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METALLIC GLASS FORMATION IN NiTiZrNbSi ALLOYS BY RAPID SOLIDIFICATION OR BALL MILLING AND ULTRA HIGH PRESSURE COMPACTION

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Abstract. New Ni-based bulk metallic glasses were synthesized in the NiTiZrNbSi system. Alloys were developed based on the quaternary alloy (A) $Ni_{48,5}$-$Nb_{21,5}$-$Ti_{16,5}$-$Zr_{13,5}$ (in at.%) applying a small addition of Si. At first, the alloy Ni_{45}-Nb_{21}-Ti_{16}-Zr_{13}-Si_5 (alloy B in at.%) was cast and then a new alloy based on the eutectic composition $Ni_{50,34}$-$Nb_{14,38}$-$Ti_{17,32}$-$Zr_{15,15}$-$Si_{2,81}$ (alloy C in at.%) has been developed. Both alloys were also prepared by mechanical alloying and melt spinning and in both cases fully amorphous structure was observed. DSC analysis of the ribbon of the alloy B shows crystallization temperature of 512 °C. In the alloy C HRTEM studies indicated presence of a few nanocrystals of size of 1-2 nm in the ribbons and 5-7 nm in the powders. DSC analysis shows crystallization temperature of 555 °C in the ribbon and 587 °C in the powder. The Vicker's microhardness measurements gave similar results for both amorphous B and C alloys close to 12 GPa. Ultra high pressure compacting performed under pressure of 4-7 GPa and temperatures several degrees below crystallization temperatures allowed to obtain compacts of dominating amorphous structure as confirmed using TEM studies and DSC measurements.

1. INTRODUCTION

Bulk amorphous alloys have been of particular interests in the past two decades because of their exceptional mechanical properties that include very high strength and elastic strain limit. Currently developed bulk metallic glasses (BMG's) have limitations, like thermal stability and elastic modules and a relatively high materials costs. As such, there has been a growing interested in developing novel BMG's with higher strength and elastic modules, higher thermal stability, lower density and lower material costs, like titanium, iron, aluminum and copper based alloys with higher GFAs and better manufacturability [1].

Ternary NiNbSn or multicomponent Ni_{60-x}-Co_x-Nb_{20}-Ti_{10}-Zr_{10} nickel base amorphous alloys [2] were obtained either by rapid solidification [3] or ball milling technique [4]. Bulk alloys exhibit a high elastic modulus, good corrosion resistance and compressive yield strength between 1,8 and 3 GPa with 2% fracture elongation. Ni_{57}-Zr_{20}-Ti_{20}-Si_3 powders obtained by mechanical alloying and consolidated into bulk metallic glasses by vacuum hot pressing method was found to have a wide supercooled region of 88K before crystallization and a microhardness of about 800 HV [4]. Surprisingly, $Ni_{59}Zr_{16}Ti_{13}Si_3Sn_2Nb_7$ as-cast BMG exhibits compressive plastic deformation of 6.5% before failure [5]. The bulk amorphous $Ni_{59}Zr_{20}Ti_{16}S_{i2}Sn_3$ alloy exhibits high compressive fracture strength of about 2.7 GPa with a plastic strain of about 2% [6]. Additions of Pt and Cu simultaneously were found to

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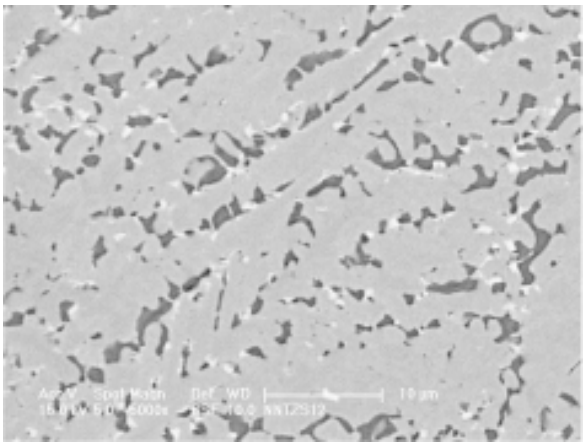

Fig. 1. SEM microstructure of the alloy C showing 4 phases eutectic structure.

increase the supercooled liquid region of the $Ni_{60}Nb_{10}Zr_{15}Ti_{15}$ alloy from 42 to 89 and 91K respectively [7].

