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) Ni₄₅₋₅,Nb₂₁₋₅,Ti₁₆₋₅,Zr₁₃₋₅ (in at.%) applying a small addition of Si. At first, the alloy Ni₄₅₋₅,Nb₂₁₋₅,Ti₁₆₋₅,Zr₁₃₋₅,Si₅ (alloy B in at.%) was cast and then a new alloy based on the eutectic composition Ni₅₀₋₃₄,Nb₁₄₋₃₈,Ti₁₇₋₃₂,Zr₁₅₋₁₅,Si₂₋₈₁ (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 Ni₅₀₋ₓ,Cox₋ₓ,Nb₂₋₁₅,Ti₁₀₋₁₀,Zr₁₀₋₁₀ 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. Ni₅₀₋ₓ,Zr₁₀₋ₓ,Ti₁₀₋ₓ,Si₃ 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, Ni₅₀₋ₓ,Zr₁₀₋ₓ,Ti₁₀₋ₓ,Si₃,Nbₓ, as-cast BMG exhibits compressive plastic deformation of 6.5% before failure [5]. The bulk amorphous Ni₅₀₋ₓ,Zr₁₀₋ₓ,Ti₁₀₋ₓ,Sn₃ 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
increase the supercooled liquid region of the Ni$_{48.5}$Nb$_{21.5}$Zr$_{16.5}$Ti$_{16.5}$ alloy from 42 to 89 and 91 K 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$_{16.5}$, alloy (B) Ni$_{48.5}$Nb$_{21.5}$Ti$_{16.5}$Zr$_{11.5}$Si$_{2.81}$, alloy (C) Ni$_{50.34}$Nb$_{14.38}$Ti$_{17.23}$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.

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$_{17.23}$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
particle's size of powders particles from about 65 $\mu$m down to 13 $\mu$m 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$_3$Ti of and Ni$_{16}$Zr$_3$ phases diffraction lines positions.

**Fig. 9.** DSC curve of UHP compacted sample of the alloy C.
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 $T_g$ 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$_3$Ti and Ni$_{10}$Zr$_2$ 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$_2$Si and Nb$_3$Ni$_2$Si 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 (NNTZ3) and C (NNTZ12).

4. CONCLUSIONS

1. Ball milling of powders corresponding to eutectic compositions Ni$_{58.5}$-Nb$_{21.5}$-Ti$_{16.5}$-Zr$_{13.5}$ and
Ni_{59.24}Nb_{14.32}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_{5}Si 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 4.0-7.5 GPa 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_{3}Ti 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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