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Consolidation of amorphous ball-milled Zr–Cu–Al and Zr–Ni–Ti–Cu powders

J. Dutkiewicz [a,*], L. Jaworska [b], W. Maziarz [a], T. Czeppe [a], M. Lejkowska [a], M. Kubíček [c], M. Pastrňák [c]

[a] *Institute of Metallurgy and Materials Science of the Polish Academy of Sciences, ul. Reymonta 25, Kraków, Poland*
[b] *Institute of Metal Cutting (IOS), ul. Wrocławska 37A, Kraków, Poland*
[c] *Vysoká Škola Báňská, Technical University of Ostrava, 17 Listopadu 1, Ostrava-Poruba 708 33, Czech Republic*

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Abstract

Consolidation of ball-milled powders of the ternary Zr–Cu–Al and quaternary Zr–Ni–Ti–Cu alloys was performed using high-temperature ultra high-pressure method (UHP) at 7.5 GPa. Easy glass forming Zr–Cu–Al and Zr–Ni–Ti–Cu alloys were investigated. The consolidation temperature was chosen between the glass transition and crystallization temperature estimated at 514 °C for Zr–Ni–Ti–Cu amorphous powder and 510 °C for Zr–Cu–Al amorphous powder using Differential Scanning Calorimetry. $CuZr_2$ nanoparticles were identified in ball-milled powders and consolidated glasses.

Keywords: ZrCuAl alloys; ZrNiTiCu alloys; Mechanical alloying; Amorphous powder consolidation

1. Introduction

Glass formation by heavy deformation and mechanical alloying has been found to be an alternative method of amorphization for several zirconium, nickel-, copper- or titanium-based alloys [1–10]. Most extensively studied using this method were ZrAlCuNi alloys [1,4,6,8]. TEM investigations [4] show amorphous stripes located at interfaces of elemental layers suggesting amorphization process is initiated at grain boundaries. However, in the paper of Djakonova et al. [8] amorphization process was accelerated when started from milling of mixture of glass compounds from ZrNiCuAl system, which suggests that intermetallic compound play an important role in this system. It is contrary to the amorphization observed in TiAl where extended solid solution formed preceding amorphization; however, not in NiAl where instantly formed intermetalllic phase is stabilized [9]. Metallic glasses with extended undercooled liquid regions are expected to allow consolidation of bulk samples using viscous flow between T_g and T_x. A possibility of manufacturing of bulk amorphous samples by uniaxial hot pressing was demonstrated in [1]. The mechanical properties of such samples are really similar to those of cast glasses [1]. Therefore, in the present paper ZrCuAl and ZrNiTiCu were ball-milled and hot consolidated using hot pressing at 7.5 GPa ultra high-pressure consolidation.

2. Experimental procedure

The ball milling process of the Zr–Cu–Al and Zr–Ni–Ti–Cu alloys was performed in planetary mill "Pulverisette 5" at 200 rpm in argon atmosphere. The elemental powders were initially blended to desired compositions of Zr, 65%; Cu, 27.5%; Al, 7.5%; and of Ti, 25; Zr, 17; Cu, 29; Ni, 29 (in at.%), respectively, and then subjected to milling. The composition of alloys was chosen the same as for the bulk amorphous Zr–Cu–Al [12] and easy glass forming Zr–Ni–Ti–Cu alloy, elaborated earlier [11].

High-pressure consolidation was performed using ultra high-pressure method (UHP) at pressures between 4.0 and 7.5 GPa and temperature between 400 and (480 ± 20) °C for 30 s in a high-pressure Bridgman type apparatus. Structure was studied using TEM Philips CM 20, SEM Philips XL 30 and X-ray diffractometer PHILIPS PW 1840. DSC analysis was performed by Q1000 equipment with a heating rate of 20 °C/min.