Previous work [8] on ZrCuAl and ZrNiTiCu prepared by ball milling and ultra high pressure 4.0-7.5 GPa (UHP) consolidation method in the temperature range between T_g - T_x proved the possibility to obtain bulk compacts using this technology. In this paper the development of a new amorphous alloys in the NiTiZrNbSi system prepared by rapid solidification or ball milling and UHP compaction and their thermal and mechanical properties are described.

2. EXPERIMENTAL PROCEDURE

The ball milling process of the Ni-Nb-Ti-Zr-Si alloys was performed in a planetary mill “Pulverisette 5” at 200 rpm under argon atmosphere. The elemental powders were initially blended to desired compositions in the glove box and then subjected to milling. The alloys of compositions (all in at.%): alloy (A) $Ni_{48,5}$-$Nb_{21,5}$-$Ti_{16,5}$-$Zr_{13,5}$, alloy (B) Ni_{45}-Nb_{21}-Ti_{16}-Zr_{13}-Si_5, alloy (C) $Ni_{50,34}$-$Nb_{14,38}$-$Ti_{17,32}$-$Zr_{15,15}$-$Si_{2,81}$ were cast using melt spinning method in a helium atmosphere and pressure of 0,14 MPa and the linear copper wheel rate of 22 m/s. Ultra high pressure compacting was performed using Bridgeman method under pressure of 4-7 GPa and temperatures several degrees below the crystallization temperatures during 3 minutes. Structure was studied using HRTEM (Tecnai G2F20 S-Twin), TEM Philips CM 20, SEM Philips XL 30 and X-ray diffractometer PHILIPS PW 1840. Thin foils for TEM studies were prepared from ribbons using electrolytic polishing in HNO_3/CH_3OH electrolyte, from powders by embedding into epoxy and microtome cutting and from UHP compacts by diamond saw cutting, grinding, dimpling and Gatan Duo Mill 660 ion beam polishing. DSC analysis was made using Perkin Elmer DSC 5 equipment at the heating rate 10 and 20 °C/min and the onset of crystallization has been determined. The dynamic microhardness test was performed using CSEM Mikro-Combi-Tester equipped with Vickers intender with maximum load of 100 mN. Elastic Modulus was calculated using Oliver and Pharr method.

3. RESULTS AND DISCUSSION

The composition of the alloy (B) was proposed by adding 5% Si and modifying previously investigated quaternary alloy (A). After casting in an iron mould allowing low crystallization rate, its microstructure was analyzed with SEM equipped with EDS to find the eutectic composition which average value was measured using EDS as $Ni_{50,34}$-$Nb_{14,38}$-$Ti_{17,32}$-$Zr_{15,15}$-$Si_{2,81}$ (alloy C in wt.%). SEM microstructure presented in Fig.1 was taken after casting in the iron mould and slow cooling of the alloy C. It does not show primary crystals, only 4 phases eutectic structure; weak darker contrast can be distinguished near the gray phase suggesting presence of a four phases together with a bright and dark ones. Alloys B and C were rapidly solidified using melt spinning method. DSC heating curves of both alloys ribbons are presented in Figs. 2 and 3. They show that in the ribbon of alloy B the value of crystallization temperature is 512 °C and that of the alloy C shows two stages of crystallization with the first crystallization temperature of 555 °C. One can see that the first crystallization peak resulting at 512 °C from primary crystals in alloy B disappears in alloy C. It indicates that the alloys with eutectic microstructure show better glass forming ability as manifested by higher crystallization temperature giving higher T_x/T_l coefficient, as observed also for zirconium base alloys [8,9]. Unfortunately, due to the DSC equipment temperature range it was not possible to calculate the heat of crystallization. The High Resolution Transmission Electron Microscopy (HRTEM) of ribbon of the alloy C shows presence of nanocrystals of size of 1-2 nm indicated by an arrow in the Fig. 4. Measurements of Vickers microhardness of the ribbons gave similar results of approximately 12 GPa for both alloys.

