Journal of Physics: Conference Series **291** (2011) 012033 doi:10.1088/1742-6596/291/1/012033

A study of structure formation in Ti-Nb-Zr shape memory alloys for medical application

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Abstract. A study of structure formation in Ti-Nb-Zr shape memory alloys was carried out by means of transmission electron microscopy. After 450 ^{o}C annealing of cold-worked specimens a very high dislocation density (10^{11} cm^{-2}) remained; after 600 ^{o}C annealing a mixed structure consisting of submicron sized grains and subgrains formed. Therefore, a nanosubgrained structure is expected to form after 500 – 550 ^{o}C annealing.

1. Introduction

Biocompatible shape memory alloys (SMA) are in the number of the most advanced metallic implant materials [1]. Titanium based and titanium intermetallic based alloys, especially Ti-Ni, are well studied. However, on account of nickel carcinogenicity, development of nickel-free alloys, e.g. solid solution Ti-Nb-(Ta, Zr) based alloys, is in a progress [2 – 4].

As the SMA functional properties are defined by the alloy structure, studies of the structure formation rules under the thermomechanical treatment comprising cold rolling + post-deformation annealing is of interest. The work was aimed at a search for the annealing temperature range to obtain nanosubgrained or nanocrystalline structures which provide the best combination of SMA functional characteristics, in particular, superelasticity [5 – 8].

2. Experimental

The study of structure formation in Ti-20.8Nb-5.5Zr (at. %) alloy was carried out by transmission electron microscopy after cold rolling and subsequent annealing under the following conditions: (1) 85 % reduction (true strain e = 2); (2) 85 % reduction + 450 ^{o}C, 1 hr annealing; (3) 85 % reduction + 600 ^{o}C, 1 hr annealing.

For structure investigation JEM 200CX transmission electron microscope was used with magnification x 15000 and x 50000. Electron diffraction patterns were obtained from selected areas with 0.5 μm in diameter. The studied samples were thin foils cut from thermomechanically treated samples and subsequently thinned by electropolishing.

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3. Results and discussion

In as-deformed state after deformation e = 2, a non-homogeneous deformed structure of β-phase is observed (figure 1). The experiments show that β-phase exhibits a very high dislocation density (not less than 10^{11} cm^{-2}). The α- or α''-phase plates are also present, their width is about 100 nm. Dark field images show that very fine (below 10 nm) round shaped ω-phase particles are distributed through the whole volume. No features of amorphous or nanocrystalline structure are detected.

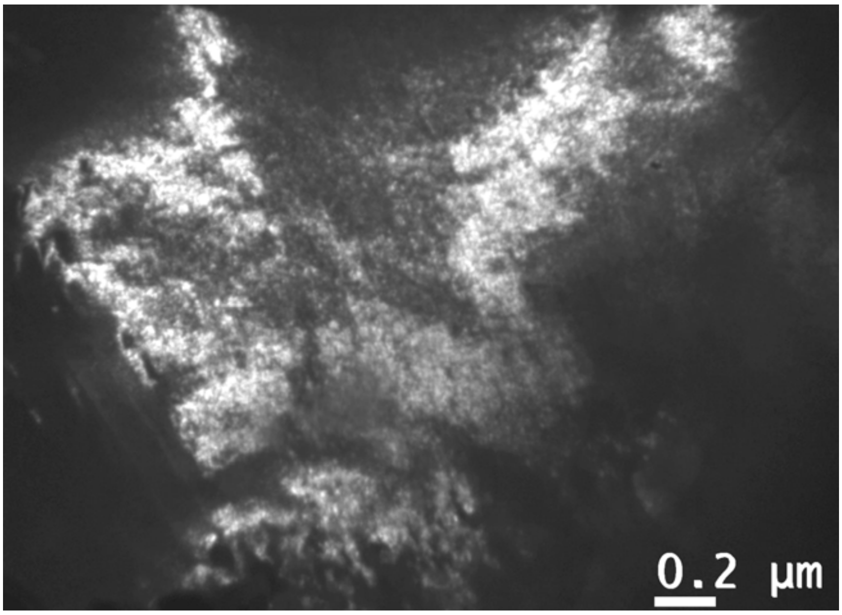

Figure 1. Dark-field image under diffraction conditions corresponding to deformed β-phase; e=2.

