MICROSTRUCTURE AND PURITY OF THE NiTiZr-BASED ALLOYS PREPARED BY A PLASMA METALLURGY PROCESS

Václav STRUNG, Ivo SZURMAN, Martin POHLUDKA, Daniel PETLÁK, Jiřina VONTOROVÁ

VŠB - Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Ostrava-Poruba, Czech Republic, EU, vaclav.strung@vsb.cz

Abstract

Alloys based of the Ni-Ti binary system have important position in a branch of shape memory alloys. Zirconium is an important alloying element giving these alloys needed stability at high-temperature applications. The aims of this paper were a preparation of the Ni-35Ti-15Zr and Ni-45Ti-5Zr (at.%) alloys, description of their microstructures and monitoring of their purity. The alloys were melted by plasma metallurgy processes. Metallographic samples were prepared from a central part of the ingot. The optical and scanning electron microscopes were used for documentation of microstructure. In both cases, the microstructure was polycrystalline with random orientation of grains. Individual grains consisted of dendrites formed by the NiTi-phase. On the contrary, interdendritic space was rich with Zr, eventually it contained undesirable inclusions of TiC and ZrO_2. They form in consequences of chosen technology of preparation in combination with high melting temperature. Because titanium is significant picker, contents of oxygen and carbon were monitored in the ingot samples of both alloys. The Ni-45Ti-5Zr alloy contained of 0.115 wt.% O_2 and of 0.013 wt.% C. For the Ni-35Ti-15Zr alloy, the content of O_2 was 0.103 wt.% and content of C was 0.012 wt. %. Compared to industrially manufactured NiTi-based memory alloys, contents of both elements should not exceed $C < 0.07$ wt.% and $O_2 < 0.05$ wt.%. We can submit that chosen method of preparation - plasma metallurgy - did not prevent the oxidation of both alloys, even though the melts were in a protective atmosphere of Ar with a purity of 4N6. By contrast, the carbon content remained in the standard.

Keywords: NiTiZr alloys, microstructure, plasma metallurgy, purity

1. INTRODUCTION

NiTi alloys are known as the most important shape memory alloys with good memory effect and pseudoelasticity. These shape memory alloys with high melting point are materials with phase transformation above 100°C. They are mainly applied in robotics, automotive, aerospace and medicine especially because of their excellent biocompatibility and corrosion resistance. The high transformation temperature of the NiTi alloys can be obtained by adding of a third element to an alloy, such as Pt, Pd, Au, Zr or Hf. From these elements, Hf and Zr appear to be most suitable because of their lower prices compared to the remaining elements. For a few reasons, practical devices have not been developed yet. One of the most serious problem of the NiTiZr alloys is their low workability. How a Zr content in these alloys increases, their hardness increases also but the workability and cold ductility significantly decrease. Improving of cold processability of the NiTiZr alloys is very important for their production in suitable sizes and shapes and for controlling of their microstructures. Therefore, NiTiZr alloys have been extensively studied in recent years [1 - 5].

One of the most important prerequisites for the practical application of these alloys is managing of production problems. This puts increased demands on purity of the raw materials as well as on the production process itself. In order to avoid unwanted impurities, the production of NiTiZr alloys is mostly carried out by melting in vacuum. Nowadays there are some different methods using for the alloy preparation (for example melting in high-frequency induction vacuum furnace, melting in an arc furnace, melting in a plasma furnace, electron beam melting etc.). Another possibility is represented by powder metallurgy. During a melting process, content of gases (oxygen) and non-metals (carbon) has a negative effect on the alloy properties. A process of solidification control is another important problem because of related minimization of micro- and macrosegregation. It is also necessary to prevent the material from non-metallic inclusions (e.g. from electrodes or melting crucibles). Formation of different carbides and oxides (especially TiC, TiO_2, $Ti_2Ni_xO_y$) in NiTi alloys effects concentrations of individual elements and is accompanied by changes of phase transformation temperatures. The formation of the low-melting phase of Ti_2Ni leads to cracking of the alloys at high temperatures. The TiC inclusions are usually found in the NiTiZr alloys after a VIM processing due to using of a carbon crucible during a melting process. Presence of these inclusions in the NiTi alloys strongly reduced their corrosion resistance [12, 13]. In the case of oxide inclusions (i.e. $Ti_2Ni_xO_y$), Liang and Huang [14] found that their presences are the main reason for pitting corrosion. For a production of the NiTiZr alloys, the most frequently used methods in industry are arc and induction melting processes in vacuum [6 - 14].

