Introduction of antibacterial function into biomedical TiNi shape memory alloy by the addition of element Ag

Y.F. Zheng
Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

Statement of Purpose: From the viewpoint of biomedical engineering, element silver is well known for its broad-spectrum antibacterial effect at very low ppb concentrations, and it possesses many advantages such as good antibacterial ability, excellent biocompatibiliy, and satisfactory stability. TiNi alloy, with around 50% Ni content, has been extensively used in dentistry, orthopedics and interventional therapy. The purpose of the present work is to testify the feasibility of introducing the antibacterial function to TiNi alloy by the effective addition of alloying element Ag.

Methods: Ternary TiNiAg alloy ingot with an actual composition of Ti49.3Ni47.3Ag1.4 (in atomic percentage as identified by EDS (energy dispersive spectrometer)) was prepared from 99.8% purity Ti (Grade 0), 99.9% purity Ni and 99.9% purity Ag by means of arc melting in vacuum with a water cooling Cu bath. The alloy button was re-melted four times for homogeneity, and the as-cast button with the height of 15mm was hot rolled at 800°C into plate of 1.5 mm in thickness. Specimens were cut using electro-discharge machining, and were mechanically polished to remove the surface oxide layer. Then the specimens were solid solution treated at 800 °C for 2h, followed by quenching in water.

TEM observation was carried out on a JEOL-2010FX transmission electron microscope operated at 200 kV using a top-entry type double-tilt specimen stage. X-ray diffractometer (XRD, Rigaku DMAX 2400) using Cu Kα radiation was employed for the identification of the constituent phases at ambient temperature. The tensile testing was performed using an Instron 3365 universal testing machine at a strain rate of 0.0004 /s. The strains of bacteria used for the present study were S. aureus (ATCC 6538), S. epidermidis (ATCC 12228) and P. gingivalis (ATCC 33277).

Results: Fig. 1(a) shows the typical bright-field TEM image of TiNiAg alloy at room temperature. The morphology of matrix is the typical TiNi martensite twinning plates (each martensite variant consists of alternating platelets with rather regular spacing), with pure Ag spheroid particles of about 150 nm in diameter precipitated inside. The phase constitution of TiNi and TiNiAg alloys are further characterized by XRD, as shown in Fig. 1(b), and the inset of Fig. 1(b) shows high resolution XRD pattern of TiNiAg alloy at a low scanning speed (here metallic Ag peaks can be observed.). These results show that TiNi and TiNiAg alloys are mainly composed of B19' monoclinic martensite and B2 structure austenite TiNi phases at room temperature. The uniaxial tensile stress-strain curves at room temperature for the experimental TiNi and TiNiAg alloys are shown in Fig. 1(c). Both alloys exhibited large plastic deformation before breakage. Similar to TiNi binary alloy, the deformation process of TiNiAg alloy could be divided into three stages according to the stress-strain behavior. The stage I is characterized by the initial linear portion due to elastic deformation of the martensite phase. Stress plateau (stage II) indicates the martensite reorientation process occurred at about 1%~4% strain. The deformation stage following stage II (stage III) can be attributed to the permanent deformation of martensite phase. Compared with TiNi binary alloy, TiNiAg alloy exhibited slightly higher yield strength and ultimate tensile strength. Fig. 1(d) illustrates the representative macroscopic images of viable adherent bacteria. The highest bacterial counts can be detected on TiNi alloy group for all bacterial types, whereas the bacterial adhesion is significantly reduced ($p < 0.05$) on TiNiAg alloy group surface when compared to TiNi alloy group. The addition of Ag into TiNi alloy shows an obvious inhibition of the growth of all bacteria types.

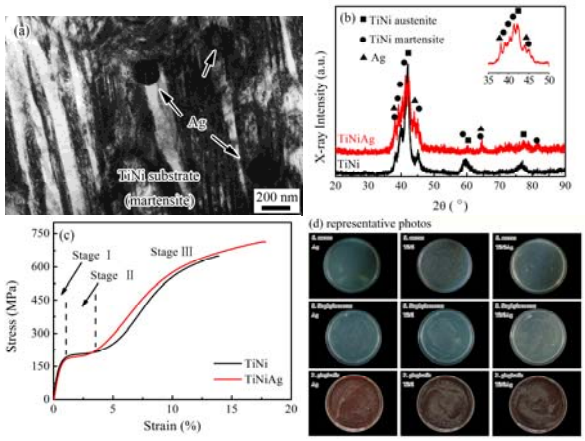

Figure 1. (a) Typical bright-field TEM micrographs of TiNiAg alloy; (b) XRD results of TiNi and TiNiAg alloys; (c) Tensile stress-strain curves of TiNi and TiNiAg alloys; (d) representative macroscopic photos of viable adherent bacteria on pure Ag, TiNi and TiNiAg alloys surface.

Conclusions: TiNiAg ternary alloy was successfully fabricated with arc-melting method with water cooling Cu bath. The Ag particles precipitate within the TiNi alloy matrix, with the size ranging from several tens of nanometers to several micrometers. The tensile tests show that TiNiAg alloy has higher strength than that of TiNi binary alloy. Compared with TiNi alloy, TiNiAg alloy possesses similar corrosion resistance and cyto-biocompatibility. Moreover, TiNiAg alloy exhibits reduced bacteria adhesion when compared with TiNi binary alloy. The antibacterial effect is attributed to the release of Ag ions from the tiny Ag precipitates. Therefore TiNiAg alloy is believed to be a functional biomaterial which combines antibacterial activity and shape memory effect, and is likely to broaden the range of the biomedical application of TiNi alloy system.