

Microstructure of phosphorus ion-implanted TiNi alloy

ZHAO XINGKE*

Harbin Institute of Technology, Harbin, 150001, China; Shanghai Institute of Applied Physics, Shanghai 201800, China

E-mail: zhaoxingke@yahoo.com

GAO ZHIYONG, CAI WEI, ZHAO LIANCHENG

Harbin Institute of Technology, Harbin 150001, China

TiNi alloy, well known for its shape memory effect, super-elasticity, corrosion resistance and biocompatibility, is a suitable material for making intravascular stent [1]. Restenosis ratio of stenting cases is quite higher (about 20 to 30% within three months to one year after stenting operation), so radiation delivered by stent is an appealing approach to reduce the restenosis rate due to the controlling of neointima hyperplasia. [2, 3]. ^{32}P is the most popular local radioactive isotope because of its pure beta-ray irradiation and a suitable half-life of 14.3d [4]. But this beta-ray energy can only provide a limited depth penetration that magnifies the radiate dose inhomogeneity between stent struts and results in "end-stent-failure" (or "candy effect") [5]. The problem of restenosis could not be overcome as had been anticipated. Attention now has been focused on improving radiate dose inhomogeneity and decreasing the end-stent-failure [6, 7].

Radiate dose inhomogeneity could be improved by making use of a mixture of ^{32}P and other radioactive isotope with a higher ray energy [6, 7]. In our recent researches, a mixed radiation has been produced by TiNi alloy treatment of phosphorous-ion-implanted (PII) followed by irradiated in slow neutron flow. PII treatment would change the surface compositions and constitutional phases, which could be of most important on biocompatibility. In the present study, microstructure of ion implanted TiNi alloys is investigated.

The experimental alloy was Ti-50.6Ni (at%). Specimens were cut from cold-rolled plates. PII treatments were carried in a plasma-merged system. The implantation voltage was 60 KV and the dose of Phosphorus was $(2-10) \times 10^{17} \text{ P/cm}^2$. Microstructures were studied with transmission electron microscopy (TEM) and high-resolution electron microscopy (HREM). Phase constitution was studied with small grazing incidence angle X-ray diffraction (GAXRD).

Before PII treatment, TiNi alloy specimen has an Ms temperature of 294 K. Therefore there is one and only parent phase (B2) at room temperature. As Phosphorous dose exceed $4 \times 10^{17} \text{ P/cm}^2$, martensite phase appears in the PII layer. Fig. 1 shows the typical microstructure of PII layer, with strip-shaped martensites ranked neatly.

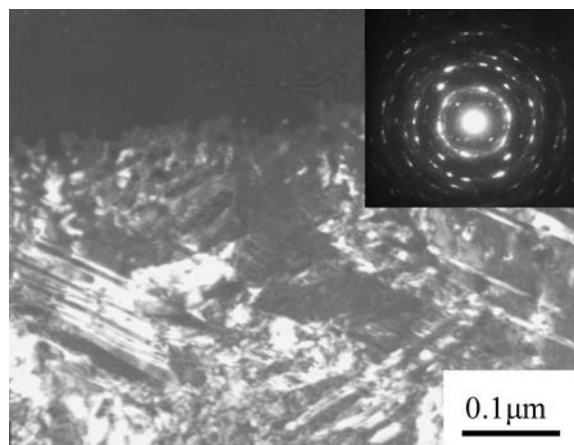


Figure 1 Martensite formed in the near surface area of P ion-implanted specimen with implanting voltage of 60 kV and the dose of $4 \times 10^{17} \text{ P/cm}^2$.

As Phosphorous dose exceed 10^{18} P/cm^2 , amorphous is the dominant phase in the PII treated layer (see Fig. 2a). The microstructure is made up of two parts: tint base and on it fuscous particulates. Fig. 2b shows an amplificatory image of fuscous particulates on Fig. 2a, with white dashed marking approximately its boundary. Regular stria are obvious on the fuscous particulates. These stria twist on the boundary of fuscous particulates, and get faintness with stretching into the tint base. The SAED patterns of tint base and fuscous particulates are shown in Fig. 2c and 2d, respectively. Fig. 2c shows hollow ring pattern, implying that the tint base is amorphous; whereas Fig. 2d shows that the fuscous particulates are crystal structure phases.

When the Phosphorous dose is within $4 \times 10^{17} - 8 \times 10^{17} \text{ P/cm}^2$, the microstructure of PII treated layer is the mixtures of amorphous and martensite. Fig. 3 shows the TEM images and corresponding SAED patterns of PII-treated layer with dose of $6 \times 10^{17} \text{ P/cm}^2$.

Fig. 4 shows the microstructure and corresponding SAED patterns of an annealed PII-treated layer. The annealing temperature is 773 K and the implanting dose is $4 \times 10^{17} \text{ P/cm}^2$. Fewer martensite plates exist in annealed specimen than in as-ion-implanted specimen (see Fig. 1). This implies that anneal could eliminate the effect of Phosphorous ion implanting.

* Author to whom all correspondence should be addressed.