Among non-contaminating melting methods, plasma arc melting represents one of the most important success in the field of high quality alloy production lasting more than three decades. Argon is used as a plasma gas. Because of the high reactivity between titanium and oxygen, there are high demands on the purity of argon. It is a decisive factor for obtaining of a quality alloy. The plasma temperature of this melting process is 4800 °C.

Advantages of plasma furnaces include:

- in comparison with arc furnaces, plasma furnaces avoid to pollution of the melted material with graphite from the used electrodes and using of an inert atmosphere prevents alloy from gasification;
- the possibility of creating low-temperature plasma from any mixture of gasses and thus the possibility of using an oxidative, reductive, inert atmosphere;
- the possibility of degassing of a metal, because a partial pressures of gasses contained in the prepared materials are very low in the inert gas;
- plasma burners can achieve high and easily controllable temperatures;
- almost hundred percent use of alloying additives due to using of the inert atmosphere in the melting space.

Industrial plasma arc furnaces are used for production of reactive, refractory metals and superalloys with high melting points for more than twenty years, as is shown in [7, 11].

2. EXPERIMENT

NiTiZr alloys with nominal composition Ni-35Ti-15Zr and Ni-45Ti-5Zr (at.%) were prepared by plasma metallurgy. The melting was carried out under an atmosphere of argon (purity 4N6), electric current and voltage were at $I = 725$ A and $U = 63$ V. Therefore, the power consumption of the plasma furnace was $P = 46$ kW. Each of the two boats placed in a cooled water crystallizer was melted four times for homogenity in the ingot axis under plasma torch. The final castings were ingot shaped. These ingots were then cut by a diagonal cut on a MIKRON 110 saw blade. A sample of the centre was taken from each ingot. The cut samples were pressed into phenol resin with graphite fibers. This operation was carried out on the device MTH Standart 30. It was followed by grinding and polishing. The samples were ground by MTH Kompakt 1031 using abrasive paper from SiC (grain 180, 220, 400, 600, 800, 1000, 1200, 1500). Finally, on the same machine, the polishing of samples was carried out using a billiard cloth and aluminium (Al_2O_3) suspension with average grain size of 1 µm and 0.3 µm.

The microstructure was etched with etchant containing 10 g $CuSO_4 \cdot 5H_2O$ + 50 ml H_2SO_4 + 50 ml H_2O + 50 ml CH_3OH. The microstructure of the samples was then observed on the inversion metallographic microscope Olympus GX51 equipped with the DP12 digital camera and the Analysis FIVE software. The equipment has been photographed on the microstructure. For the determination of the chemical composition, a QUANTA FEG 450 scanning electron microscope (SEM) equipped with an APOLLO X probe was used. EDS analysis was perform on this equipment and photographic documentation of samples of both NiTiZr alloys was taken here. At the last stage, gas and interstitial elements were measured in these two alloys.

3. RESULTS

Observing the effect of the composition on the material structure of the NiTiZr - based alloy ingots, the structure was found to be largely inhomogenous. This inhomogeneity is associated with the own nature of plasma melting, when on the one side the process takes place at very high temperatures and, on the other side, the alloy is intensively cooled. The microstructure of both alloys was first documented by optical microscopy, but the inappropriately chosen etchant only led to etching of zirconium rich phases without any effect on grain boundary visibility (**Figures 1, 2**).The structure of both samples was clearly polycrystalline. Due to the fact that etching was not fully successful, etchings containing 26 ml of glycerol, 6 ml of concentrated HNO_3, 1 ml of concentrated HF and inaqueous solution of HF + HNO_3 will be used according to the work of Carl et al., Katona et al. [15, 16].