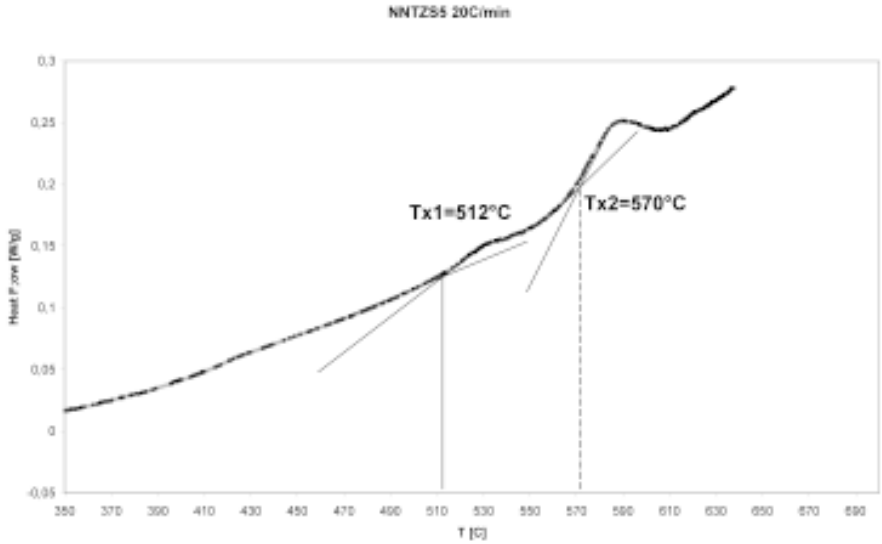

Fig. 2. DSC Analysis of Ni_{45}-Nb_{21}-Ti_{16}-Zr_{13}-Si_5 (alloy B) ribbon.

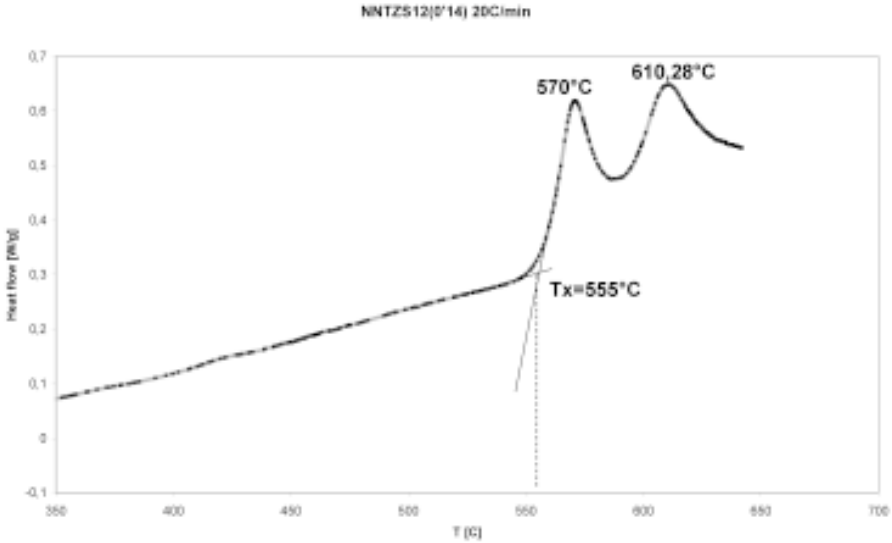

Fig. 3. DSC Analysis of $Ni_{50,34}$-$Nb_{14,38}$-$Ti_{17,32}$-$Zr_{15,15}$-$Si_{2,81}$ (alloy C) ribbon.

