MICROSTRUCTURE OF NiTi ORTHODONTIC WIRES OBSERVATIONS USING TRANSMISSION ELECTRON MICROSCOPY

This work presents the results of the microstructure observation of six different types of NiTi orthodontic wires by using Transmission Electron Microscopy (TEM). Within these analyses the chemical compositions of each wire were observed in different places by applying the EDS detector. Namely, the chemical composition in the orthodontic wires is very important because it shows the dependence between the phase temperatures and mechanical properties. Microstructure observations showed that orthodontic wires consist of nano-sized grains containing precipitates of Ti_2Ni and/or TiC. The first precipitated Ti_2Ni are rich in Ti, while the precipitated TiC is rich in C. Further investigation showed that there was a difference in average grain size in the NiTi matrix. The sizes of grains in orthodontic wires are in the range from approximately 50 to 160 nm and the sizes of precipitate are in the range from 0,3 μm to 5 μm.

Key words: NiTi orthodontic wire, microstructure, TEM, EDS, average grain size

INTRODUCTION

The Shape Memory Alloys (SMA-s) nickel – titanium (NiTi) are very useful materials in medical use because they have good biocompatibility and functional properties [1]. In particular, this alloy is used in the field of orthodontics for orthodontic wire in orthodontic appliances. The reasons for this are that they have the lowest force delivery (small modulus of elasticity) and they have a large recoverable strain for time continuous orthodontic treatment (superelasticity) [2,3].

The commercially available wires are in superelastic and shape memory forms [4]. The properties of SMA wires depend on the characteristics of the austenitic phase (body centred cubic structure) and martensite phase (monoclinic structure) [5]. For clinical conditions the austenite - finish (A_f) temperature is important. This temperature in the NiTi SMA for orthodontic use is usually lower than the human body temperature (37 °C). The reason for this is that these alloys at temperatures above A_f have characteristic behaviour called superelasticity, which means a material property that has a lot of recoverable elongation. A special feature of these alloys is the transformational plateau, where due stress caused a diffusion-less phase transformation from austenite to detwinned martensite while, in SMA, it greatly increases the elongation at low changes of stress. In the case when

such a wire is inserted into the oral environment and deformed it is transformed from austenite to martensite. This means that the material caused the gentle and time continuous force which we want in orthodontic treatment, especially in the initial stage of treatment [6-8].

In SMA-s NiTi the temperatures of a phase have a great influence on the chemical composition of the transformation. Moreover, the mechanical properties are also strongly dependent on the phase temperatures [5]. For these purposes the characterisation of microstructure for SMA NiTi was studied using Transmission Electron Microscopy (TEM) in many studies [9, 10]. However, there are not many studies that deal with the comparable TEM microstructural analysis of orthodontic wires which have similar chemical composition.

The aim of this work was to observe the TEM microstructures and to determine the chemical compositions of six commercially available SMA NiTi orthodontic wires in stress free conditions and on different regions within the volume. With this analysis we want to observe the starting microstructure and it final influence on the functional behaviour of each orthodontic wire.

MATERIALS AND METHODS

We investigated and analysed six commercially available orthodontic wires from SMA NiTi with a diameter 0,014 '' (0,305 mm): 1. Damon Copper NiTi (Ormco, USA), 2. Thermo NiTi (Dentaurum, Germany), 3. Sentalloy (GAC, Japan), 4. Truflex (Ortho Technology, USA), 5. Truflex Thermal (Ortho Technology, USA), and 6. Rematitan (Dentaurum, Germany).

Previously we analysed the phase transformation temperatures of each orthodontic wire [11] and results

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showed that all of the wires have a phase transformation temperature A_f below the body temperature in a range from approximately 14 to 27 °C.

