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CHARACTERIZATION OF THE CARBIDES IN A Ni-Ti SHAPE-MEMORY ALLOY WIRE

KARAKTERIZACIJA KARBIDOV V ŽICI ZLITINE S SPOMINOM Ni-Ti

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The microstructure of a commercially available Ni-Ti shape-memory alloy was investigated with Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS) and Electron Backscatter Diffraction (EBSD) patterns. The material investigated was a Ni-Ti shape-memory alloy with the chemical composition in the mass fraction: C 0.1 %, Ni 45 % and Ti 54.9 %. The microstructure of the alloy consisted of nanosized crystal grains of the Ni-Ti phase and particles of titanium carbides. The majority of the particles were aligned in the longitudinal direction parallel to the wire's axis. The problems occurring during the EBSD analysis of the Ni-Ti phase are discussed and some orientational relationships between the carbides and the matrix are suggested.

Key words: shape memory alloy, Ni-Ti, TiC, EBSD, EDS

Raziskali smo mikrostrukturo komercialne zlitine s spominom Ni-Ti z uporabo vrstične elektronske mikroskopije (SEM), energijsko disperzijske spektroskopije (EDS) in uklona sipanih elektronov (EBSD). Preiskovani material je bila zlitina s spominom Ni-Ti s kemijsko sestavo v masnih deležih: C 0.1 %, Ni 45 % in Ti 54.9 %. Mikrostruktura zlitine je bila sestavljena iz nanokristalnih zrn faze Ni-Ti in titanovih karbidov. Večina karbidov je bila usmerjena vzdolžno z osjo žice. Opisani so problemi EBSD-analize faze Ni-Ti in predlagane orientacijske odvisnosti med karbidi in matrico.

Ključne besede: zlitina s spominom, Ni-Ti, TiC, EBSD, EDS

1 INTRODUCTION

Porous Ni-Ti shape-memory alloys are widely used in numerous biomedical applications (orthodontics, cardiovascular, orthopedics, urology, etc.) because of their good biocompatibility, unique shape-memory properties, mechanical properties, superior damping capability, excellent corrosion resistance and wear resistance [1–6]. They combine their special functional properties with a high mechanical strength [7]. These characteristics are due to the martensitic transformation and its reversion, which can be activated by thermal or mechanical loads [7]. The Ni-Ti alloy has similar mechanical characteristics to natural biomaterials, e.g., a high recoverable strain and a low elastic modulus [8,9], both of which are very similar to bone. This makes the alloy an ideal biological engineering material for orthopedic surgery and orthodontics [10]. Despite these advantages, the high Ni content (50 %) in the Ni-Ti shape-memory alloy is a major health concern [11]: the toxicity, carcinogenicity and allergic hazards associated with Ni have been the subject of a number of studies [12,13]. One of the most effective and obvious solutions is to improve the surface microstructure and modify the properties. Of course, one of the basic requirements for any metallic implant is that it should not exhibit any toxicity and that it should be biocompatible.

The properties of a Ni-Ti shape-memory alloy depend strongly on the exact chemical composition, the processing history, and the level of impurities [7]. For example, contaminants such as oxygen and carbon can dramatically affect the properties of the alloy; their penetration tends to occur during the production and processing of the alloy [7].

To obtain a good shape-memory effect it is crucial to have a good chemical homogeneity of the material, which then leads to single-phase Ni-Ti formation. The usual process to produce Ni-Ti shape-memory alloys is called Vacuum Induction Melting (VIM), using high-density graphite crucibles to minimize the carbon contamination of the melt. The carbon combines with the titanium, which results in the precipitation of TiC particles. The consequence is an alloy matrix that is richer in nickel than the nominal composition, which means a lowering the martensitic transformation temperatures [3,14–16]. The higher concentration of Ni in the Ni-Ti matrix increases the risk of allergic and toxic reactions [1] as well as reducing the shape-memory effect. The precipitated titanium carbides have been reported to have a certain orientational relationship with the matrix [16].