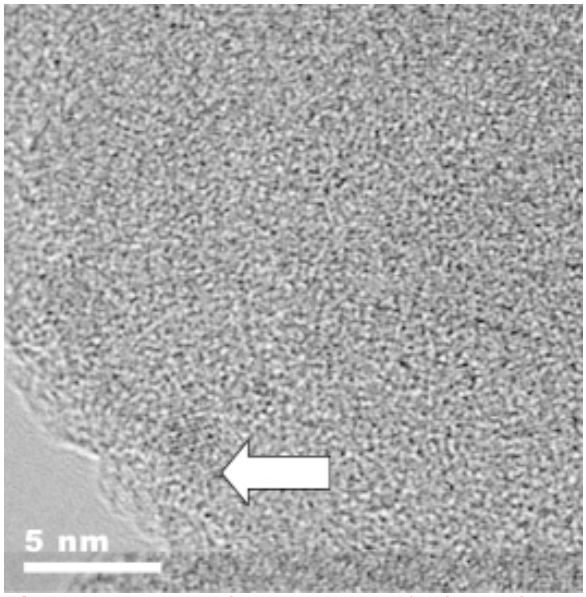

Fig. 4. HRTEM microstructure of $Ni_{50,34}$-$Nb_{14,38}$-$Ti_{17,32}$-$Zr_{15,15}$-$Si_{2,81}$ (at.%) (alloy C) ribbon cast at the linear drum rate of 8 m/sec.

Powders of compositions corresponding to alloys B and C were milled for the maximum time of 60 hours. Structure of milled powders was studied using X-ray diffraction taking samples of the powders after 0, 5, 10, 20, 40, and 60 h of milling. Fig. 5 shows X-ray diffraction curves of the alloy C and it indicates that gradual broadening and a decrease of the intensity of peaks from pure elements occurs up to 20 hours and after longer milling time only a broad amorphous hallow can be seen. Changes in particles size measured by optical microscopy and microhardness are presented in Fig. 6 for the alloy C. It shows a decrease of the

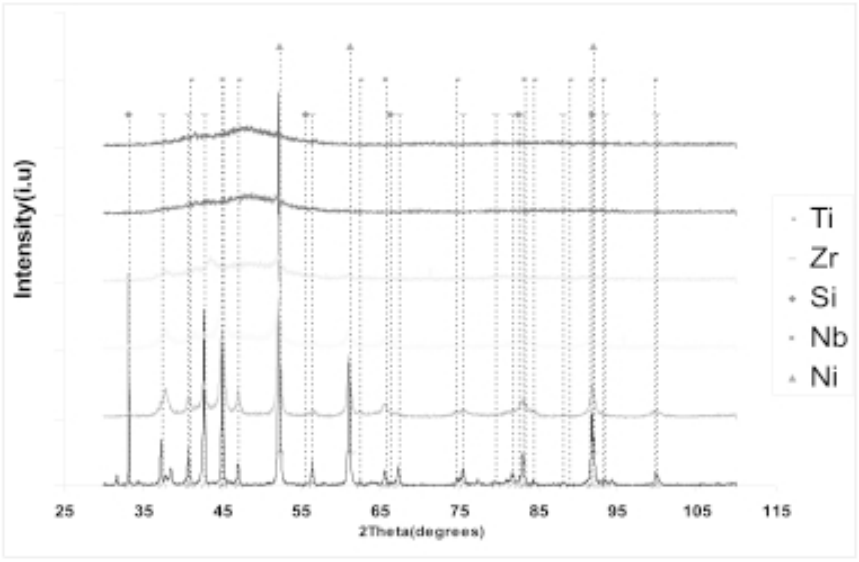

Fig. 5. X-Ray diffraction curves of alloy C powder after indicated milling times.