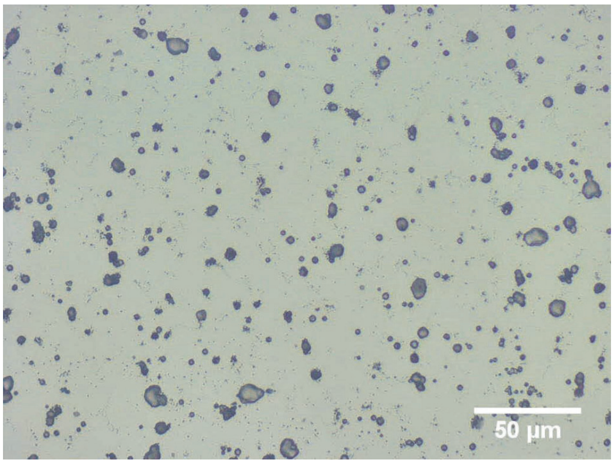

Figure 1 Optical micrographic microstructure of etched Ni-45Ti-5Zr alloy

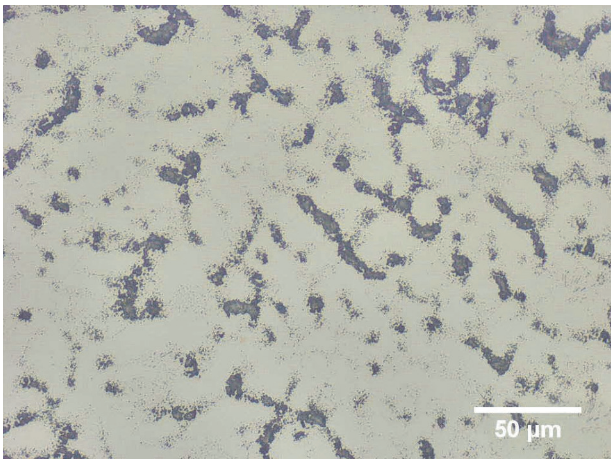

Figure 2 Optical micrographic microstructure of etched Ni-35Ti-15Zr alloy

For better observation and determination of individual phases, we used electron microscopy (**Figures 3, 4**).

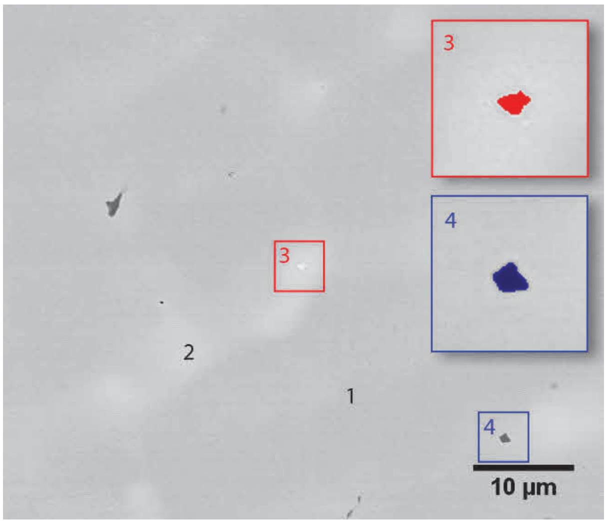

Figure 3 SEM micrograph of Ni-45Ti-5Zr alloy: 1,2) (Ti, Zr)Ni phase; 3) $Ni_{10}Zr_7$+NiTi+Ni_3Ti phase; 4) TiC phase;

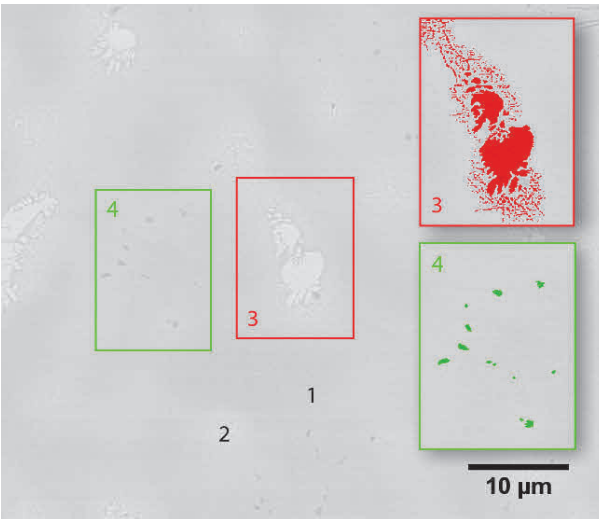

Figure 4 SEM micrograph of Ni-35Ti-15Zr alloy: 1, 2) (Ti, Zr)Ni phase; 3) $Ni_{10}Zr_7$+NiTi+Ni_3Ti phase; 4) ZrO_2 type phase