In the present study the microstructure of a commercial Ni-Ti orthodontic wire produced by vacuum induction melting was examined with Scanning Electron Microscopy and Electron Backscatter Diffraction (EBSD) patterns. The problems occurring during the indexing of the EBSD patterns of the Ni-Ti phase are described and some of the orientational relationships between the carbide particles and the matrix are suggested.

2 EXPERIMENTAL

The material used was a Ni-Ti shape-memory alloy with the following chemical composition in mass fractions: C 0.1 %, Ni 45 %, Ti 54.9 %. An orthodontic archwire specimen (ϕ 0.2 mm × 100 mm) was hot mounted in conductive Bakelite, ground and polished. The usual diamond polishings with 3 µm and 1 µm particles were prolonged to 10 min each; these were followed by colloidal silica oxide polishing for 5 min and then cleaning in an ultrasonic bath. The specimen was analyzed in a FE-SEM JEOL JSM 6500F field-emission scanning electron microscope using energy-dispersive X-ray spectroscopy (EDS), an INCA X-SGHT LN2-type detector, INCA ENERGY 450 software, and an HKL Nordlys II EBSD camera using Channel 5 software. The microstructure was revealed with etching in 85 % H_20, 5 % HF and 10 % HNO_3. For the EDS analyses a 15-kV accelerating voltage and a probe current of 0.7 nA were used. The parameters chosen represent a good compromise between the size of the analyzing volume and the overvoltage needed to detect the elements present. The EBSD was performed at a 15-kV accelerating voltage and a 2.6 nA probe current. The analysis was made using 40 reflectors and 4 × 4 binning. For the noise reduction, 10 frames were used, and each frame was obtained at 20 ms. The obtained crystallographic data were analyzed using the Channel 5 software and the ICSD 2003 database.

3 RESULTS AND DISCUSSION

The thermomechanical behavior of shape-memory alloys is obtained with the martensitic-austenitic phase transition, which depends on the temperature and the stress, and occurs as a result of the martensitic twinning at low temperatures. The hysteresis loop of the analyzed shape-memory alloy has a martensite start at 2 °C and a martensite finish at –15 °C, and an austenite start at 18 °C and an austenite finish at 36 °C, in order to achieve the phase transformation from martensite to austenite, which is typical for applications at human-body temperature [17]. The microstructure of the investigated alloy consists of the Ni-Ti phase with a number of titanium carbide particles (**Figure 1**). The high carbon content of 0.1 % is due to the dissolution of carbon from the crucible graphite in the melt during the vacuum induction melting [16]. The titanium carbides might lower the concentration of nickel in the matrix; however, a beneficial effect of increased hardness may occur, particularly if the interface between the titanium carbide and the Ni-Ti phase is semi-coherent [16].

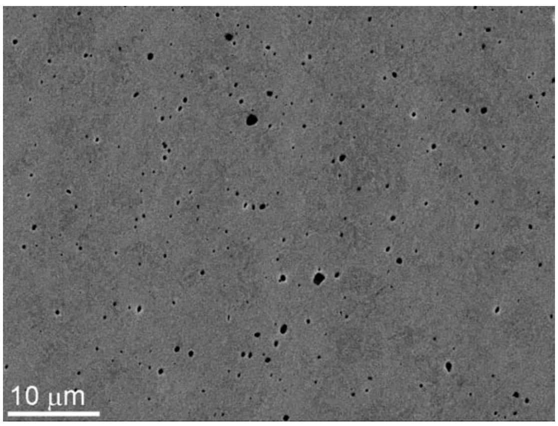

Figure 1: Polished transversal cross-section of NiTi wire. Black spots represent titanium carbides in the NiTi matrix. Micrograph obtained in scanning electron microscope using backscattered electrons.

Slika 1: Prikaz poliranega prečnega prereza NiTi žice. Temna področja so titanovi karbidi v NiTi matrici. Slika je bila posneta v vrstičnem elektronskem mikroskopu z odbitimi elektroni.

