STRUCTURALLY PHASE ANALYSIS OF A NiTi-Zr-Nb-BASED ALLOY

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Abstract

NiTi-based alloys belong to progressive materials which exhibit so called a shape memory phenomenon. These alloys are frequently used at high-temperature applications and automotive industry. Structurally complex phase analysis of TiNi-based alloys was carried out. The chemical composition of the prepared alloy was 49.5Ni-25.5Ti-10Zr-15Nb (at.%). The alloy was prepared by a vacuum induction melting with gravity casting and examined by methods of optical microscopy, scanned electron microscopy, X-ray diffraction and thermo-evolution method of interstitial element analysis.

Keywords: NiTi Alloy, vacuum induction melting, scanned electron microscopy

1. INTRODUCTION

NiTi based super-elastic shape memory alloys are increasingly used in many areas, from bridge structures, medical implants, for the production of tiny sensors and actuators in micro-electromechanical systems. These alloys have their applications also in building structures and in vibration dampening [1]. Alloys of the system Ni-Ti-Nb are characterised by a big hysteresis of transition. With sufficient strain in the martensitic state, the TiNi matrix will be pseudo-elastically deformed while in soft Nb-precipitates plastic deformation takes place. The matrix must during reverse transformation to austenite overcome significant internal tensions => new possibilities of use of such alloy are e.g. in the coupling technique, where greater temperature differences are needed [2, 3]. When substituting titanium and zirconium in a range of approx. 10 to 30 at.%, the transformation temperatures increase above 200 °C. Due to the good hot formability and relatively low manufacturing costs, these alloys could offer interesting possibilities for high-temperature applications [4].

2. EXPERIMENT

Experimental alloy Ti-Ni-Nb-Zr was prepared by vacuum induction melting in the graphite crucible and it was then cast into the mould by gravity casting. The charge consisted of lump material formed of pure metals. The melting temperature was 1500 °C. The samples for metallographic observations were prepared by standard metallographic methods including sanding with the use of abrasive paper of the grain size from 60 to 2000 and polishing by slurry of Al_2O_3 with a particle size from 1 to 0.3 µm. For observation of the microstructure and for analysis of the chemical composition the optical microscope Olympus GX51 was used with digital camera DP12 and scanning electron microscope QUANTA 450 FEG equipped with the probe EDAX APOLLO X. The content of interstitial elements (oxygen, nitrogen) was measured the thermo-evolution method using the instrument ELTRA ONH-2000. At least 3 pieces of the samples were always used for the measurement. The carbon content was measured on the instrument SpectroMaxX.

3. RESULTS AND DISCUSSION

Table 1 presents the chemical composition of the alloy after vacuum induction melting determined by the EDS method, including standard deviation measurements. This is a surface analysis. The results show that we managed to prepare an alloy, the composition of which differed only slightly from the nominal composition.

Table 1 Results of surface EDS microanalysis of the alloy 49.5Ni-25.5Ti-10Zr-15Nb

Chemical composition (at.%)	Elements			
Alloy	Ni	Ti	Zr	Nb
49.5Ni-25.5Ti-10Zr-15Nb	48.64 ± 0.03	25.91 ± 0.09	9.50 ± 0.01	15.95 ± 0.13

The microstructure of the alloy 49.5Ni-25.5Ti-10Zr-15Nb is shown in **Figures 1** and **2**. The structure is formed by a matrix (phase 1) shown in **Figure 3a)**, the composition of which corresponds to the intermetallic compound TiNi (B2 high-temperature cubic modification in binary alloys), in which Zr and Nb are also dissolved. Furthermore, it is possible to observe in the structure the less represented phase 2 (it represents in the binary alloys the low-melting phase Ti_2Ni) with a higher amount of dissolved Nb and a smaller amount of Zr in comparison with the matrix. It can be also see inclusions of the complex carbide type (Ti-Nb-Zr)C,O. The exact type of the crystal lattice and its parameters will be moreover determined by an X-ray diffraction analysis within the frame of other experiments.