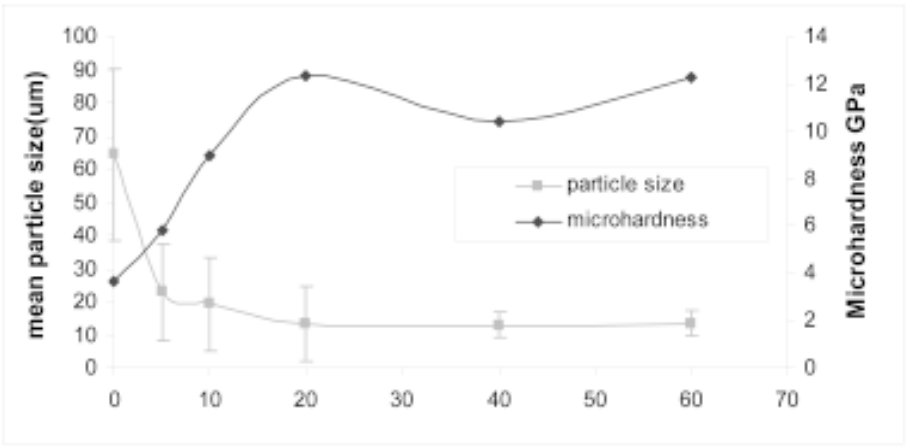

Fig. 6. Mean particle size and microhardness changes during milling time of the alloy C.

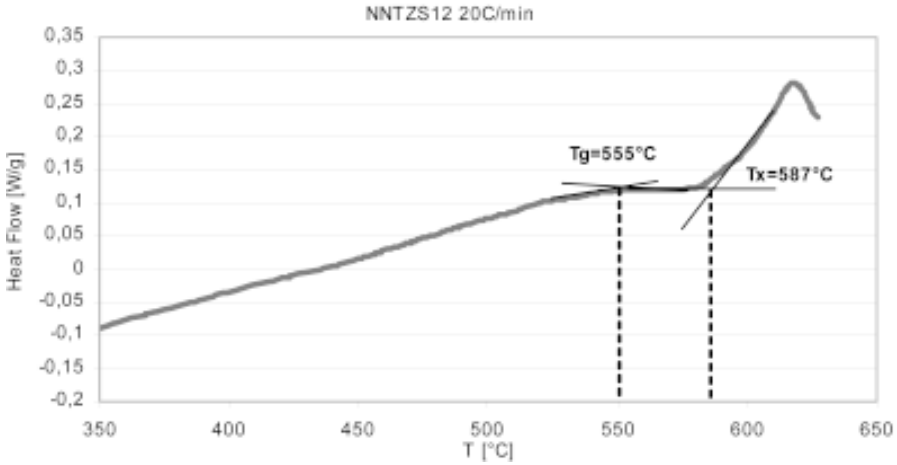

Fig. 7. DSC Analysis of the powder of alloy C milled for 60 hours.

particle's size of powders particles from about 65 μm down to 13 μm and the Vickers Microhardness increase from 3 to 12 GPa with the milling time, i.e. to the same value as for the ribbon is attained.