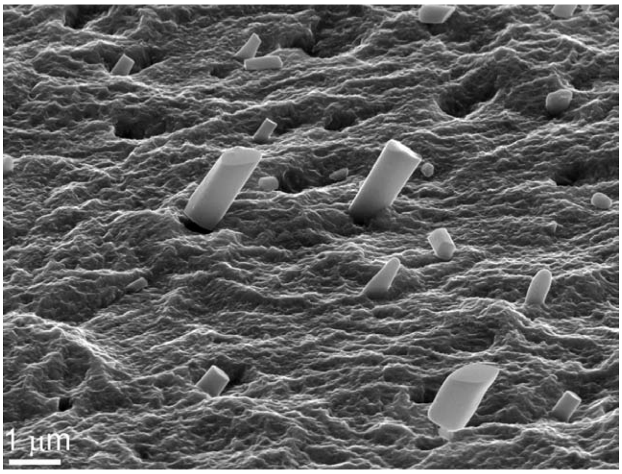

Figure 2: Etched transversal cross-section of NiTi wire with visible carbides in longitudinal direction. Micrograph obtained from secondary electrons in 60° tilted mode.

Slika 2: Prikaz jedkanega prečnega prereza NiTi-žice z vidnimi karbidi v vzdolžni smeri. Slika je bila posneta s sekundarnimi elektroni, vzorec nagnjen za 60°.

Chemical etching of the Ni-Ti surface prior to the surface characterization causes a rapid attack on the NiTi matrix, while the titanium carbides were not affected. Therefore, in the highly tilted mode in the Scanning Electron Microscope the carbide particles, and especially their shape, become clearly observable (**Figure 2**). The longitudinal direction of the carbide is parallel to the wire's longitudinal direction. This specific situation may result from two possible factors concerning the precipitation of carbide particles. The first one is related to the manufacturing of the shape-memory Ni-Ti alloy, which is associated with the casting and the plastic deformation of the wire at elevated temperatures. The carbides might precipitate during the casting solidification [16] and later during the plastic working with hot rolling and drawing when the non-deformable particles are aligned in the longitudinal direction of the wire. In this case, the carbide particles have no orientational relationship with the matrix because of the re-crystallization during or after the wire drawing. On the other hand, the particles may have precipitated during the wire drawing, which would impact on the specific growth direction of the particles. The titanium carbides have a rod-like shape; however, the transversal cross-section is not completely circular; in some cases it is closer to a square with rounded edges. It is most likely that the wire was manufactured by continuous casting and drawing, so that the carbides precipitate during the casting and have a specific orientation due to the tension gradient in the drawing direction. This can explain why the carbides are not broken into small pieces, which is what usually occurs with aluminum or silicon non-metallic inclusions in steels during plastic deformation. Some of the carbide particles are slightly thinner at their ends, which is typical evidence that the precipitation and the drawing took place at a high enough temperature to allow plastic deformation also of the carbides.

The EBSD analysis was performed on highly polished surfaces where the carbide particles formed just a slight topography. Based on the available ICSD 2003 database [18,19], the EBSD patterns were solved almost equally as TiC or Ti_8C_5. However, a slightly better MAD (mean angular deviation) number was obtained for the TiC phase. Zhang et al. reported the lattice of titanium carbide particles as being cubic TiC [16]. TiC is in a wider region according to the phase diagram calculated using the Thermo Calc program [20]. TiC can have the B1 (or NaCl-type) lattice with the titanium atoms situated in a face-centered-cubic, closed-packed arrangement with the octahedral interstitial sites occupied by carbon atoms [21]. The equilibrium phase diagram exhibits only one carbide phase, TiC, which is characterized by a wide region of composition (from $TiC_{0.48}$ to $TiC_{1.00}$) and melts congruently at 3068 °C [22]. The reason why both carbides create almost identical patterns from the interaction of electrons with the crystal structure is that in both lattices the atoms are in a close-packed formation and the similar ordering creates similar electron refraction. Because of the very similar EBSD patterns of both the equilibrium and non-equilibrium carbides, it is not possible to exclude the existence of the Ti_8C_5 carbide. Nevertheless, the shape of the carbide rods, with their slightly square transversal shape, might be more indicative of the equilibrium cubic TiC. The internal stress can have an influence on the carbide growth at high temperature and might change the bulky crystal shape. Some hexagonal form, for instance an angle of 120°, is to be expected also. **Figure 3** shows the EBSD pattern of a typical TiC particle. The orientation of the crystal is such that the longitudinal direction of the carbide is parallel to the wire.