Table 2 EDS analysis of Ni-45Ti-5Zr alloy

Ni-45Ti-5Zr -area and spot EDS analysis (at.%)				
	Ni	**Ti**	**Zr**	**C**
area	53.51 ± 0.16	41.85 ± 0.26	4.64 ± 0.13	
spot 1	53.53± 0.10	43.10 ± 0.40	3.37 ± 0.30	
spot 2	55.47 ± 0.11	31.31 ± 0.40	13.23 ± 0.29	
spot 3	59.07 ± 0.63	21.87 ± 2.64	19.06 ± 2.02	
spot 4	5.35 ± 0.85	46.65 ± 1.22	3.12 ± 0.09	44.88 ± 0.45

Table 3 EDS analysis of Ni-35Ti-15Zr alloy

Ni-35Ti-15Zr -area and spot EDS analysis (at.%)				
	Ni	**Ti**	**Zr**	**O_2**
area	54.35 ± 0,40	32.01 ± 0,15	13.64 ± 0,27	
spot 1	54.12± 0.19	35.06 ± 0.20	10.82 ± 0.41	
spot 2	55.52 ± 0.08	28.76 ± 0.68	15.72 ± 0.60	
spot 3	60.45 ± 0.02	17.28 ± 0.05	22.27 ± 0.09	
spot 4	6.20 ± 0.80	4.90 ± 0.80	21.74 ± 1.12	67.16 ± 0.48

Using SEM microscopy, it has been found that the grains in the selected alloys are made from dendrites of (Ti, Zr)Ni phase. However the interdendritic space was rich on zirconium, possibility containing unwanted elements in the form of TiC carbides, ZrO_2 oxides (**Table 1**, spot 3 and **Table 2**, spot 4). Mentioned unwanted elements arise due to the chosen preparation technology combined with high melting temperatures.

An EDS analysis was performed to determine the chemical composition of the area and individual phases of the investigated alloys (**Tables 1, 2**). From the analysis of the area it is possible to say, that the nominal composition was observed. Compared with the ternary diagram [17, 18] and works by Hsieh et al. [19], it can be argued, that the gray matrix (spot 1) for both alloys samples correspond to the phase (Ti, Zr)Ni. The light gray phases (spot 2), also occurring in the both alloys, represent again the (Ti, Zr)Ni phase according to [19]. Since the white phases (spot 3 for Ni-45Ti-5Zr and Ni-35Ti-15Zr) are in the ternary diagram in an area, that is not experimentally explored, the ternary diagram calculated using the CALPHAD method [18] was used for these phases. It follows, that these phases are found in three phase area with the composition $Ni_{10}Zr_7+NiTi+Ni_3Ti$.If it goes of the dark phase (spot 4) in the alloy Ni-45Ti-5Zr, it is the TiC carbide phase. Similarly, the gray phase (spot 4) in alloy Ni-35Ti-15Zr is the inclusion of ZrO_2 type.

Since some phases of the selected alloys have not been uniquely determinated, it is planned for the future, subjecting these phases to a more detailed examination. X-ray diffraction analysis or TEM microscopy will be used for the future experiments.

Since titanium is a significant picker, the contents of the gases (oxygen) and interstitial elements (carbon) have been monitored in ingot samples of both alloys (**Table 3**).

Table 4 Content of carbon and oxygen in investigated alloys

Alloy	**C** (wt.%)	**O_2** (wt. %)
Ni-45Ti-5Zr	0.0129	0.115
Ni-35Ti-15Zr	0.0122	0.103

Compared to ASTM F2063 - 00 [20], which states that the minimum of oxygen levels in industry can be $O_2 <0.05$ wt.%, we can state, that the chosen methodology of preparation - plasma metallurgy failed to fully prevent the oxidation of alloys even if the process was carried out in a protective atmosphere of argon purity of 4N6. Tuissi et al. [11], however, had in their work the value of oxygen in the standard. It is shown that the reason for the increased oxygen content in NiTiZr alloys is the higher the amount of oxygen contained in the starting metals, any leakage in the furnace armature. Conversely, the carbon values according to [20] ($C < 0.07$ wt.%) remained in the standard.