For investigation we used (TEM) equipped with the Energy - Dispersive X-ray Spectroscopy (EDS) which enables the detection of chemical composition. Namely, TEM/EDS techniques are very useful tools for the quantitative analysis of a sample on the nanometre scale [12,13]. TEM analyses were performed at room temperature. From the general analysed phase temperatures it can be seen that the material at this temperature has, in most cases, an austenitic structure with minimum martensite structure due to temperature. For the determination of the average austenite grain size we used the standard ASTM E112 – 10 [14]. We measured the grain sizes which are related to the average diameter of each grain. Because it is impossible to calculate the diameter from each individual grain in whole volume in wire, we calculated these grain sizes from the surfaces respectively from cross-sections of wires. Next we used test methods which covered the measurements including the comparison procedure, the planimetric or Jeffries procedure. In this procedure we inscribed a circle on a micrograph. We considered that in the circle are around 50 grains. Then we counted the number of grains included completely within this area plus one half of the number of grains which were intersected by the circumference. From the number of grains we calculated the average gain area. Finally, we calculated the average grain diameter or grain size from the average gain area. The technique used for preparation of thin foils for TEM was argon ion-slicing with an Ion Slicer (Jeol EM-09100IS). The Ion Slicer thins the specimen partly. It is possible to prepare cross-section or plan-view thin foil specimens. The instrument irradiates an argon ion beam on the specimen, which is masked partially with a shield belt. After argon ion-slicing the specimens were examined with TEM (Jeol JEM-2100, HR) at 200 kV using conventional TEM (CTEM), high-resolution TEM (HRTEM), electron diffraction, and Energy Dispersive X-ray Spectroscopy (EDS).

Specimens for TEM were cut out of a bulk material (orthodontic wires) in lengths of approximately 2,8 – 3,0 mm. The thickness (or diameter) of specimens was around 351 – 360 μm which was reduced further to around 86 – 160 μm with a Jeol Handy Lap using grinding papers SiC 1 200, 2 400, 4 000 and distilled water. Specimens were then mounted on an Ion Slicer specimen holder, masked partially with a shield belt (bulk cross-section preparation) and thinned additionally with an argon ion beam. The slicing process started at the pressure of 10^{-5} Pa or 10^{-4} Pa, and alternated between the front and the backside of the specimen while it was rotating. The beam was tilted between 2,0, 2,5 or 3,5 °. Accelerating voltage 6 kV, argon gas flow rate between 6,8 and 7,3 (arbitrary units) and side change interval of 30 s were chosen. After a large thin area of the specimens up to 500 × 500 μm or more was obtained, a hole was generated in the thinnest region of the specimens.
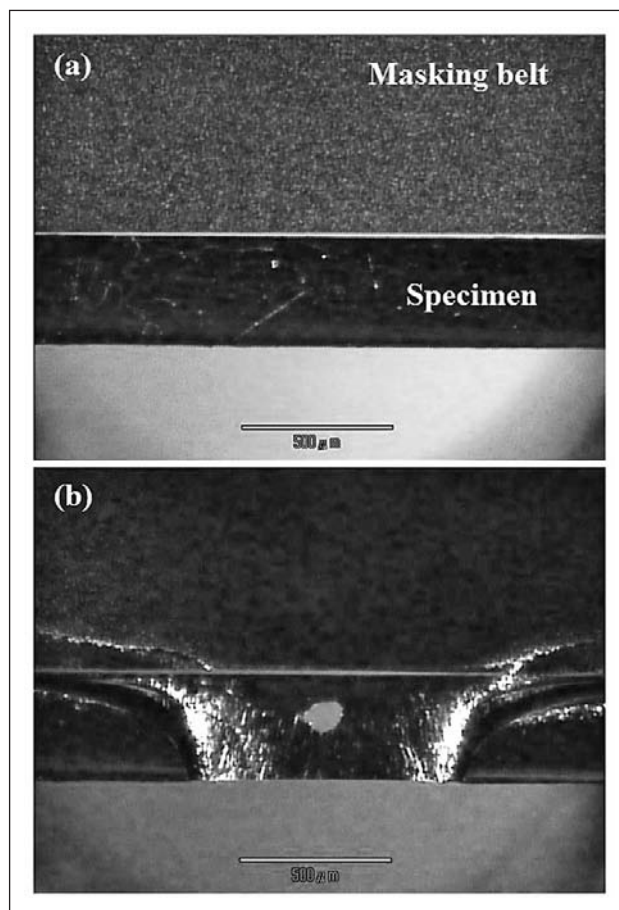

Figure 1 Images of specimen of orthodontic SMA NiTi wires before (a) and after (b) Ar ion-slicing using an Ion Slicer

Polishing was used with a tilt angle of 0,8 or 1,5 °, at the accelerating voltage of 2 kV and side change interval of 30 s for 10 or 12 min. The total time of slicing was between 4 h and 8 min and 10 h and 19 min. An example of a specimen before and after argon ion-slicing using an Ion Slicer is shown in Figure 1.