3. Results

The structure of milled powders was studied using X-ray diffraction after increasing milling times from 5 to 80 h (Fig. 1). Broadening of reflections occurs up to 10 h of milling, then after

* Corresponding author.
E-mail addresses: nmdutkie@imim-pan.krakow.pl (J. Dutkiewicz), jaworska@ios.krakow.pl (L. Jaworska), nmmaziar@imim-pan.krakow.pl (W. Maziarz), nmczeppe@imim-pan.krakow.pl (T. Czeppe), nmlejkow@imim-pan.krakow.pl (M. Lejkowska), martin.kubicek.fs@vsb.cz (M. Kubíček), martpastr@post.cz (M. Pastrňák).

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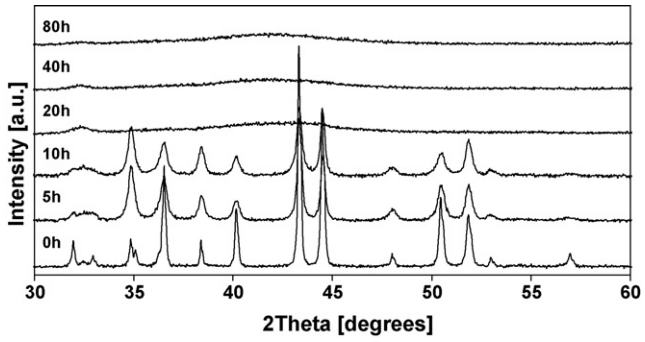

Fig. 1. X-ray diffraction patterns of mechanically alloyed Ti–Zr–Ni–Cu powder.

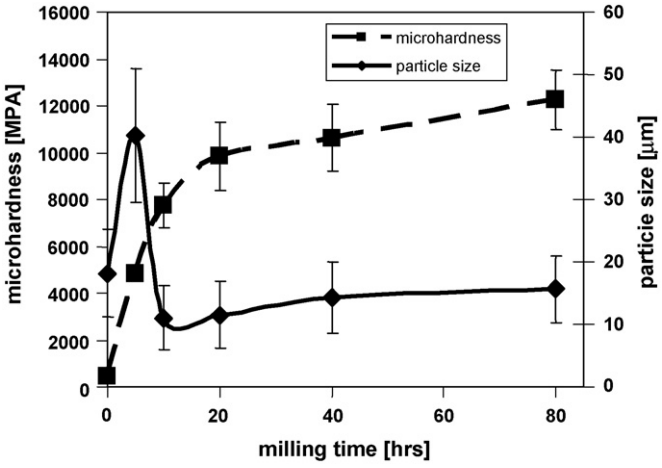

Fig. 2. Changes of particle's size and microhardness HV_{20} vs. milling time of ZrCuAl alloy composition.

20 h only broad amorphous hallow can be seen. The changes of particle's size and micro-hardness of Zr–Cu–Al alloy are presented in Fig. 2. Particles are growing from 20 to 40 μm during the first few hours of milling, then decrease down to 10 μm and remain at approximately the same value after 40 h of milling. Changes of HV_{20} of Zr–Cu–Al powders during milling (Fig. 2) show rapid growth from initial average 50 up to about 1000 MPa HV_{20} after 25 h of milling and stabilize at about 12 GPa after 80 h of milling. Similar microhardness is attained in the case of Zr–Ni–Ti–Cu-milled powders.

The analysis of heat flow data of Zr–Cu–Al powder milled for 80 h (Fig. 3) shows relaxation process at the beginning between