4. CONCLUSION

This work deals with NiTiZr - based alloys with nominal composition Ni-45Ti-5Zr and Ni-35Ti-15Zr (at.%), which with their composition occur at the edge of known area in ternary diagram. Due to their lucrative nature in the field of industry, these alloys have been extensively studied in recent years. The alloys were made using plasma metallurgy, where homogenization was sought. As this operation has become unsuccessful, in the near future, it plans to remelt these ingots with VIM technology (vacuum induction melting) to guarantee homogenity. The study of structure, which was performed by SEM microscopy and EDS analysis, indicates that the grains in selected alloys form dendrites rich on (Ti, Zr)Ni phase. Interdendritic space is on the other hand rich on zirconium, possibility including TiC or ZrO_2 inclusions. Since titanium is a significant picker, carbon and oxygen measurements have been performed on alloys. From the results it can be stated, that plasma metallurgy failed to fully prevent oxidation of alloys. Oxygen values in alloys exceeded the permitted industrial values ($O_2 < 0.05$ wt.%) roughly twice (Ni-45Ti-5Zr $O_2 = 0.115$ wt.% a Ni-35Ti-15Zr $O_2 = 0.103$ wt.%). The carbon content values remained in the alloys in the standard. Since EDS analysis is not fully sufficient with respect to the determination of the phase in alloys, its planned to subject these alloys X-ray diffraction analysis or TEM microscopy.

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REFERENCES

[1] KIM, S., PARK, CH. and HONG, J. Fracture toughness of TiNiHf alloys: A hybrid study using In-situ transmission electron microscopy. Experiments and finite element analyses. *Materials Science & Engineering A* [online]. 2016. vol. 655, pp. 363-372. [viewed 2018-05-09]. Available from: DOI: 10.1016/j.msea.2016.01.016

[2] HSIEH, S. F., HSUE, W. S. and CHEN, S. L. Surface characteristics and shape recovery ability of Ti35.5Ni48.5Zr16 and Ni60Al24.5Fe15.5 ternary shape memory alloys. *Journal of Alloys and Compounds* [online]. 2013. vol. 571, no. 6, pp. 63-68. [viewed 2018-05-09]. Available from: DOI: 10.1016/j.jallcom.2013.03.111

[3] KIM, J.I., INAMURA, T, KIM, H.Y., HOSODA, H. and MIYAZAKI, S. Shape memory characteristics of Ti-22Nb-(2-8)Zr(at.%) biomedical alloys. *Materials Science and Engineering* [online]. 2005. vol. 405, pp. 334 - 339. [viewed 2018-05-09]. Available from: DOI: 10.1016/j.msea.2005.05.050.

[4] KIM, H.Y., MIZUTANI, M. and MIYAZUKI, S. Crystallization process and shape memory properties of Ti-NiZr thin films. *Acta Materialia* [online]. 2009. vol. 57, pp. 1920-1930. [viewed 2018-05-09]. Available from: DOI: 10.1016/j.actamat.2008.12.036.

[5] KIM, H.Y., JINGUU, T., NAM, T. and MIYAZAKI, S. Cold workability and shape memory properties of novel Ti-Ni-Hf-Nb high-temperature shape memory alloys. *Acta Materialia* [online]. 2011. vol. 65, pp. 846-849. [viewed 2018-05-09]. Available from: DOI: 10.1016/j.scriptamat.2011.07.049.

[6] FILIP, P., CÍŽEK, L., KURSA, M., KUCHAŘ, L. and MAZANEC, K. Basic technological data of preparation TiNi equiatomary alloy. In *Collection of scientific papers of VSB - Technical University in Ostrava* [online]. 1988. no. 1, pp. 125-139. [viewed 2018-05-09]. in Czech.

[7] KURSA, M., SZURMAN, I., DRÁPALA, J., LOSERTOVÁ, M. and GREGER, M. *Shape memory materials on the base of Ni-Ti-Me and possibilities of controlling their transformation characteristics*. 1st. ed. Ostrava: VŠB - Technical University of Ostrava, 2005. 155 p. ISBN 80-248-0894-3. In Czech.