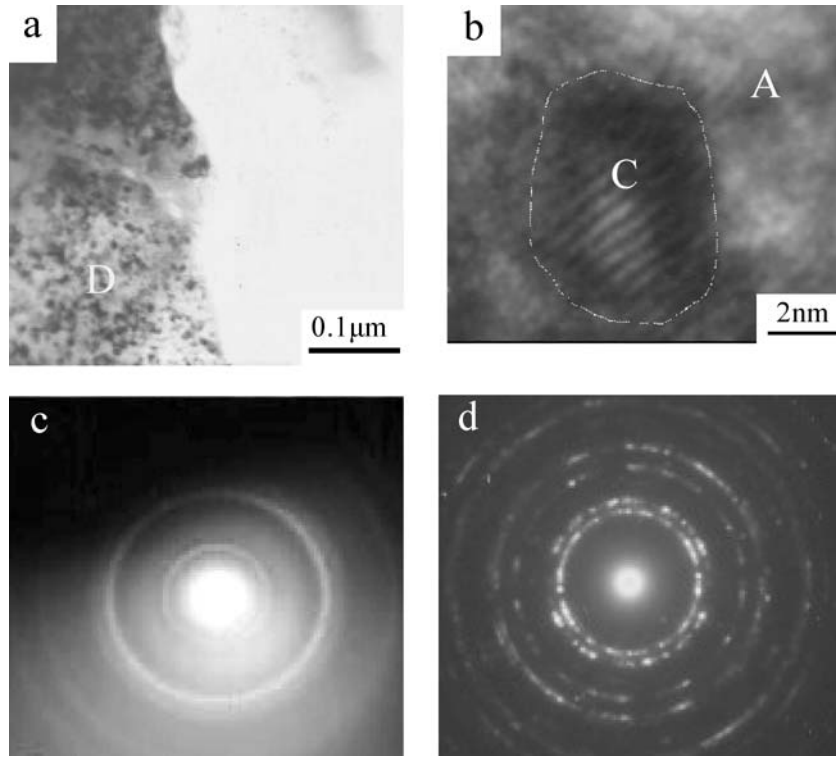


Figure 2 TEM images and corresponding SAED patterns of PII layer with dose of 10^{18} P/cm² (a) Bright field image; (b) enlarged image of area D in (a); (c) SAED pattern taken from area A in (b); (d) SAED pattern taken from area C in (b).

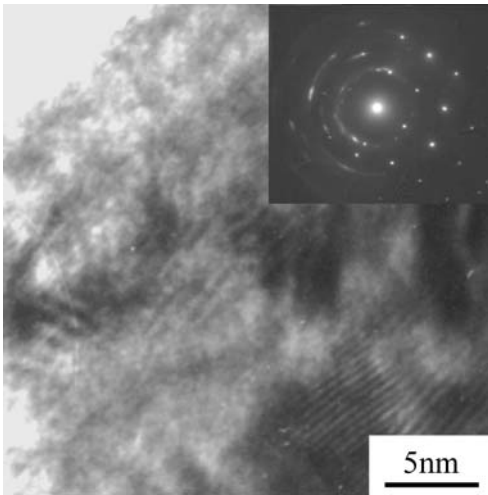


Figure 3 TEM image and SAED patterns for mixture of martensite and amorphous formed in P implanted specimen with dose of 8×10^{17} P/cm².

The phase constitution of PII layer is tested by GAXRD. As the thickness of PII layer is very small (about 40 nm measured by X-ray photon spectra), the GAXRD spectra give not only the phase constitution of PII layer but also that of base alloy beyond PII layer. Fig. 5 shows the GAXRD spectra of layer of TiNi specimens before (Fig. 5a) and after PII treatment (Fig. 5b). Fig. 5a shows that parent phase (B2) is one and only phase in TiNi specimen before PII treatment; Whereas Fig. 5b shows few phosphides (mainly P₂O₅) and martensite (B19') in the PII layer. The intensity peak in Fig. 5b is broader than that in Fig. 5a, which implies that stress and crystal structure aberration occur during PII treatment.

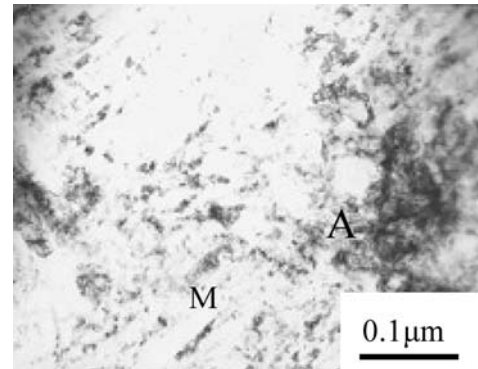


Figure 4 Microstructure of PII treated layer after annealed at 773 K for 30 min.