After 450 °C annealing, the alloy structure does not change significantly, but becomes more uniform. Mainly the regions with deformed β-phase and the regions with alternate α- and β-phase plates are observed; in all cases dislocation density remained very high. There are fine ω-phase particles inside β-plates. There are also very fine (less than 20 nm) lamellar crystals inside α-plates which morphology is similar to α''-phase crystals (figure 2). Obviously, annealing temperature of 450 °C corresponds to recovery stage, a polygonization in dislocation substructure does not yet develop.

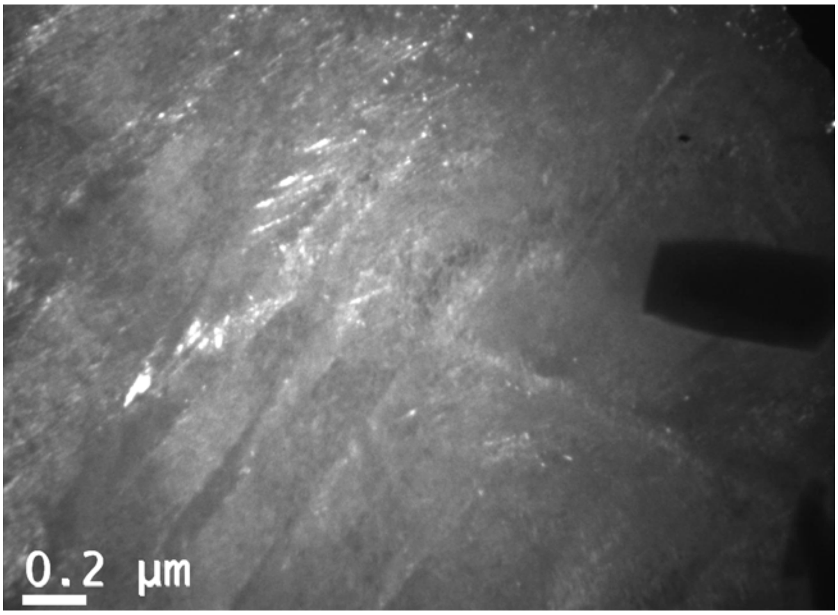

Figure 2. Dark-field image of plate-like α''-phase crystals after post-deformation annealing at 450 °C.

After annealing at 600 °C, an ultrafine-grained structure is observed (figure 3). Dark-field images obtained under diffraction conditions corresponding to α- and β-phase indicate that some grains belong to α-phase, while the greater fraction of grains, including the largest ones, belong to β-phase. According to these electron diffraction patterns, the visible structure elements (size 0.1 – 0.5 µm) are separated by high-angle and low-angle boundaries (see azimuthal misorientations between reflexes in figure 4). Obviously, annealing at 600 °C corresponds to transition to recrystallization. At this stage grain structure and polygonized substructure with submicro-sized structure elements (subgrains and grains) coexist.

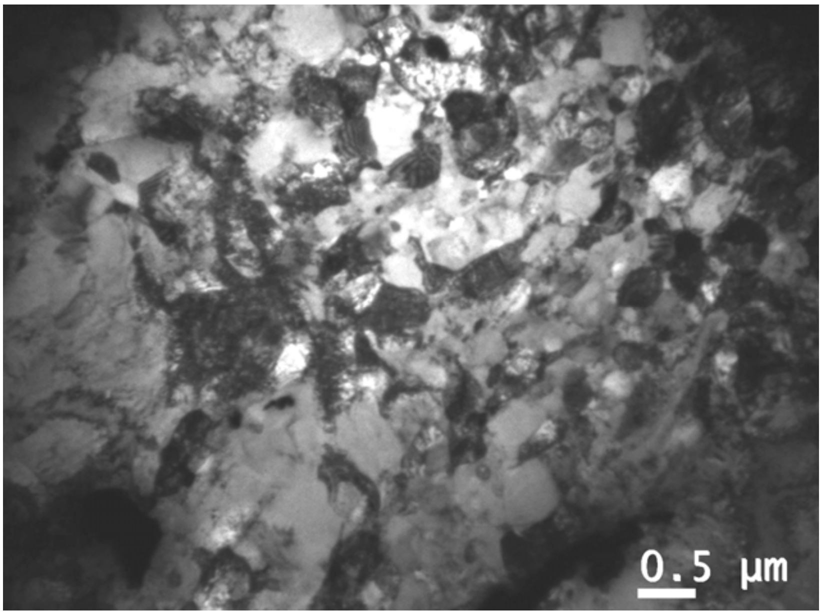

Figure 3. Bright-field image of structure after 600 °C annealing.