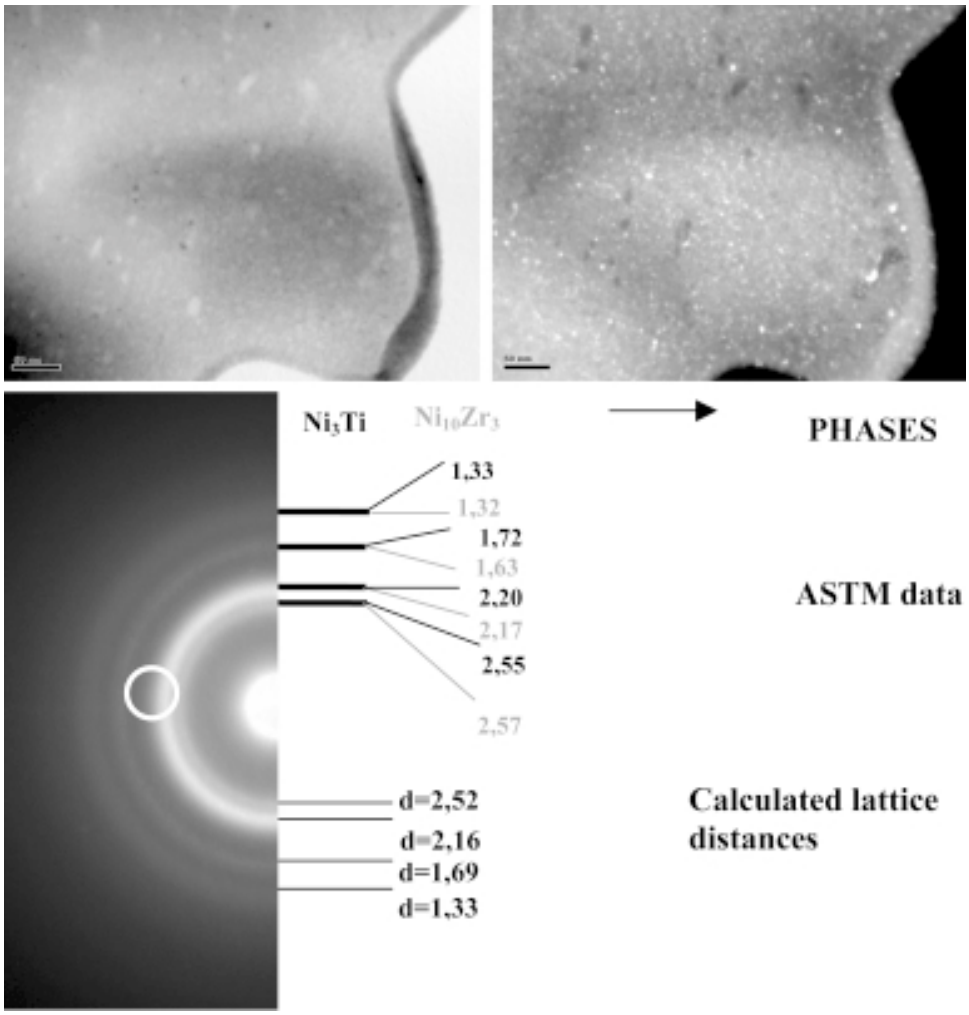

Fig. 8. UHP compacted milled powder of alloy B (a) TEM Bright field, (b) Dark field and (c) Selected area electron diffraction pattern with marked positions Ni_3Ti of and $Ni_{10}Zr_3$ phases diffraction lines positions.