EDS microchemical analyses were performed on some carbide particles. However, an accurate EDS carbon analysis is always a challenge. The system used has no liquid-nitrogen trap and therefore some excess carbon due to contamination is always observed. Depending on the material analyzed, some carbon build up under the electron beam is usually observed during the EDS measurement in the range of mole fractions 10 % or 15 % in steels and Ni-Ti alloys, respectively. The carbon in the vacuum analyzing chamber originates mostly from the oil vapor in the diffusion pumps. Taking into account this particular fact and from the EDS measurements on titanium carbides, it is possible to conclude that the carbides are closer to TiC than Ti_5C_8. Unfortunately, using the WDS technique gives no improvement in such conditions; on the contrary, it makes the measurements even less reliable. The phenomenon of carbon build up is even more intense due to the higher current. **Figure 4** shows EDS spectra from typical carbides in the Ni-Ti shape-memory alloy and the calculated chemical composition of the carbide. From the EDS spectra the calculated atomic ratio of Ti to C is approximately 1:1. There is, however, some excess amount of carbon due to the vacuum problem mentioned above. A certain amount of oxygen was also observed in

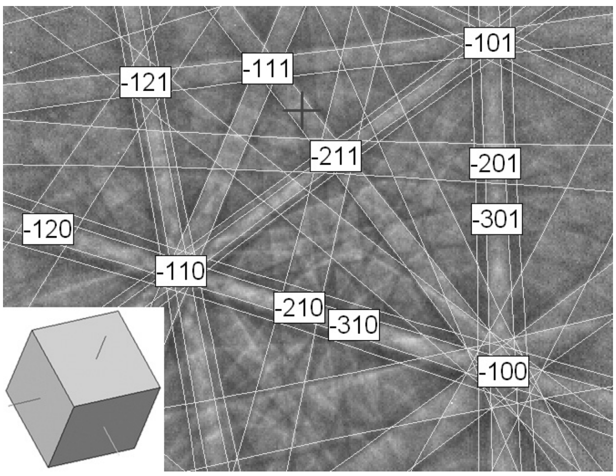

Figure 3: EBSD pattern of typical TiC carbide in longitudinal direction of the wire. The pattern was solved as TiC with the orientation of the crystal shown in the figure.

Slika 3: EBSD-slika tipičnega TiC-karbida v vzdolžni smeri žice. Elektronska uklonska slika prikazuje TiC s kristalno orientacijo, prikazano na sliki.

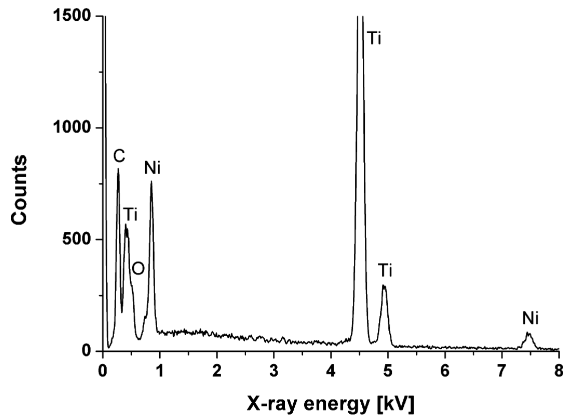

Figure 4: EDS spectrum of carbides shows slightly larger amount of carbon that belongs to the TiC. The excess amount is due to carbon build up under the electron beam.