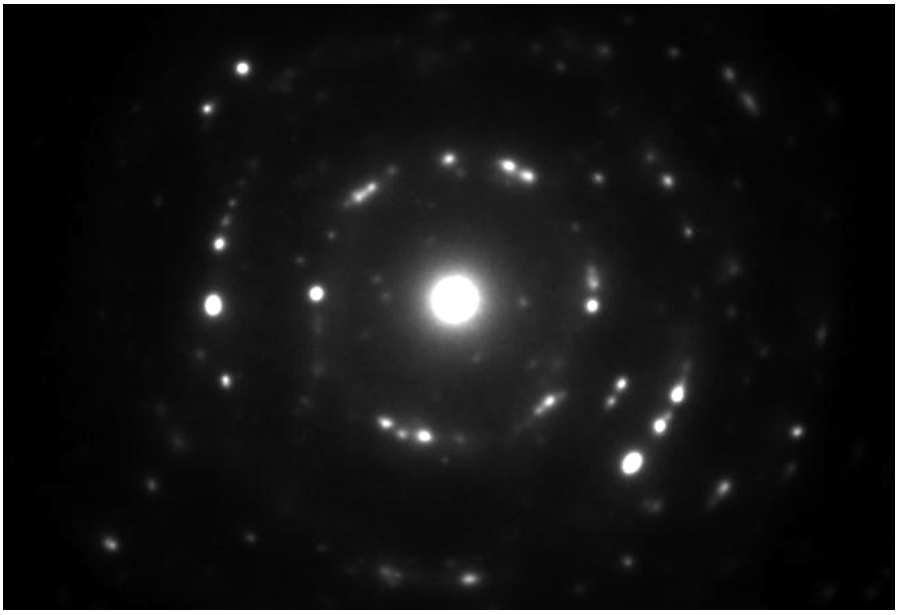

Figure 4. "Ring" diffraction pattern corresponding to fine-grained structure after 600 °C annealing.

The results of the TEM studies indicate that to obtain nano-sized (less than 100 nm) structure elements, the post-deformation annealing should be carried out at 500 – 550 °C; the obtained structure elements will rather be subgrains (surrounded by low-angle boundaries) than grains (surrounded by high-angle boundaries).

A preliminary study of electrochemical behavior of Ti-Nb-Ta alloy which is analogous with Ti-Nb-Zr was carried out. It was shown that the alloy exhibits inclination for self-passivation in artificial saliva solution, with an electrode potential more positive than those for pure titanium that is known to be corrosion resistant material. Passivation rate of Ti-Nb-Ta is relatively low compared to those for titanium; it may indicate lower concentration of defects in passive film on Ti-Nb-Ta that may influence the film's resistance in the biofluid positively.

It is well known that electrochemical behavior of an alloy depends on its structure and, consequently, on thermomechanical treatment conditions. It was clearly shown for Ti-Ni [9] and Ti-6Al-4V [10] alloys. Therefore among the directions of the further biomedical Ti-Nb-Zr alloys research there is study of structure, including nanostructure, influence on the alloys' electrochemical behavior, as well as optimization of their treatment conditions concerning combination of mechanical, functional and electrochemical properties.

4. Conclusions

A study of structure formation in biomedical Ti-Nb-Zr shape memory alloy (SMA) was carried out by means of transmission electron microscopy after thermomechanical treatment under different conditions.

- Cold deformation of Ti-Nb-Zr SMA with true strain e = 2 forms dislocation substructure with very high dislocation density (not less than 10^{11} cm^{-2}) in β and α''-phases. High dislocation density remains after annealing at 450 °C, 1 hr, that denotes the preservation of significant strain hardening.
- After annealing at 600 °C, 1 hr in the case of initial strain e = 2 a mixed β-phase structure consisting of submicron sized (0.1 – 0.5 μm) grains and subgrains is observed. A nanosubgrained structure is expected to form after during post-deformation annealing at 500 – 550 °C.

Acknowledgements

The present work was carried out with the support of Ministry for Science and Education of Russian Federation (ADTP "Development of scientific potential of the higher school (2009-2010)", project 2.1.2.7129, FTP "Scientific and scientific-educational personnel of innovative Russia", projects 16.740.11.0014 and 14.740.11.0465), Ministry of Economic Development of Quebec, Natural Science and Engineering Research Council of Canada, and the Programme of Creation and Development of the National University of Science and Technology "MISIS".

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