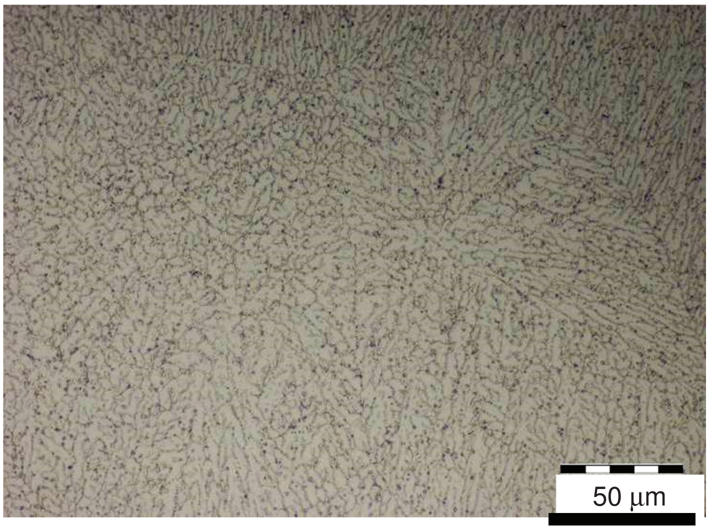

Figure 1 The microstructure of TiNiZrNb alloy, induction melting, OM

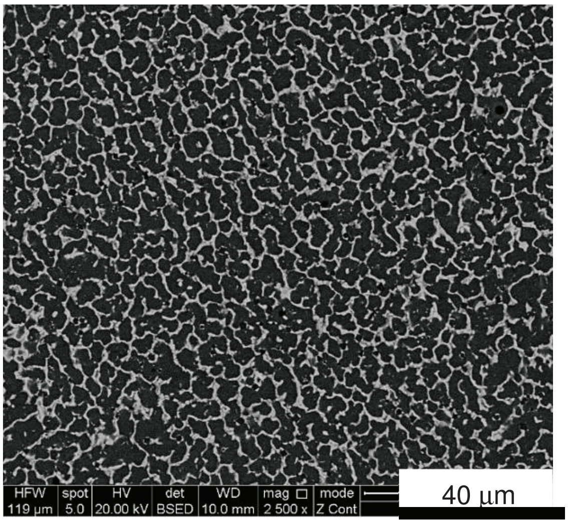

Figure 2 TiNiZrNb alloy, induction melting, SEM

Table 2 shows the composition of individual phases and of the complex carbide. These phases are shown in **Figure 3a)**. The phase marked as 3 is a complex-carbide, the detail of which is shown in **Figure 3b)**.

Table 2 Results of spot EDS microanalysis of the alloy 49.5Ni-25.5Ti-10Zr-15Nb

Spots analysis	Chemical composition (at.%)					
Sample	Ti	Ni	Zr	Nb	C	O
1	28.91 ± 0.22	50.03 ± 0.11	10.38 ± 0.11	10.68 ± 0.22	-	-
2	18.24 ± 0.84	45.41 ± 0.66	7.21 ± 0.44	29.15 ± 0.26	-	-
3	25.07 ± 1.64	26.42 ± 1.19	6.40 ± 0.23	14.60 ± 0.41	18.80 ± 0.71	8.71 ± 0.05