Slika 4: EDS-spekter karbidov, ki prikazuje nekoliko povišan delež ogljika glede na TiC. Presežek ogljika je zaradi nalaganje pod elektronskim curkom.

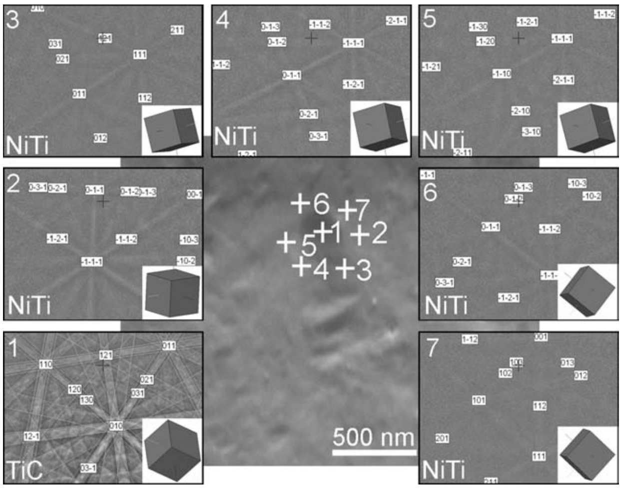

Figure 5: Marked area of EBSD spot analysis with corresponding EBSD pattern. Spot 1 shows the carbides, spots 2 to 7 show Ni-Ti matrix with nanograins.

Slika 5: Označeno mesto EBSD točkovne analize s pripadajočo EBSD uklonsko sliko. Mesto 1 prikazuje karbid, mesta od 2 do 7 prikazujejo Ni-Ti matrico z nanozrni.

the EDS spectra. It was reported previously that the presence of carbon and oxygen can result in the formation of different titanium carbides and oxides [23].

To prepare the Ni-Ti alloy for the EBSD investigation was a demanding task. Two different approaches were tested: polishing of the surface with argon ions and polishing by using silica oxide nanoparticles. The latter was more successful, however. It is believed that the highly energetic ions may affect the lattice and induce some internal stresses, which could be reflected in the EBSD pattern, as observed during the EBSD mapping. In these analyses the indexing and the band-contrast image constantly deteriorated during the EBSD mapping. The explanation for this may also be found in the austenite-martensite transformation as well as the martensite twining caused by the interaction of electrons and the specimen being analyzed. Most likely this problem is related to the contamination of the surface during EBSD analysis as well as local oxidation of the surface.

The orientational relationship of the titanium carbides (with the B1 crystal structure) and the Ni-Ti matrix (with the B2 crystal structure) was established (**Figure 5**). It was found that the majority of the TiC particles have the same orientation, and without any clear relationship with the NiTi matrix lattice. However, it is related to the longitudinal direction of the wire, as the EBSD analysis showed that majority of titanium carbides had the longitudinal direction [111]. The grain size of the Ni-Ti phase was in the range of 200 nm.

4 CONCLUSIONS

The present study was conducted in order to characterize a commercially available Ni-Ti shape-memory alloy. It was found that the microstructure of the analyzed shape-memory alloy consisted of nanosized crystal grains of the Ni-Ti phase with a number of titanium carbides. The chemical analyses confirmed that the excess amount of carbon originated from the induction-melting process in the graphite crucible, which decreased the shape-memory effects due to the formation of TiC precipitates. The titanium carbides were rod shaped, while the transversal cross-section shape was in the form of a modified circle, although in some cases it was close to a square with rounded edges. The majority of the carbides were aligned parallel to the wire axis, which can be associated with an orientation change during the plastic deformation. It is also possible that the particles grow faster in the longitudinal direction due to the stresses produced by the wire drawing. The grain size of the Ni-Ti phase was in the range of 200 nm, and the majority of the carbides had a direction parallel to the wire's longitudinal direction [111].

Acknowledgements

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