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Microstructure studies of ball milled and vacuum hot pressed NiZrTiAl powders

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ABSTRACT

Purpose: To determine microstructure and hardness of hot pressed mechanically alloyed MA NiZrTiAl powders well known as a good glass formers.

Design/methodology/approach: Powders has been ball milled r 40 hours starting from pure elements. Changes of particle's size and crystallographic structure of nanocrystals embedded in the amorphous matrix during milling has been determined using High Resolution Transmission Electron Microscopy HRTEM.

Findings: The MA particles first grow, then decrease after 40 hours of milling, when powders possess amorphous structure. HRTEM studies of powders allowed to reveal small nanocrystals of $NiTi_2$ within milled powders which were not detected using X-Ray diffraction. The powders show crystallization peak at temperature T_x near 553°C. Consolidation of powders was performed under vacuum using uniaxial hot pressing method at temperature slightly below T_x. Mean microhardness was determined near 430 HV and the mean Young´s modulus as 81 GPa.

Practical implications: It was shown a possibility of hot densification in vacuum of amorphous Ni base alloys allowing to obtain bulk amorphous compacts with embedded nanocrystals.

Originality/value: The size and structure of nanmocrystals within the amorphous matrix after MA and after hot vacuum densification has been determined. The microhardness and Young's modulus of compacts show perspectives of application of such materials.

Keywords: Amorphous metals; Metallic glasses; Ni- based alloys; Mechanical alloying

MATERIALS

1. Introduction

Ni – based amorphous alloys (Ni – 50 at.%) have been considered as potential engineering materials with good mechanical properties, particularly high elastic limit. Many binary, ternary and higher order of Ni – based amorphous alloys have been prepared by rapid quenching techniques [1,2]. However, only a few Ni – based amorphous alloys have the undercooled liquid region (URL) that relates to thermal stability of the amorphous alloy [3,4]. These new alloys are expected to expand the application fields of bulk amorphous alloys due to the unique properties, such as high tensile strength and relatively high corrosion resistance at room temperature [5]. The supercooled liquid region is defined by temperature range, $\Delta T = T_x - T_g$, between the glass transition temperature (T_g) and crystallization temperature (T_x). The increase of ΔT means that stability of the supercooled liquid state increases against crystallization and therefore enables formation of bulk amorphous alloys by conventional casting techniques at low cooling rates ranging from 1.5 to 100 Ks^{-1} [4]. Recently, new metallic amorphous alloys with a wide supercooled liquid region exceeding 20 K have been prepared in a number of Ni – based alloy systems, such as $Ni_{76}M_5P_{19}$ (M = Ti, Zr, Hf or Nb), $Ni_{75-x}Nb_5M_xP_{20-y}B_y$ (M = Cr, Mo), and Ni-Ti-Zr-(Al,Sn) [1-4]. Fairly large ULR in the Ni – based bulk amorphous alloys have been reported indicating high stability of the amorphous phases. It should be noted however, that a large amount of metalloids needs to be added in the above Ni – based amorphous alloys (Ni – X – P, X = Pd, Zr, Ti, Nb) and it can be maximized by the addition of about 20 at% P [6,7]. The addition of metalloids such as P, B, and Si significantly improves the GFA (glass forming ability) of Ni – based amorphous alloys [1,2]. Moreover, since the glass transition temperature (T_g) tends to decrease as the metalloid content increases [4], the temperature range for practical applications can be limited to lower temperatures (in general, < T_g). Various techniques have been used to obtain amorphous alloys, but most of the research is focused on the the rapid solidification and solid state reactions [5]. Mechanical alloying, a relatively simple technique, has been used successfully to synthesize amorphous Ni and Zr base alloy powders [8-13]. In [10] behavior of $Ni_{57}Zr_{20}Ti_{18}Al_5$ alloy powders synthesized by mechanical alloying is reported. The complete amorphization is feasible after 5 h of MA and powders exhibit a wide supercooled liquid region of 54 K. Therefore in the present work this alloy has been chosen for amorphization using ball milling and compaction in vacuum using hot pressing.