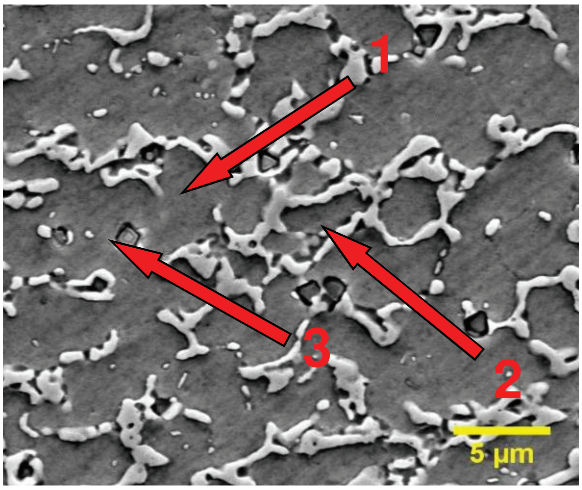

Figure 3 a) The microstructure of TiNiZrNb and marking phases, SEM

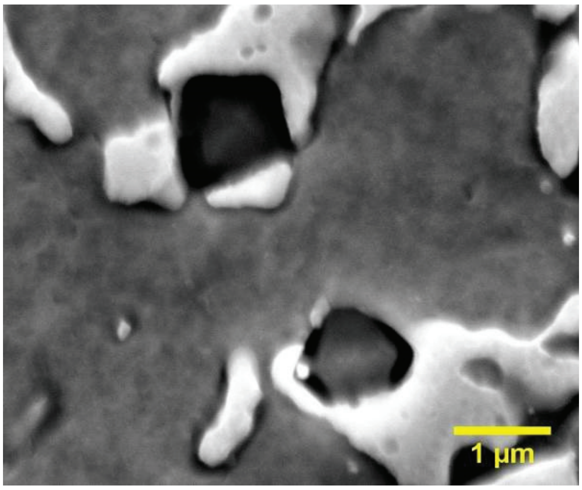

Figure 3 b) Detail of complex-carbide inclusions

On the scratch pattern, three phases were observed by electron microscopy and an image analysis of these phases was created (**Figure 4**):

blue phase - (phase 1) matrix (50Ni-29Ti-10Zr-11Nb at.%)
red phase - (phase 2) (46Ni-18Ti-7Zr-29Nb at.%)
green phase - (phase 3) carbide + oxide (26Ni-25Ti-6Zr-15Nb-9O-19C at.%)

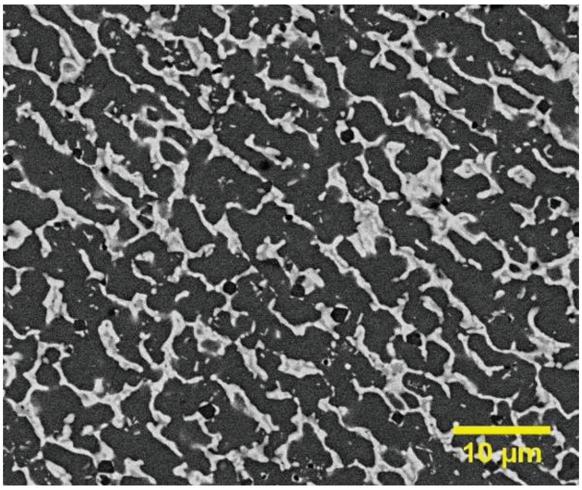

Figure 4 a) The structure of the NiTiZrNb alloy

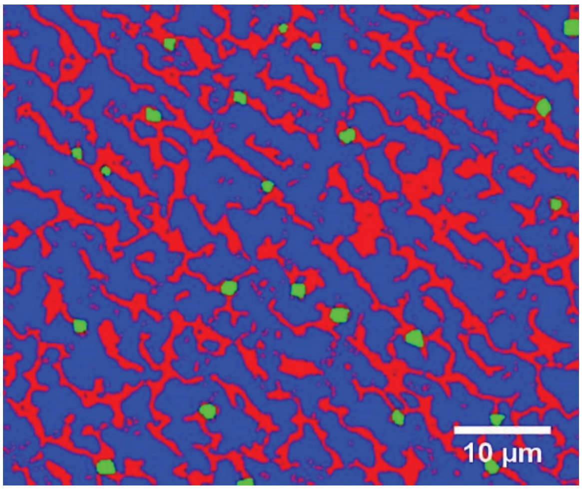

Figure 4 b) Viewing the structure of **Figure 4 a)** in false-color (for contrast enhancement)

The structure of the NiTiZrNb alloy is formed by the blue and red phases at a ratio of 3:1 (**Table 3**). Unfortunately, the structure contains also undesired inclusions of the oxide-carbide nature (green phase), the volume fraction of which is 1.45% (**Table 3**).

Table 3 The volume fraction of the phases in the alloy NiTiZrNb

	Blue phase	Red phase	Green phase
Volume (%)	73.60 ± 0.27	24.95 ± 0.14	1.45 ± 0.28

The content of the gases and carbon in the alloy after vacuum induction melting in the graphite crucible: The amount of oxygen was 0.083 wt.%, which can be evaluated as successful. The content of nitrogen, namely 0.0068 wt.% is also satisfactory, as well as the carbon content of 0.053 wt.%. This quantity of carbon was caused by the graphite crucible [5].