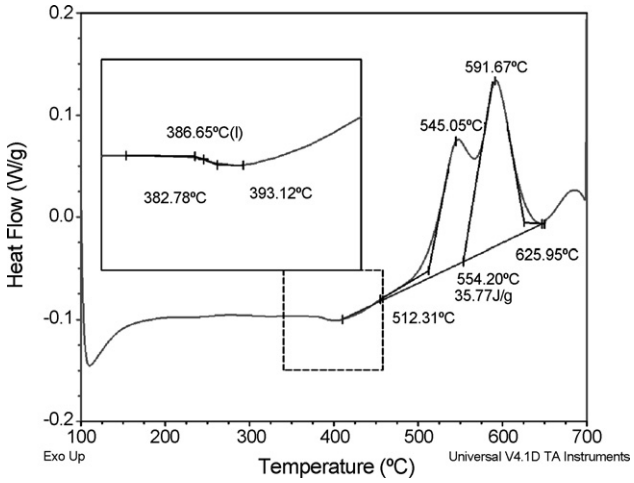

Fig. 3. DSC curve obtained during 20 °C/min heating of ZrCuAl powder.

100 and 300 °C. Then, at about 386 °C glass transition starts. It is followed by the first crystallization starting at 512 °C, which continues with secondary crystallization starting at 591 °C. Similar crystallization path was observed in ZrNiTiCu alloys. TEM studies of Zr–Cu–Al ball-milled powders have shown the presence of nanocrystallites of size 2–5 nm within amorphous matrix. Electron diffraction patterns were similar for both investigated alloys and showed intense diffused rings due to the presence of the amorphous phase and some weak spots along rings due to nanocrystalline phases. The nanocrystalline phases are difficult to identify due to the presence of only a few diffused rings and a possibility of crystallization of several phases like $CuZr_2$, CuZr, $NiZr_2$, NiZr and Cu_3Ti [13].

TEM studies of investigated alloys after UHP consolidation (Figs. 4 and 5) have shown amorphous structure with a few nanocrystalline inclusions of size between 10 and 26 nm in the ZrNiTiCu specimen (Fig. 4). As can be seen from the selected area diffraction patterns (SADP), the best fit gives hexagonal $CuZr_2$ phase in agreement with [2,9]; however, appearance of other phases like Ni_2Zr is also possible due to appearance of single spots in other distances. TEM studies of UHP consolidated ZrCuAl alloy (Fig. 5) show almost perfect amorphous structure with very weak spots from crystalline phases included in the amorphous hallow. Dark field shows a few bright crystals of size of a few nanometers. In accordance with structural investigations, DSC curves show clear crystallization effects. Fig. 6 shows

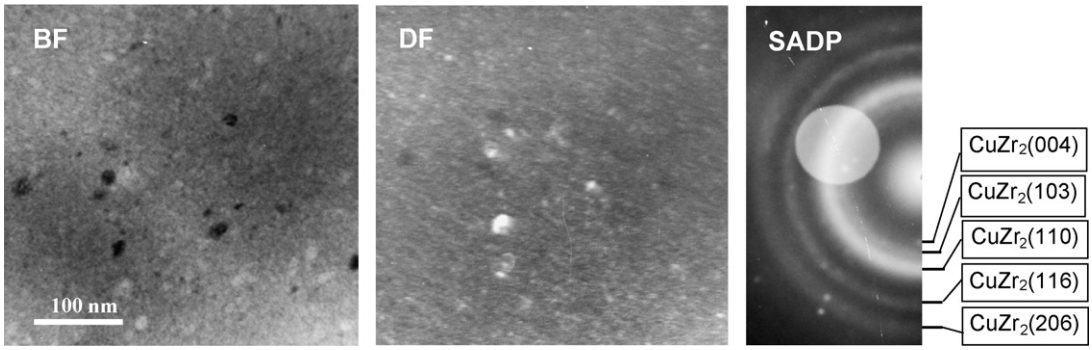

Fig. 4. Bright field (BF) and dark field (DF) micrographs and corresponding selected area diffraction pattern (SADP) from UHP consolidated ZrNiTiCu specimen.