2. Experimental procedure

Mechanical alloying of high purity elements powders (≥ 99,7%) with composition of $Ni_{57}Zr_{20}Ti_{18}Al_5$ was performed in a high-energy ball mill "Pulverisette 5" at a rotational speed of 200rpm. All powders were handled in a glove box under a purified argon atmosphere. The milling cycle includes 15min of milling followed by 45min of cooling down. The consolidation of amorphous powder was performed by a vacuum hot pressing in a specially constructed chamber. Disc shape bulk amorphous alloy compact with diameter of about 20mm and a thickness of 4-5mm was prepared. Conditions of the consolidation of amorphous powder by vacuum hot pressing are 560°C / 500 MPa / 12 min. The Vickers microhardness was measured using CSM tester applying Oliver & Pharr method. Microstructure analysis was performed using optical microscope Leica and transmission electron microscope TEM Philips CM 20 and Tecnai G2F20 S – TWIN. The structure was identified using X-ray diffractometer PHILIPS PW 1840 with Cu Kα radiation. DSC analysis was performed using Q1000 equipment with a heating rate of 20ºC/min.

3. Results

Structure of ball milled powders of composition corresponding to the alloy $Ni_{57}Zr_{20}Ti_{18}Al_5$ was studied using X-ray diffraction after increasing milling times (5, 10, 20, and 40 hours of milling). As one can see in Figure 1, the powder is almost amorphous after 10 hours and full amorphization of powder occurs already after 20 or 40 hours of milling, where only a broad peak is seen in the graph.

The quantitative optical microscopy measurements of $Ni_{57}Zr_{20}Ti_{18}Al_5$ milled powder particles size was performed in relation to the milling time. The change of particle's size of the alloy is presented in Figure 2. It can be seen that, at the beginning the grain size of $Ni_{57}Zr_{20}Ti_{18}Al_5$ powder particles increases during the early stages of milling (up to 5 h), but with further milling, the size of particles decrease from 48,9 to 22,2 µm.

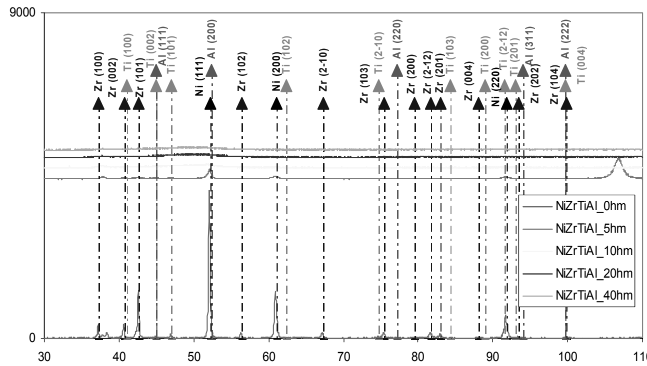

Fig. 1. X -ray diffraction after milling of $Ni_{57}Zr_{20}Ti_{18}Al_5$ powder

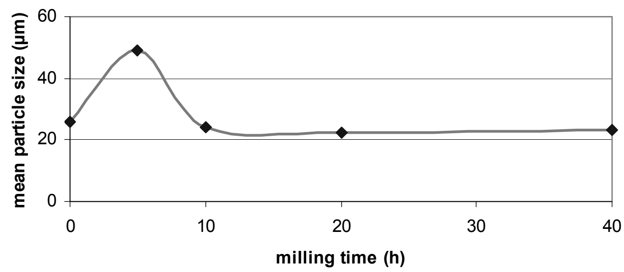

Fig. 2. Evolution of size of $Ni_{57}Zr_{20}Ti_{18}Al_5$ alloy particles during milling

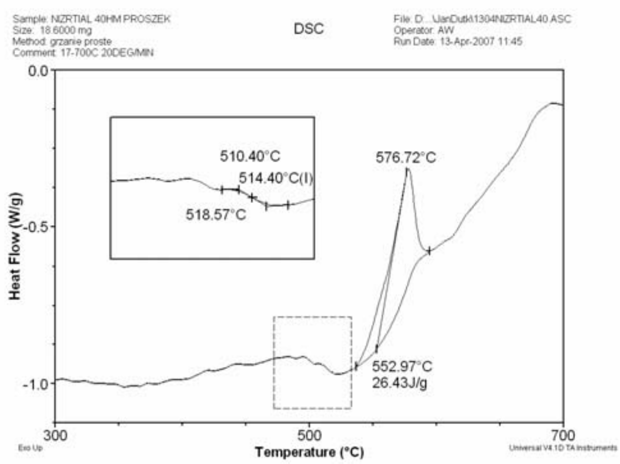

Fig. 3. DSC analysis of $Ni_{57}Zr_{20}Ti_{18}Al_5$ amorphous powder after milling

