



On the mechanically induced crystallization of FCC phases by mechanical milling in ZrAlNiCu bulk metallic glasses

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ABSTRACT

In the present study, amorphous–nanocrystalline phase transformation induced by mechanical milling of full monolithic bulk metallic glasses (based on $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{58}Al_{16}Ni_{11}Cu_{15}$ alloys) has been investigated using X-ray diffraction as well as transmission electron microscopy. Nanocrystals having an FCC structure and a grain size of several 10 nm precipitate in the early stages of the milling process and remain stable for long milling duration. The structure changes induced by milling give a new insight on the preparation of amorphous-related alloys when using the method of mechanical milling.

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1. Introduction

Over the last two decades, bulk metallic glasses (BMGs) have received increasing interest due to their unique combination of some mechanical and chemical properties [1,2]. Attempts on BMG-based composites [3–6], by inducing the reinforcement phases to the metallic glass matrix via a routes of casting [3,5], annealing [7], and mechanical milling (MM) [8,9], have been made to improve their plastic properties. Formation of a structural mixture of amorphous–nanocrystalline composites by MM [9–12] has been investigated for subsequent powder consolidation. Under ball milling, a cyclic sequence (crystalline–glassy–crystalline) was observed in the CoTi [12] and ZrNi [13] systems while the devitrification of glassy ZrAlNiCuPd [14] and ZrAlNi [15] alloys was reported. These results indicate that metallic glasses can become unstable against MM. However, the effects induced by MM on metallic glasses have not been considered sufficiently and clarified. This aspect is very important to decide on the best process parameters of MM when preparing BMG-related products.

The quaternary ZrAlNiCu BMGs are considered as “classic” metallic glasses and their glass forming abilities [16,17], crystallization behaviors [18,19], and mechanical properties [1,2] are well depicted. The formation of nanocrystals in Zr-based BMGs can lead to improve mechanical properties [9–11] and the fabrication of these BMGs and their composites by MM have also received some

attention [10,11,20,21]. In contrast, little work has concentrated on the phase stability of metallic glasses during MM. This paper present the first results of an ongoing study dedicated to the influence of mechanical milling on ZrAlNiCu BMGs.

2. Experimental procedure

Master ingots with nominal compositions $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{58}Al_{16}Ni_{11}Cu_{15}$ (at.%) were prepared by arc melting under argon atmosphere. The purity of the elements was 99.9 wt% for Zr, 99.999 wt% for Al, and 99.99 wt% for Cu and Ni. Rods with a diameter of 3 mm were then produced from the master alloys by copper mould suction casting. These rods were crushed into 3 mm long blocks and milled at room temperature using the vario-planetary mill Pulverisette 4 of Fritsch. In this machine the shock energy and the shock frequency can be independently selected and controlled. Here, the absolute rotation speeds of the disk (Ω) and vials (ω) were set, respectively, at 350 and 200 rpm. The powders were sealed in stainless steel vials of volume 125 ml to avoid significant oxidation and milled using five stainless steel balls (15 mm in diameter for a 14 g weight).

The structural evolution was identified by X-ray diffraction (XRD) with Cu $K\alpha$ radiation using a RU300 rotating anode and an INEL CPS120 position sensitive detector. Microstructure was also investigated by transmission electron microscopy (TEM, Philips CM20).

3. Results and discussion

Fig. 1(a) shows XRD traces of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ milled alloys for different milling time. The initial as-cast amorphous rod is also shown for comparison. Sharp diffraction peaks corresponding to crystalline phases appear after milling. The analysis reveals that, from 1 to 4 h of milling, a big cubic phase [13–15] together with a phase having FCC features form from the metallic glass matrix. However, only the peaks of the FCC-type phase remains after 12 h