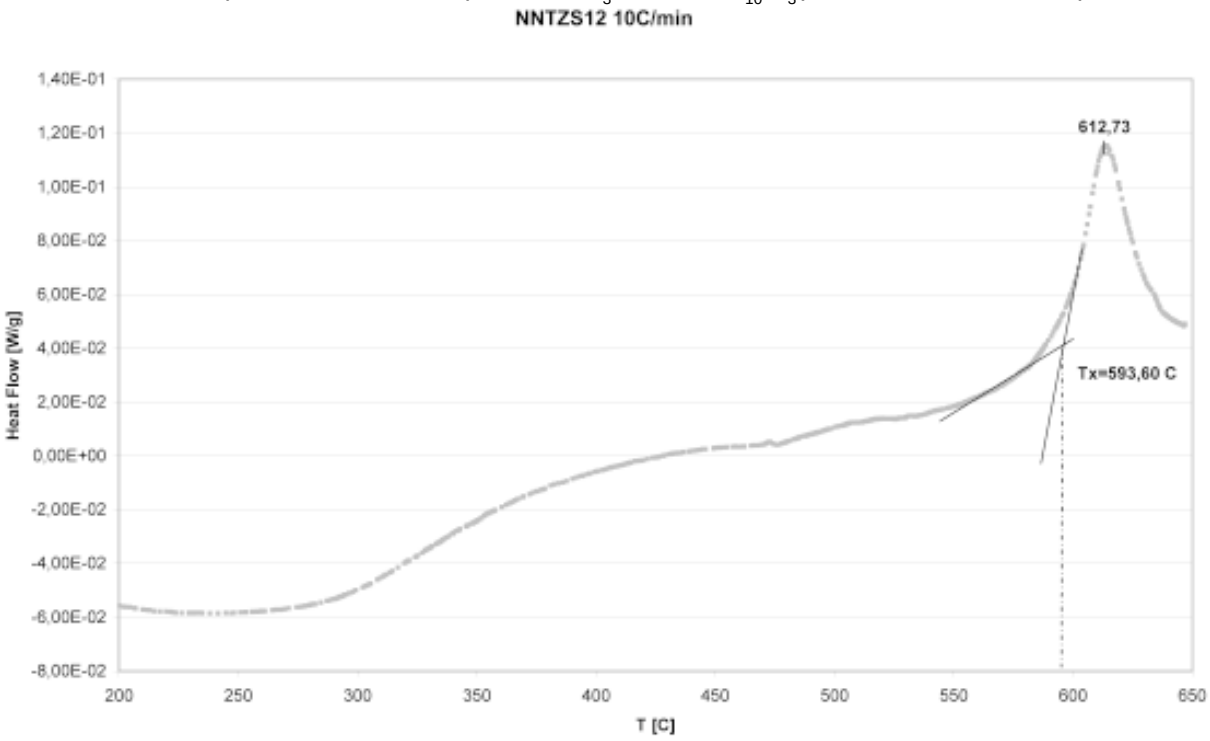

Fig. 9. DSC curve of UHP compacted sample of the alloy C.

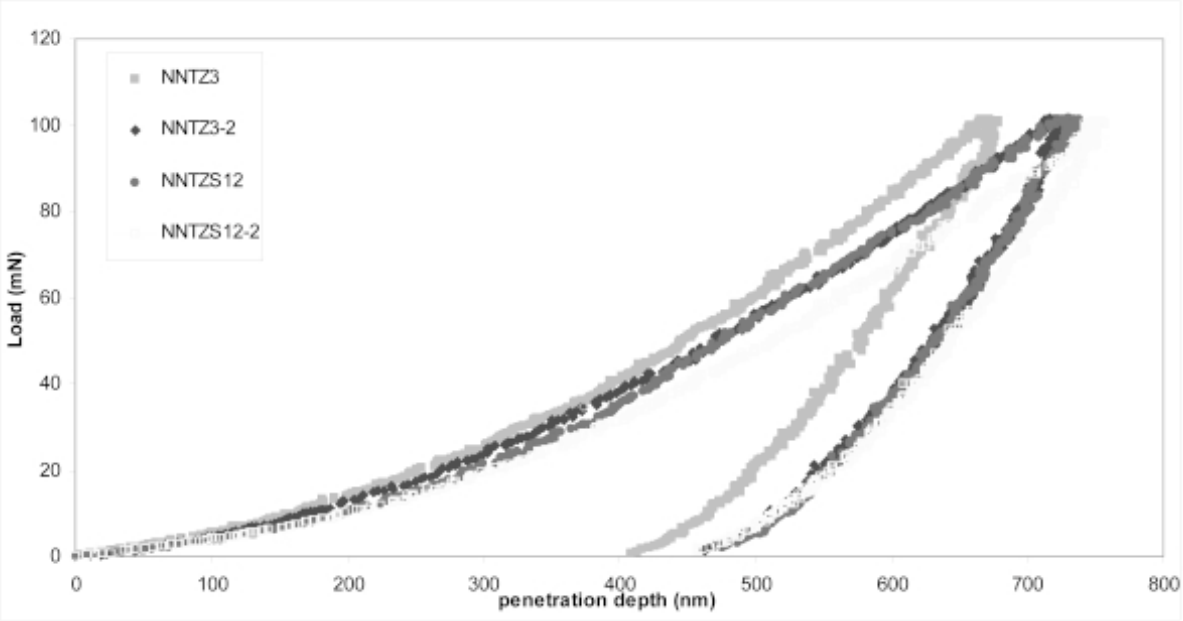

Fig. 10. Depth-Load curves recorded during dynamic microhardness test of UHP compacted investigated alloys B (NNTZ3) and C (NNTZ12).