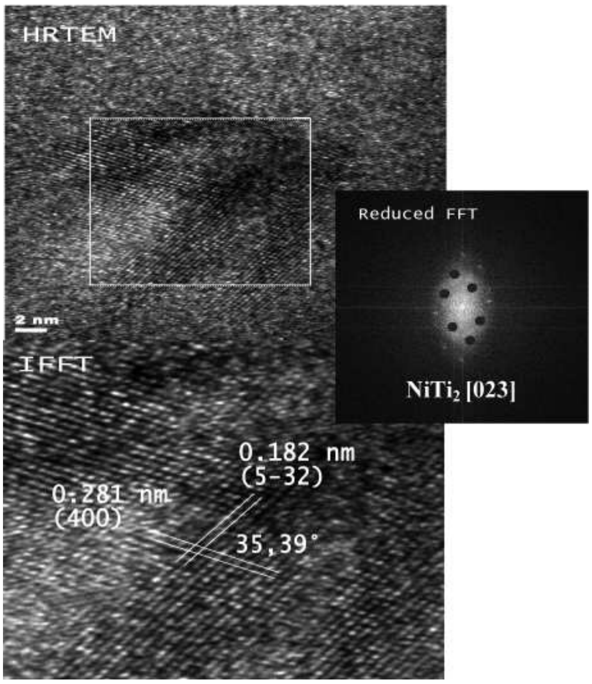

Fig. 4. HRTEM analysis of $Ni_{57}Zr_{20}Ti_{18}Al_5$ powder

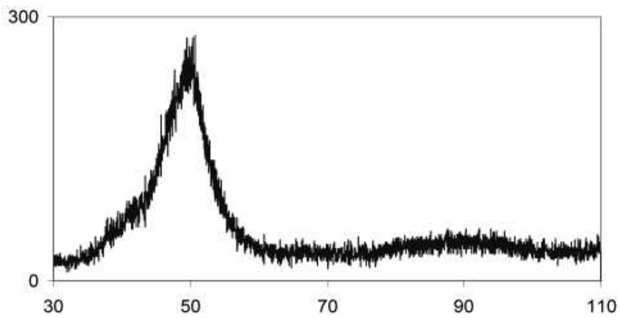

Fig. 5. X-ray diffraction patterns of the consolidated $Ni_{57}Zr_{20}Ti_{18}Al_5$ compact at 560°C under pressure 500 MPa

Figure 3 shows the DSC curve of $Ni_{57}Zr_{20}Ti_{18}Al_5$ ball milled powder. The onset temperature of crystallization (Tx) was 553°C. Below the onset of crystallization, the glass transition (Tg) can be seen however it overlaps with the exothermal relaxation effects. It is shown as an endhotermic reaction in the DSC curve, at about 514°C. This means that in this case fairly large supercooled liquid region (ΔTx) is observed approaching about 39°C.

The milled amorphous powder was examined using HRTEM. Interplanar distance was measured in the image obtained using IFFT (Inverse Fast Fourier Transform) of the atomic planes what allowed to obtain better contrast. Following the analysis of HRTEM micrograph including lattice spacing and angles of cross grating, the structure of the particle can be identified as $NiTi_2$ cubic crystalline phase of orientation close to [023] zone axis (Figure 4).

3.1. Consolidation of amorphous powder

The consolidation of amorphous powder was performed using uniaxial vacuum hot pressing described in [11]. Figure 5 shows the X-ray diffraction patterns of compacted $Ni_{57}Zr_{20}Ti_{18}Al_5$ sample. The X-ray diffraction patterns clearly show that the sample is amorphous even after hot pressing at 560°C. The trace of crystalline phase formation in $Ni_{57}Zr_{20}Ti_{18}Al_5$ compacts is manifested by a presence only one weak peak at this consolidation condition.

The porosity [%] of the $Ni_{57}Zr_{20}Ti_{18}Al_5$ consolidated compact was investigated using optical micrographs (OM) from cross-section of a polished surface. As shown in Figure 6, relatively large amount of pores or voids was observed at polished cross-section of the sample. This indicates that the consolidated compact was not fully densified at these consolidation conditions. The mean porosity of this sample was estimated at 12 %.

The Vickers hardness was measured on the polished surface of sample. The mean hardness value is about 279 HV as measured on the surface of polished $Ni_{57}Zr_{20}Ti_{18}Al_5$ compact. Figure 7 shows the results of microhardness measurement of the sample. The mean Vickers microhardness is about 430 HV and the mean Young´s modulus was determined at 81 GPa.