RESULTS AND DISCUSSION

Results of microstructure observations for all orthodontic wires are shown in Figures 2(a) to 2(f), where the bright field (BF) images technique was used, respectively.

From the surfaces of these wires the chemical compositions of the matrix were detected by TEM/EDS. The results of the average value for chemical composition of the matrix are presented in Table 1.

The first orthodontic wire contained, besides nickel (Ni) and titanium (Ti), also copper (Cu). In all other orthodontic wires the microstructure is enrich in Ni. It is very important to mention that the original bulk composition of the orthodontic wires (through the whole volume) was different. Namely, to achieve a Shape Memory Alloy it is expected that alloys have a composition of Ni between 50 and 51 at.% [5]. The values for Ni in these wires vary in the range from 52 to 54,4 at.%. Detectable change occurs due to the formation of precipi-
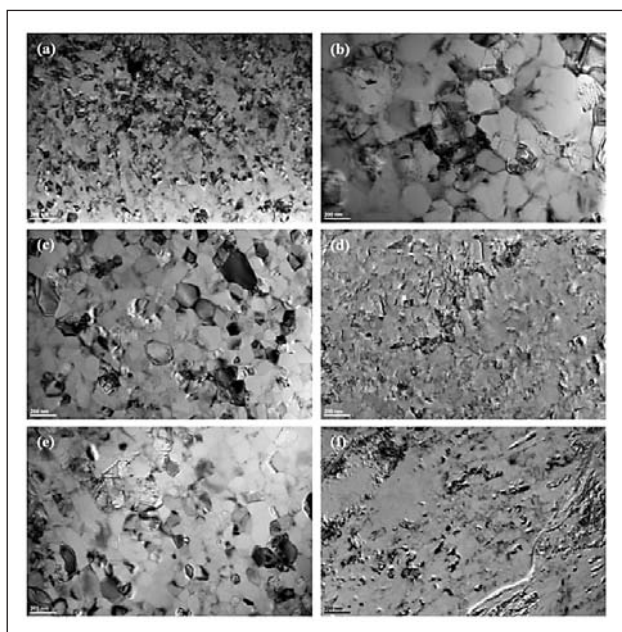
Figure 2 TEM bright - field (BF) micrograph images of different orthodontic wires from SMA NiTi showing small austenite particles in the matrix
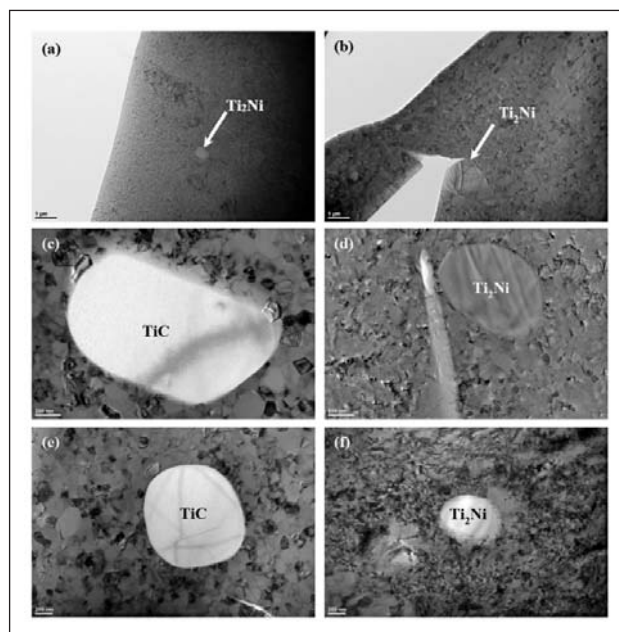

Figure 3 TEM bright - field (BF) micrographs showing precipitates in SMA orthodontic NiTi wires

Table 1 **Results of chemical composition for SMA orthodontic NiTi wires by TEM-EDS / %**

