Crystallization and mechanical properties of the NiNb(ZrTi)Al amorphous alloys with 10 and 25 at % of Nb and 3 to 7 at % Al content.

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Abstract. The results of the investigations of alloys of compositions Ni₅₈Nbₓ(ZrTi)₃₉₋ₓₐ₉ and Ni₅₈Nbₓ(ZrTi)₃₂₋ₓₐ₇ with x = 10, 25 and y = 3, 7 respectively, are presented. The structure of the all melt spun ribbons was amorphous, however the crystallization process proceeded in a very different way in the ribbons with x= 10, y= 7 and ribbons with x= 25 and y= 3. In the first compositions typical primary crystallization of the 50 nm grains of the NiTi(Zr) cubic phase was observed while the ribbons containing 25 at.% of Nb and 3 at.% of Al revealed very stable thermally amorphous phase, nano-crystallizing at the range of primary crystallization but preserving large fraction of the amorphous phase high above the primary crystallization temperature. The tensile curves were determined for ribbons of both compositions and were different, but revealed quite large range of the plastic elongation. The HREM experiments did not reveal any crystallization in the shear bands, after the fracture of the ribbons.

1. Introduction
Ni-base Nb containing amorphous alloys reveals high glass forming ability, fracture strength and high corrosion resistance [1]. In case of the metallic glasses inhomogeneous deformation realized by the shear bands formation, together with large elastic deformation range and practical lack of plasticity may cause premature fraction [2, 3]. In many cases together with the shear bands formation the nanocrystallization was observed, especially when the compressive strains were present [2]. In some other amorphous compositions or deformation modes no mechanically induced crystallization occurred [2]. In the following paper two different NiNbZrTiAl alloys, with 10 and 25 at% of Nb content, were studied from the point of view of the microstructure of the melt spun ribbons, crystallization, tensile properties and microstructure of the deformed amorphous phase.

2. Experimental procedure
The ingots of composition Ni₅₈Nb₁₀Zr₁₃Ti₁₂Al₇ (alloy S1) and Ni₅₈Nb₂₅Zr₅Ti₆Al₃ (alloy S2) were made by melting components of high purity, and casting. The ribbons 50 µm thick and 5 mm wide were prepared by melt spinning after re-melting of the ingots several times with use of the levitation method. The scanning electron microscope Philips XL 30, transmission electron microscopes Philips CM 200 and TECNAI were applied for the micro-structural and high resolution characterization. To
determine thermal stability of the amorphous phase the DSC DuPont 910 and SDT Q600 were used while the heating rate 0.3 K/s was applied. The tensile test on the samples shaped from the ribbons was performed on the Instron 3382 testing machine with the rate of 0.1 mm.s⁻¹. The pneumatic side-action grips were applied. At least ten samples were tested for load-elongation curve. Thin foils for HREM were prepared by electropolishing and additionally thinning with ion gentle milling system. The fine ion beam technique (FIB) was used for the preparation of the foils from the fractured cross-sections of the tensile specimens.

3. Experimental results and discussion

3.1. The structure and crystallization of the ribbons

The structure of all ribbons was amorphous. The bright field (BF), dark field (DF) and diffraction patterns (SADP) from the ribbons, typical for the glassy state, are shown in Fig.1a-f. The amorphous structure of the ribbons was also confirmed by X-ray diffraction. Further high resolution (HREM) observation of the ribbons, performed after additional gentle milling, also did not revealed any crystalline phase.

Fig.1. TEM micrographs (bright and dark fields) and electron diffractions from the amorphous structures of the following ribbons: S1 (a-BF, b-SADP, c-DF) and S2 (d-BF, e-SADP, f-DF).