[8] BENAFAN, O. and BIGELOW, G. S., et. al. Additive manufacturing of NiTiHf high temperature shape memory alloy. *Scripta Materialia* [online]. 2018. vol. 145, pp. 90-94 [viewed 2018-05-09]. Available from: DOI: 10.1016/j.scriptamat.2017.10.016

[9] SCHETKY, L. and WU, M. H. Issues in the further development of Nitinol properties and processing for medical device applications. *Proceedings of the Materials & Processes for Medical Devices Conference 2003 (ASM International)* [online]. 2004. Available from: https://pdfs.semanticscholar.org/2a2f/b9e1bf07bf7c0c0dfcb96d576bceb6a197bf.pdf.

[10] PORTER, D.A. and K.E. EASTERLING. *Phase transformations in metals and alloys*. 2nd ed. London: Chapman&Hall, 1993. 520 p. ISBN 9780442316389.

[11] TUISSI, A., G. RONDELLI and P. BASSANI. Plasma arc melting (PAM) and corrosion resistance of pure NiTi shape memory alloys. *Shape Memory and Superelasticity* [online]. 2015, vol. 1, no. 1, pp. 50-57. [viewed 2018-05-09]. Available from: DOI: 10.1007/s40830-015-0011-6.

[12] KIMURA H. and SOHMURA T. Surface coating on TiNi shape memory implant alloys. *The Journal of Osaka University Dental Scholl* [online]. 1987, vol. 27, pp. 211-223. [viewed 2018-05-09]. Available from: https://www.ncbi.nlm.nih.gov/pubmed/3506079

[13] SHABALOVSKAYA, S., ANDEREGG, J. and VAN HUMBEECK, J. Recent observations of particulates in Nitinol. *Materials Science and Engineering A* [online]. 2008. vol. 481-482, pp. 431-436. [viewed 2018-05-09]. Available from: DOI: 10.1016/j.msea.2007.01.177.

[14] LIANG, C. and HUANG, N. Electrochemical characteristic of TiNi shape memory alloy in artificial body fluids. *Journal of Biomedical Materials Research. Part A* [online]. 2009, vol. 89A, no. 1, pp. 266-269. [viewed 2018-05-09]. Available from: DOI: 10.1002/jbm.a.32062.

[15] CARL, M., SMITH, J., VAN DOREN, B. and YOUNG, M. Effect of Ni-content on the transformation temperatures in NiTi-20 at. % Zr high temperature shape memory alloys. *Metals* [online]. 2017, vol. 7, no. 11, pp. 511-526. [viewed 2018-05-09]. Available from: DOI: 10.3390/met7110511. ISSN 2075-4701.

[16] KATONA, B., BOGNÁR E., BERTA, B., NAGY, P. and HIRSCHBERG, K. Chemical etching of Nitinol stents. *Acta of Bioengineering and Biomechanics* [online]. 2013. vol. 15, no 4, pp. 3-8. [viewed 2018-05-09]. Available from: DOI: 10.5277/abb130401.

[17] GUPTA, K.P. The Ni-Ti-Zr system (Nickel-Titanium-Zirconium). *Journal of Phase Equilibria*. 1999. vol. 20, no. 8, pp. 441-448.

[18] TOKUNAGA, T., MATSUMOTO, S., OHTANI, H. and HASEBE, M. Thermodynamic calculation of phase equilibria in the Nb-Ni-Ti-Zr quarternary system. *Materials Transaction* [online]. 2007. vol. 48, no. 2, pp. 89-96. [viewed 2018-05-09]. Available from: DOI: https://doi.org/10.2320/matertrans.48.89.

[19] HSIEH, S.F. and WU, S.K. Room-temperature phases observed in Ti_{53}-$xNi_{47}Zr_x$high - temperature shape memory alloys. *Journal of Alloys and Compounds* [online]. 1998. vol. 266. pp. 276-282. [viewed 2018-05-09]. Available from: http://ntur.lib.ntu.edu.tw/bitstream/246246/86724/1/62.pdf.

[20] MORGAN, N., WICK, A., DICELLO, J. and GRAHAM, R. Carbon and oxygen levels in nitinol alloys and the implications for medical device manufacture and durability. In *Proceedings of International Conference on Shape Memory and Superelastic Technologies, SMTS - 2003* [online]. 2006. pp. 821-828. [viewed 2018-05-09]. Available from: DOI: 10.1361/cp2006smst821.