No growth of particle's size was observed as in the case of zirconium alloys [8] most probably due to addition of Si preventing welding of particles. The DSC analysis of the heat flow of the alloy is presented in Fig. 7. It shows a diffused relaxation exothermal peak between 400-550 °C and the crystallization temperature starting at 587 °C. The position of T_g is not well established due to presence of elongated relaxation peak. It might also shift the crystallization peak to higher temperatures since in the previous work [8] on zirconium base alloys, estimated T_x temperature was similar for the same composition amorphous ribbons and milled powders. Fig. 8 shows TEM microstructures and electron diffraction pattern from the UHP compacted milled 80 hours powder of the alloy B. It shows small nanocrystals visible as dark in the bright field and bright in the dark field taken using aperture placed in the broad peak with position marked in Fig. 8c. Diffuse Debye-Scherrer rings typical for amorphous and nanostructured materials indicate presence of mixed amorphous and nanocrystalline phases. The lattice spacings corresponding of Ni_3Ti and $Ni_{10}Zr_3$ phases from ASTM data give the best fit to the measured distances in the SADP and in addition are in agreement with the phases observed in [4]. Similar microstructures were observed in UHP compacted alloy C, however in addition $NiNb_4Si$ and Nb_3Ni_2Si were identified there due to the presence of silicon.

Fig. 9 shows the DSC curve of the alloy C after UHP hot pressing of milled powder at 550 °C. One can see clear crystallization peak starting at 593 °C and diffused relaxation peak extending from 280 to 500 °C. It is similar to the curve obtained from the milled powder. DSC results support the TEM studies that the amorphous phase is preserved to a large extend after hot pressing. Fig. 10 shows the depth-load curves recorded during dynamic microhardness test of UHP compacted investigated alloys B and C. The HV values of 9.4 MPa and 9.3 MPa are close for the UHP compacted alloys A and C, however the Young's modulus decreases in alloy with Si addition down to 163 from 152 GPa as can be calculated from Fig. 10. The hardness is slightly lower than that for the ribbons and milled powders what might result from the partial crystallization of UHP compacts.

4. CONCLUSIONS

1. Ball milling of powders corresponding to eutectic compositions $Ni_{48,5}$-$Nb_{21,5}$-$Ti_{16,5}$-$Zr_{13,5}$ and

$Ni_{50,34}$-$Nb_{14,38}$-$Ti_{17,32}$-$Zr_{15,15}$-$Si_{2,81}$ lead to formation of the amorphous structure after melt spinning or 40 hours ball milling as confirmed by X-ray diffraction, and DSC techniques. TEM technique allows to identify nanocrystals of $NiTi_{0.6}Zr_{0.4}$ and $NiNb_4Si$ phases embedded in the amorphous matrix in ball milled powders.

2. Amorphization is accompanied by substantial increase of ribbon or powder microhardness approaching 12 GPa. The powders show clear diffused exothermal relaxation effect in the range 250-500 °C and crystallization temperature about 587 °C. The ribbon shows a two step crystallization starting at the temperature of 555 °C and the second one close to observed in the milled powder sample.
3. Ultra high pressure consolidation performed in the pressure range 4,0-7.5GPa and temperature several degrees bellow crystallization temperature allowed to obtain compacts of mixed amorphous and nanocrystalline microstructure. The nanocrystals of size of a few nm were identified as Ni_3Ti and $Ni_{10}Zr$. The microhardness of compacts is close to 9.5 GPa, slightly lower than that of ribbons and milled powders. The addition of silicon caused a decrease of the Young's modulus of the compacts from 163 GPa to 152 GPa.

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