The temperature range of the complete crystallization process of the investigated amorphous compositions exceeded 700°C. The range of the crystallization determined with SDT revealed two crystallization effects in case of the composition S1 and three thermal effects for the composition S2. The primary crystallization temperatures were 865 and 878 K (Fig.2) and the processes were completed until 983 and 1063 K respectively for both compositions. The increase of the niobium content increased all the characteristic temperatures of transformations but reduced undercooled liquid range ΔT (by -4 K), while reduced glass transition temperatures Tg/Tm remained 0.62. To investigate the changes of microstructure during crystallization the samples were heated and aged in the desired temperatures in the calorimeter before thin foils were prepared for the transmission electron microscopy. The first temperature T1 was chosen just at the start of the primary crystallization, at 853 K in case of alloy S1 and 877 K in for the alloy S2. As the crystallization process revealed to be very different, the alloy S2 was studied also after short ageing at temperature T2= 903 K between the first and the second crystallization effect and 50 K above the end of the process of crystallization, at temperature T3 = 1123 K.

The microstructures of the ribbons S1 achieved after 120 s annealing and S2 after annealing 600 s at temperatures T1 are shown in the Figs. 3 and 4a. In the case of the amorphous phase S1 the of equiaxial crystalline grains of the average size of 55 nm formed. Also respectful ring-type of SADP characteristic for polycrystalline structure was observed. The primary crystallizing phase was identified as the cubic ( Pm-3m) NiTi(Nb), frequently noticed after crystallization of Ni-based amorphous alloys containing Ti, Zr or Nb [4], with the lattice constant a₀ = 0.299 nm.
After 600 s annealing at the analogous T1 temperature the S2 amorphous phase revealed only small amount of nanocrystallization (Fig.4a). As is seen crystallites up to 5 nm in diameter were formed at this temperature. Similar crystallites were observed also at temperature T2. Even when crystallization was completed at temperature T3, still not complete nanocrystallization was observed (Fig.4b, c, d) but still large amount of the amorphous phase remained.

Fig.4. HREM and TEM microstructures of the sample S2: a) after annealing 600 s at temperature T1= 877 K (HREM); b, c, d) at temperature T3= 1123 K, b) BF, c) SADP, d) DF (TEM).

3.2. Mechanical properties of the amorphous ribbons
To determine mechanical properties of the ribbons the room temperature tensile tests were performed. The sharp grips imprints on the samples confirmed lack of any sliding between the grips and the sample. The load-elongation curves for S1 and S2 ribbons, revealed differences. In both cases the ribbons showed quite large range of the plastic elongation. The ribbon S1, maximally elongated up to 0.6, after the stress peak relaxation, with no breaking (Fig.5a, curve a) and the second cycle was performed until fracture (Fig.5a, curve b). The range of the stress relaxation should be identified with the shear band formation, further leading to the micro-cracks formation [5]. However the range of the localized, inhomogeneous plastic deformation was quite large, as for the amorphous phase. The structure of the fracture surface is shown in Fig.5b. The river-like pattern interpreted as ductile fracture event [6] and melted droplets of the material due to the high local temperature increase [3] are marked by the arrows. In the Fig.5c, slip lines roughly parallel to the tensile axis are also visible, related to the thin surface layers on the fracture cross-sections. The plastic deformation between yield stress and stress peak relaxation is probably related to them (the range between the first and second arrow in Fig.5a, curve a).

In the case of the ribbon S2 the stress-elongation curve was more characteristic for the metallic glass (Fig.5a, curve c), the observed maximal elongation was slightly shorter and something like a hardening effect was following it. Hardening effect is hard to explain in case of the metallic glasses but some information concerning such an event is available in literature [3, 7].
As an athermal nanocrystallization caused by the fracturing was commonly reported in case of metallic glasses [3] the HREM investigations were performed. The HREM microstructures observed on the edges and fracture surfaces prepared with FIB technique were similar both for S1 and S2 tensile samples, however no crystallization was observed (Fig.5d, e).

4. Conclusions
In case of the investigated amorphous alloys increase of the Nb content above 20 at% greatly increases thermal stability of the amorphous phase while relatively good ductility remained. This may be promising for the bulk metallic glasses or for the amorphous matrix composites.

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5. References
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