Orthodontic wire	Chemical element	Matrix	
		Average	Standard deviation
1	Ni	46,9	0,667
	Ti	47,8	0,777
	Cu	5,3	0,469
2	Ni	53,5	1,580
	Ti	46,5	1,580
3	Ni	52,2	0,335
	Ti	47,8	0,335
4	Ni	53,3	1,040
	Ti	46,7	1,040
5	Ni	53,0	0,689
	Ti	47,0	0,689
6	Ni	54,4	2,712
	Ti	45,6	2,712

Table 2 **Grain sizes of austenite for SMA orthodontic NiTi wires**

Orthodontic wire	Average grain size / nm	Standard deviation	Relative accuracy / %RA
1	50,4	2,2	5,3
2	157,2	10,7	8,5
3	95,0	7,5	9,8
4	71,3	5,7	9,9
5	97,9	7,7	9,8
6	49,6	3,0	7,7

tates Ti_2Ni which finally resulted in the fact that SMA orthodontic wires became rich in Ni [15]. Detailed TEM examination of orthodontic wires at room temperature indicated the existence of an austenite phase. The BF in all Figures 2 show fine-scale austenite particles which are distributed almost homogeneously in the microstructure. The grain sizes are different for each orthodontic wire and are written in Table 2 including the standard deviation of the individual measurements. Orthodontic wire number 6 had the smallest grains at 49,6 nm, while orthodontic wire number 2 had the largest size of grains at 157,2 nm. Because the measurement of determination grain size is not exact, due to having a problem with the precise calculation within the determined surface, we considered that the actual average grain sizes are representative. In Table 2 is presented also the calculated percent's relative accuracy %RA of carried out measurements.

The general rule of RA is that the value in the range of 10 %RA or lower is considered to be acceptable precision for most purposes [14]. With our calculation we obtained RA values less than 10 % (from 5,3 to 9,9 % RA) which showed the adequateness of this method. The reduction of grain size improves the pseudoelasticity and facilitates the orientation of neighbour grains and its stiffness is related to the number of martensite plates which are produced [16]. Figures 3(a) to 3(f) show the TEM images of Ti_2Ni and TiC particles which precipitate in different positions within the volume of the orthodontic wire.

The chemical compositions of these particles, including average values of the presenting chemical elements, are shown in Table 3.

The particles of Ti_2Ni are rich with Ti - more than 64 at.% in all orthodontic wires. In Figures 3(c) and 3(e) we can see particles of titanium carbide (TiC) which contain a different amount of carbon (C). In orthodontic wire 3 the C content 73 at.% represents a maximum value, while in orthodontic wire 5 the content of C 53 at.% is minimal. In Table 4 are shown the results of particles size analysis with their extreme values: the minimal and maximum sizes. These particles are approximately from 0,3 to 5 μm in size. The size of TiC precipitations are in the range 0,2

Table 3 **Analysis of chemical composition on precipitates in SMA orthodontic NiTi wires by TEM-EDS / %**

Orthodontic wire	Chemical element	Precipitates		
		Average	Standard deviation	Precipitate
1	Ni	31,9	0,222	Ti_2Ni
	Ti	64,8	0,288	
	Cu	3,3	0,099	
2	Ni	35,4	0,644	Ti_2Ni
	Ti	64,6	0,644	
3	Ni	0,4	0,065	TiC
	Ti	26,4	6,474	
	C	73,2	6,492	
4	Ni	35,3	0,37	Ti_2Ni
	Ti	64,7	0,37	
5	Ni	0,5	0,467	TiC
	Ti	46,7	0,156	
	C	52,8	0,311	
6	Ni	35,8	0,362	Ti_2Ni
	Ti	64,2	0,362	

to approximately 2 μm. The TiC particles resulted from the use of a graphite crucible during the casting and melting of NiTi SMA alloys. Frenzel reported in literature [17,18] the thermodynamic and kinetics of TiC formation due to the reaction between molten NiTi and the graphite crucible and/or mould. According to literature and other findings [19], these particles did not have any role in influencing the mechanical or superelastic properties. In reference [20] it is reported that with the addition of graphite the martensite transformation temperature decreased noticeably.