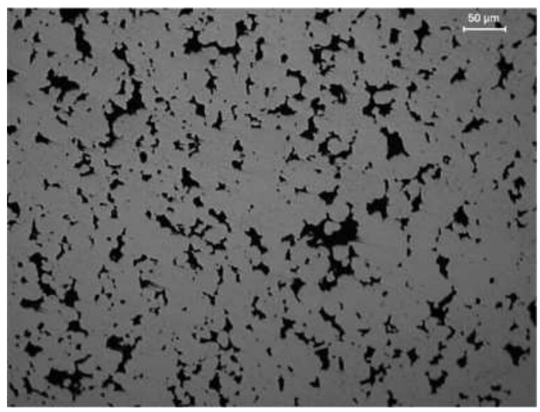

Fig. 6. Optical micrograph of $Ni_{57}Zr_{20}Ti_{18}Al_5$ consolidated compact cross-section

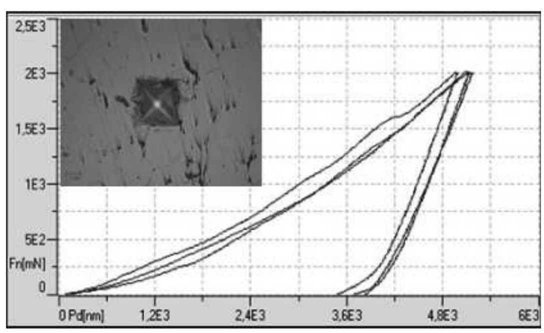

Fig. 7. Results of microhardness measurement of $Ni_{57}Zr_{20}Ti_{18}Al_5$ consolidated compact and the imprint of indenter (Fn is normal force, Pd is penetration depth)

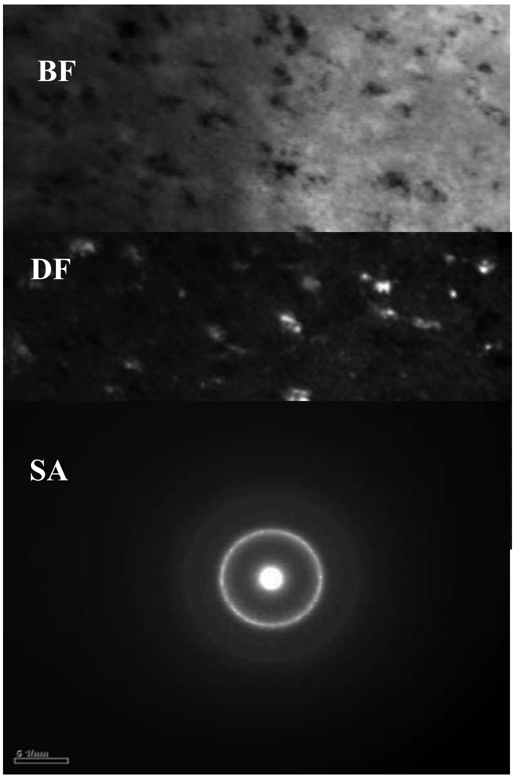

Fig. 8. TEM analysis of $Ni_{57}Zr_{20}Ti_{18}Al_5$ compact hot pressed at 560 °C for 12 min under 500MPa

The microstructure of $Ni_{57}Zr_{20}Ti_{18}Al_5$ consolidated compact was analyzed using TEM. Thin foils were prepared by mechanical polishing and ion beam thinning. Figure 8 shows BF (bright field), DF (dark field) and SADP (selected area diffraction patterns). Conventional microstructures of consolidated compact show an amorphous matrix with a small nanocrystals of size close to 11 nm. Electron diffraction rings from crystallites are too diffused to allow identification of crystals.

4. Conclusions

1. $Ni_{57}Zr_{20}Ti_{18}Al_5$ alloy ball milled from elemental powders in a planetary mill shows first grow, then decrease of particle's size. After 40 hours of milling powders possess already amorphous structure. The powders show crystallization peak at temperature T_x near 553°C and glass transition temperature T_g near 514°C. HRTEM studies of powders allowed to reveal small nanocrystals within milled powders which were identified as $NiTi_2$ cubic phase.
2. Consolidation of powders was performed under vacuum using uniaxial hot pressing method at temperature slightly below the T_x. TEM studies of the massive $Ni_{57}Zr_{20}Ti_{18}Al_5$ alloy show an amorphous matrix with a small nanocrystals. Microhardness measurements of $Ni_{57}Zr_{20}Ti_{18}Al_5$ consolidated compact has shown that the mean Vickers microhardness was about 430 HV and Young's modulus 81 GPa.

Acknowledgements

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