may thus expect that the reversion process during heating to the irradiation temperature was complex and non-uniform. Moreover, if the reversion modes were different, the resulting crystal would also exhibit a fairly non-uniform distribution of defects. These defects remained in the matrix at the relatively low temperatures to which the specimens were heated for irradiation. However, if the density of those defects was high in certain regions and they were strong point defect sinks, they could have acted as described above and favored the rapid buildup of complex defects capable of destabilizing the crystalline structure. This would explain the plate-like morphology of the earlier amorphized regions in a material that did not contain any plates at the time that it was subjected to irradiation. It also explains the difference of amorphization kinetics among regions.

The occurrence of preferential amorphization in the sample underlines a basic feature of the irradiation induced process, viz., that amorphization is a highly localized phenomenon similar to a nucleation process. The view that amorphization is extremely sensitive to the local crystalline imperfections and their interaction with radiation induced point defects is consistent with that feature. This affects both the kinetics and the morphology of the transition. The effects on the kinetics are further emphasized by the post-irradiation

annealing experiments, which showed that crystallization of the amorphous portions occurred independently of changes in the damaged crystalline regions. After the rapid amorphization of the more defective portions of the specimen, further irradiation of the amorphous regions modified their structure as well as induced further damage in the remaining crystal.

We conclude that radiation-induced amorphization closely depends on the microstructure of the specimen. The cutoff temperature for amorphization is also a function of the microstructure. There is an upper cutoff temperature above which recovery of a very defective specimen will occur at a rate fast enough to prevent the occurrence of amorphization. In our NiTi compounds, this upper cutoff is about 250°C.

REFERENCES

1. K. Otsuka, T. Sawamura, and K. Shimizu, *Phys. Stat. Sol.* **5**, 457 (1971)
2. M. Matsumoto and T. Honma, in New Aspects of Martensitic Transformations, JIM Int. Symp (The Japan Institute of Metals, Kobe, Japan, 1976) p.199
3. V.N. Kiachin, Yu. A. Paskal', V.E. Gunter, A.A. Monasevich, and V.P. Sivokha, *Phys. Met. Metall.* **46**, 49 (1979)
4. W.J. Buehler and F.E. Wang, *Ocean Eng.* **1**, 105 (1968)
5. A.I. Lotkov, V.N. Grishkov, A.V. Kuznetsov, and S.N. Kulkov, *Phys. Stat. Sol. (a)* **75**, 373 (1983)
6. K.H.J. Buschow, *J. Phys. F: Met. Phys.* **13**, 563 (1983)
7. A.J. Pedraza, M.J. Godbole, E.A. Kenik, D.F. Pedraza, and D.H. Lowndes, in Beam-Solid Interactions and Transient Processes, edited by S.T. Picraux, M.O. Thompson and J.S. Williams (North Holland, 1987) p.185
8. H. Mori and H. Fujita, *Jpn. J. Appl. Phys.* **21**, L494 (1982)
9. H. Mori and H. Fujita, and M. Fujita, *Jpn. J. Appl. Phys.* **22**, L94 (1983)
10. J. Cheng and A. Ardell, in press in *Nucl. Instr. and Methods in Phys Res B* (1989)
11. J.L. Brimhall, H.E. Kissinger and A.R. Pelton, in Ion Implantation and Beam Processing of Materials, ed. by G.K. Hubler, O.W. Holland, C.R. Clayton and C.W. White (North Holland, 1984) p.163
12. P. Moine, J.P. Riviere, M.O. Ruault, J. Chaumont, and A. Pelton, *Nucl. Instr. and Methods in Physics Res.* **B7/8**, 20 (1985)
13. P.J. Maziasz, N. H. Packan, D.F. Pedraza, and E.H. Lee, in Proceedings of the 45th Annual EMSA Meeting, (San Francisco Press, 1987) p.220
14. P.J. Maziasz, D.F. Pedraza, J.P. Simmons, and N. H. Packan, submitted to *J. Mater. Res.*
15. P.J. Maziasz and D.F. Pedraza, *Scr. Met.* **23**, 1743 (1989)
16. D.F. Pedraza, in press in *Metal. Trans.* (1989)
17. G.J.C. Carpenter and E.M. Schulson, *J. Nucl. Mater.* **73**, 180 (1978)
18. D.F. Pedraza, *J. Mat. Res.* **1**, 425 (1986)
19. D.F. Pedraza and L.K. Mansur, *Nucl. Instr. and Meth. B*, **16**, 203 (1986)
20. D.F. Pedraza, *J. Less Common Metals* **140**, 219 (1988)
21. D.F. Pedraza, *Mater. Sci. & Eng.* **20**, 69 (1987)

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