Table 4 **Minimal and maximal size of precipitates**

Orthodontic wire	Precipitates	d_{min} / μm	d_{max} /μm
1	Ti_2Ni	0,7	4,9
2	Ti_2Ni	1,7	2,7
3	TiC	0,2	1,6
4	Ti_2Ni	0,6	0,9
5	TiC	0,3	1,9
6	Ti_2Ni	0,3	3,3

In the present TEM/EDS study we have provided determination of the chemical composition and observation of NiTi orthodontic wire's microstructure. We found out that, in orthodontic wires, different types of precipitation could be connected to the casting and melting of the NiTi SMA alloys. We observed the particles of Ti_2Ni and TiC, which are larger than the grain of a matrix consisting of an austenite phase. In the microstructure no other particles were observed which could be Ni_2Ti and Ni_3Ti according to the literature [20].

CONCLUSIONS

Under the conditions of this study we can draw the three main following conclusions:

- NiTi alloy for orthodontic wire is composed of an austenitic phase and Ti_2Ni and/or TiC particles.
- The particles sizes are in the range from 0,2 to approximately 5 μm.
- The austenitic phase represents some kind of matrix and is crystallized fully with grain sizes from approximately 50 to 160 nm.

REFERENCES

[1] T. W. Duering, K. N. Melton, D. Stoeckl, C. M. Wayman. Engineering Aspects of Shape Memory Alloys, Butterworth – Heinemann, London, 1990.

[2] R. Rudolf, J. Ferčec. Military Technical Courier, 61 (2013) 2, 105-122.

[3] J. Ferčec, B. Glišić, I. Šćepan, E. Marković, D. Stamenković, I. Anžel, J. Flašker, R. Rudolf. Acta Physica Polonica A, 122 (2012), 659-665.

[4] A. W. Brantley, G. Wenhua, A.T. William Clark, I. Masahiro. Dental Materials, 24 (2008), 204–210.

[5] D. C. Lagoudas. Shape Memory Alloys: Modeling and Engineering Applications. Springer, Berlin, 2010.

[6] W. R. Proffit, H. W. Fields, D.M. Sarver. Contemporary Orthodontics. Mosby, St Louis, 2007.

[7] A. A. Shirazdi, H. Abreu, L. Pocock, D. Klobčar, P.J. Withers, H.K.D.H. Bkadeshia. International Journal of Materials Research, 100 (2009) 1, 40 – 45.

[8] J. Ferčec, I. Anžel, R. Rudolf. Materials and Design, 55 (2014), 699-706.

[9] I. Budak, M. Soković, M. Barišić. Measurement, 44 (2011) 6, 1188-1200.

[10] R. Delville, B. Malard, J. Pilch, P. Sittner, D. Schryvers. International Journal of Plasticity, 27 (2011) 2, 282–297.

[11] J. Ferčec, R. Rudolf. IRT3000, 48 (2013), 26-29.

[12] M. Nacucchi, M. Alvisi, D. Altamura, V. Pfister, M. Re, M. A. Signore, M. Vittori Antisari. Materials Science and Engineering, 7 (2010) 1, 1 – 12.

[13] S. Matera, E. Anelli. Microscopy Microanalysis Microstructures, 6 (1995), 633-646.

[14] ASTM E112 – 12. Standard Test Methods for Determining Average Grain Size: http://materials.mcmaster.ca/faculty/malakhov/4L04/ReferenceMaterials/ASTM%20standards/ASTM%20E112-10%20Average%20Grain%20Size.pdf

[15] K. N. Lin, S. K. Wu, L. M. Wu. Martensitic Materials Transactions, 50 (2009) 11, 2637-2642.

[16] B. Karpe, B. Kosec, A. Nagode, M. Bizjak. Journal of Mining and Metallurgy, Section B: Metallurgy, 49B (2013) 1, 83-89.

[17] J. Frenzel, Z. Zhang, K. Neuking, G. Eggeler. Journal of Alloys and Compounds, 385 (2004) 1-2, 214-223.

[18] J. Frenzel, Z. Zhang, C. Somsen, K. Neuking, G. Eggeler, Acta Materialia, 55 (2007) 4, 1331-1341.

[19] O. Mortagy, M. Farag. Effect of Heat Treatment On The Superelasticity And Hardness of NiTi. International Conference on Modeling and Optimization of Structures, Processes and Systems (ICMOSPTS' 07), Durban, 2007.

[20] F. Chen, Y.X. Tong, X.L. Lu, X. Wang, B. Tian, L. Li, Y.F. Zheng, C.Y. Chung. Materials Letters, 65 (2011), 1073-1075.