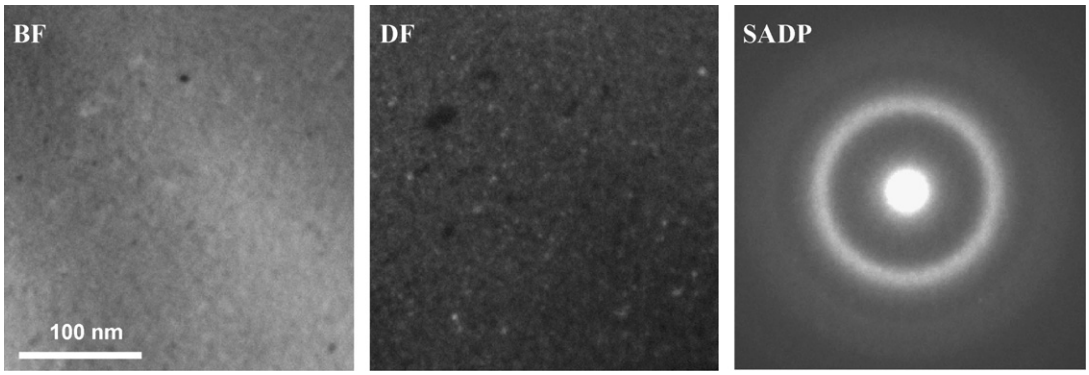

Fig. 5. Bright field (BF) and dark field (DF) micrographs and corresponding selected area diffraction pattern (SADP) from UHP consolidated ZrCuAl specimen.

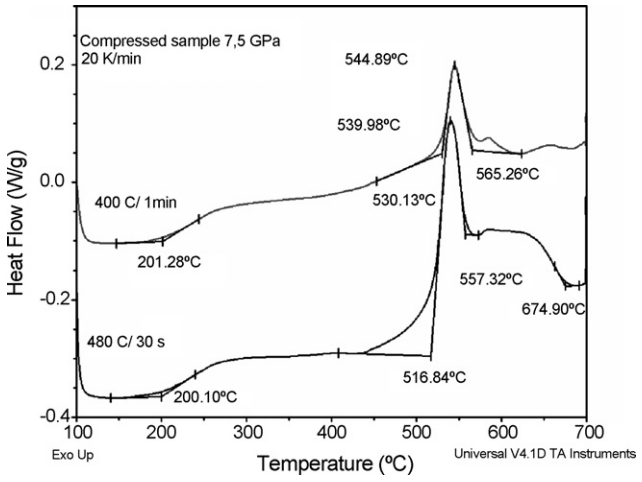

Fig. 6. DSC curves of ZrNiTiCu alloy UHP consolidated at 4 GPa (upper curve) and 7.5 GPa (lower curve) at 400 °C.

a DSC curve taken from ZrNiTiCu alloy UHP consolidated at 4 and 7.5 GPa at 400 °C. Similarly to the DSC curve for milled powders, a relaxation exothermal peak is observed between 180 and 350 °C, which is followed by a glass transition T_g at 450 °C and crystallization starting at 506 °C, i.e. exactly the same temperatures as observed in ZrNiTiCu powder. Similar DSC curve was observed in the ZrCuAl UHP consolidated sample.

4. Conclusions

Ball milling of easy glass forming ZrCuAl and ZrNiTiCu alloys leads to formation of amorphous structure identified by X-ray diffraction. Amorphization is accompanied by substantial increase of powder microhardness approaching 12 GPa. The powders show clear diffused exothermal relaxation effect in the range 200–350 °C, glass transition effect and a few stages of crystallization starting above 500 °C.

Ultra high-pressure consolidation performed in the range 4.0–7.5 GPa and temperature in the range 400–480 °C allows to obtain bulk compacts showing only a few cracks at triple grain joints revealed using SEM studies. TEM studies have shown almost completely amorphous structure in ZrCuAl alloys and nanocrystalline/amorphous in ZrNiTiCu compacts. The structure of nanocrystals was identified as $CuZr_2$. Both consolidated samples show clear glass transition and crystallization peaks in the same range as observed in the milled powders.

Acknowledgements

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