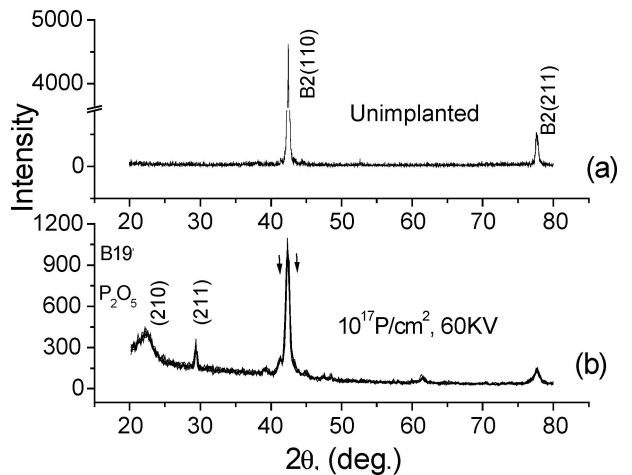


Figure 5 GAXRD spectra of TiNi specimens (a) before and (b) after PII treatment.

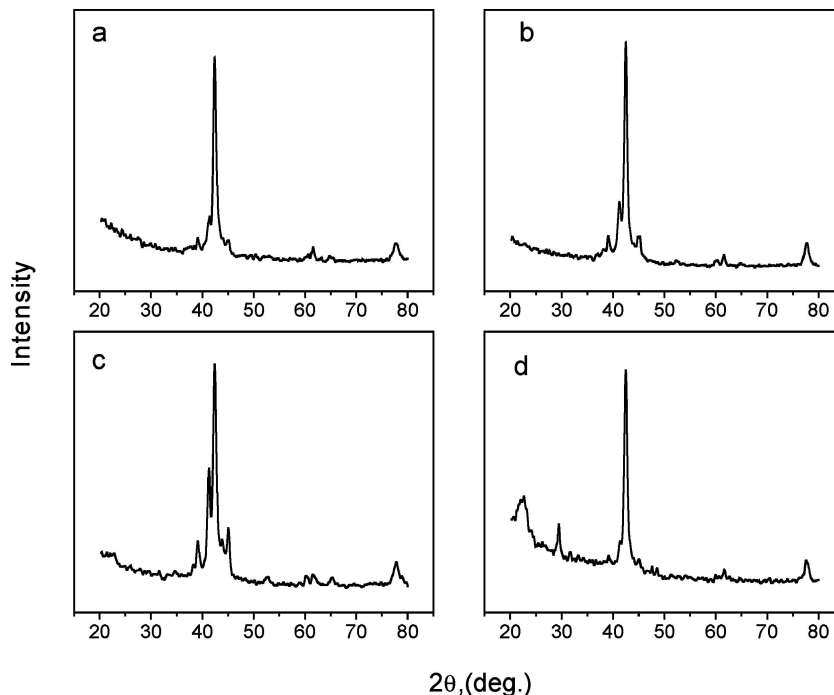


Figure 6 GAXRD spectra as a function of phosphorus implant doses. (a) 0, (b) 1×10^{17} P/cm², (c) 4×10^{17} P/cm² and (d) 1×10^{18} P/cm².

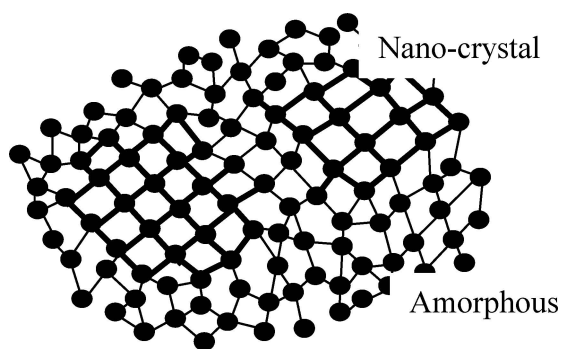


Figure 7 Structure model of amorphous and nano-crystal in PII layer

Fig. 6 shows a series of GAXRD spectra evolving with Phosphorus dose increasing from 10^{17} to 10^{18} P/cm². In the middle Phosphorous dose (see Fig. 6c, and 6d), the intensity peak of martensite is clearest compared to small and large amount of Phosphorous dose. From this fact we could deduce that martensite formed easier than amorphous phase during PII treatment, in other words, amorphous phase forms from martensite.

Parkhomenko *et al.* had calculated formation energies and values of displacements of atoms for various versions of radiation defects [8]. The defect complexes of Ti atoms in place of Ni atoms plus vacancies in place of Ni atoms have the minimum formation energy (approximately 20 times smaller than other defects and defect complexes). Phosphorous ion implanting should have the similar affect on crystal as radiation. Crystal defect will induce martensite phase transformation by the reason of higher stress status and easier atom movement. As the implantation dose increase, displacements of Ni and Ti atoms will be sufficient for amorphization.

Fig. 7 shows the structure model of amorphous and nano-crystal in PII layer. It is quite natural that packing of atoms and typical distances in such amorphous matter should not differ significantly from those parameters in a crystal before ion implanting. This can explain very well the effects of Phosphorous dose on the microstructure of PII layer.

In conclusion, Martensite and amorphous phases were formed in succession as Phosphorous ion implanting dose increasing from 10^{17} to 10^{18} P/cm². Annealing at a temperature above 773 K can mitigate the PII treatment effect and recover the microstructure.

Acknowledgments

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