Preparation of the NiTiZrNb alloy took place in a graphite crucible at the temperature of approx. 1500 °C. Dwell at such a high temperature increases the probability of erosion of the graphite crucible and enrichment of the melt with carbon [6]. In this case, various inclusions of carbide nature were observed. **Figure 3b)** shows examples of such inclusions, for which three- or four-axis symmetry was characteristic.

Statistical analysis proved that the surface of a metallographic polished section of NiTiZrNb with an area of 3042 μm^2 contains on average 34 carbide inclusions with size ranging from 0.6 to 2.1 μm. **Figure 5** shows a normal distribution of the average size of inclusions. Approximately 24% of complex-carbide inclusions are located at the maximum of this distribution, i.e. within the interval from 1.20 to 1.35 μm. This conclusion is also supported by the average size of inclusions, which was 1.31 ± 0.17 μm.

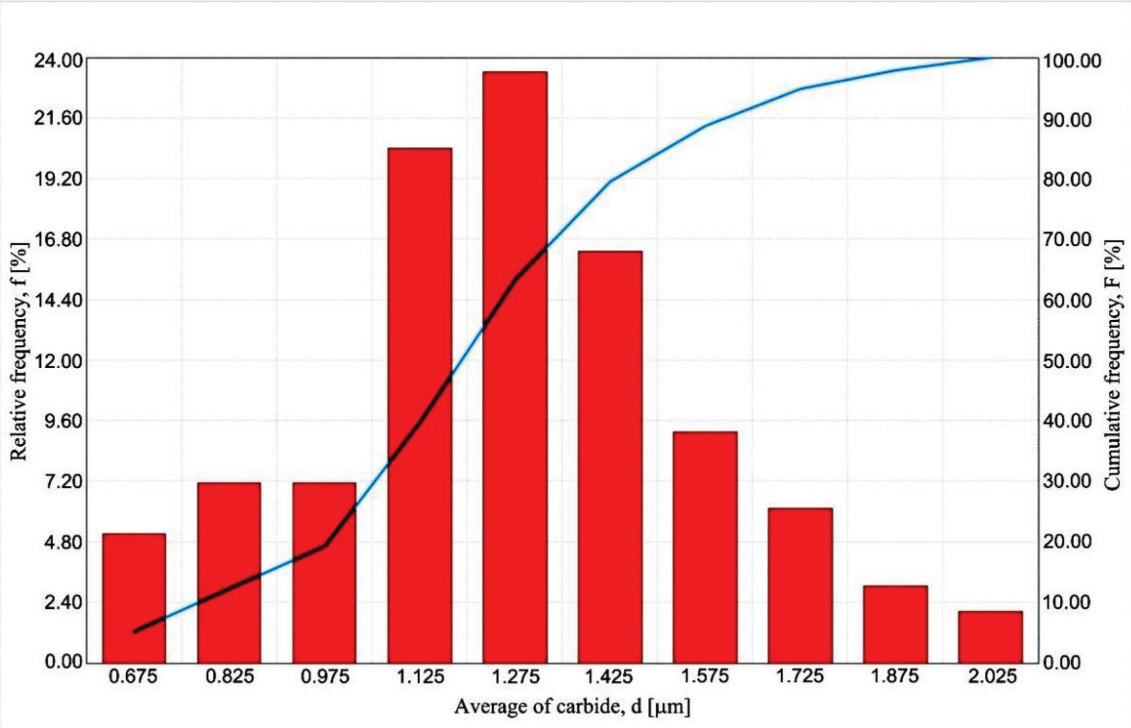

Figure 5 Average distribution of complex-carbide inclusions in the matrix of NiTiZrNb alloy

4. CONCLUSION

An alloy with composition 49.5Ni-25.5Ti-10Zr-15Nb by the method of vacuum induction melting at the temperature 1500°C was prepared. The alloy was composed of a matrix phase about the content (50Ni-29Ti-10Zr-11Nb at.%), of the phase rich in Nb about the content (46Ni-18Ti-7Zr-29Nb at.%) and of complex-carbide type (26Ni-25Ti-6Zr-15Nb-9O-19C at.%). An image analysis of these phases was created. Phases 1 and 2 were in the ratio 3:1 with a volume fraction phase 3 of 1.45 %. Furthermore, measurements were performed of the gas and carbon content in this alloy. Future progress of the work will focus on the study of the mechanical properties.

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