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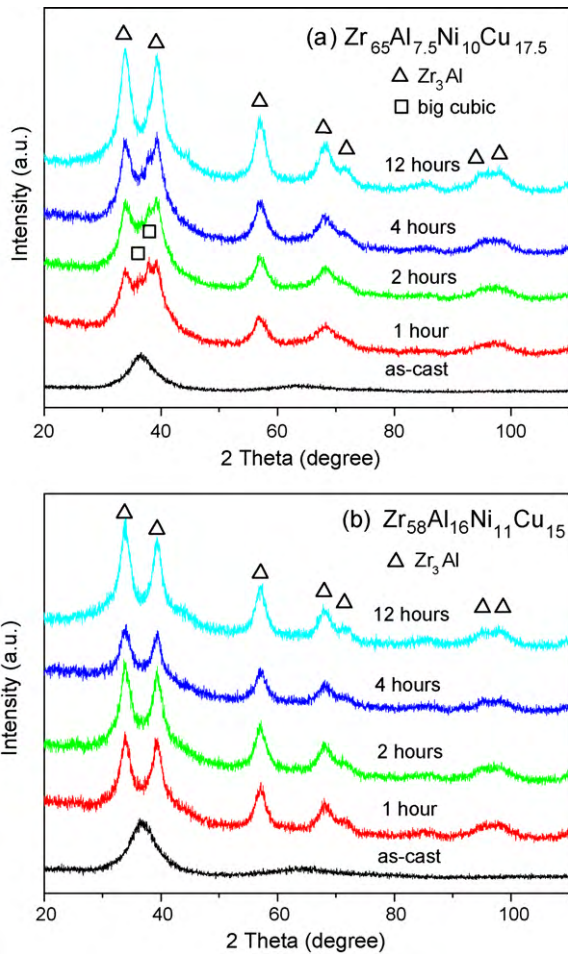


Fig. 1. XRD traces of (a) $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and (b) $Zr_{58}Al_{16}Ni_{11}Cu_{15}$ after different milling times.

of milling. Fig. 1(b) displays the XRD results corresponding to the $Zr_{58}Al_{16}Ni_{11}Cu_{15}$ samples. In this case, only the FCC-type phase can be detected by XRD during the whole milling process ranging from 1 to 12 h. This indicates a high stability of the FCC-type phase against milling. It should also be noted that the crystalline peaks in Fig. 1 are broadened. This can be attributed to the effects of stress and fine grains, as will be confirmed by TEM.

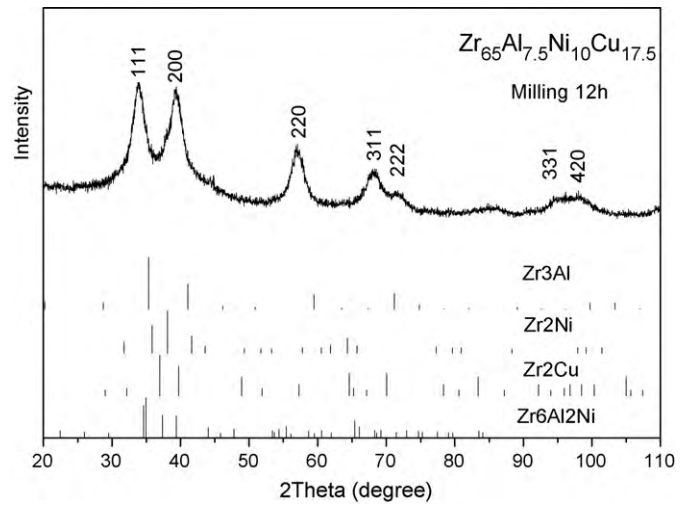


Fig. 2. XRD traces of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ powder milled for 12 h and comparison with typical standard phases.

It is interesting to notice here that this type of FCC phase has never been reported under thermal crystallization conditions [18,19]. In general, quasicrystals, FCC Zr_2Ni , and tetragonal Zr_2Cu phases are the phases that can precipitate at the first stage of thermal crystallization for $ZrAlNiCu$ metallic glasses. In particular, the metastable FCC Zr_2Ni phase can be triggered more easily in O containing alloys [19]. Correspondingly, the tetragonal Zr_2Cu and the hexagonal Zr_6Al_2Ni phases are the final stable products on high temperature annealing in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy even when contaminated by oxygen [18]. As an example, Fig. 2 shows the details of an XRD trace of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ MM alloy (milled for 12 h) and the comparison with some of the above phases. It is clear that, in the case of both MM BMGs investigated here, there is no phase separation between Zr–Cu and Zr–Ni phases and the final product after 12 h of milling is an FCC phase different from the phases produced under annealing. The best match with theoretical phases was obtained for the Zr_3Al phase. The lattice parameter of our FCC phase is however slightly higher than that of the theoretical Zr_3Al phase (about 3.2% differences). These results indicate that the mechanically induced transformations produced changes in the phase transformation sequence that are different from those occurring under annealing. The formation of FCC phases was reported under ball milling of amorphous $ZrAlNiCuPd$ [14] and $ZrAlNi$ [15] powders. In these cases, the alloys were very homogeneous and

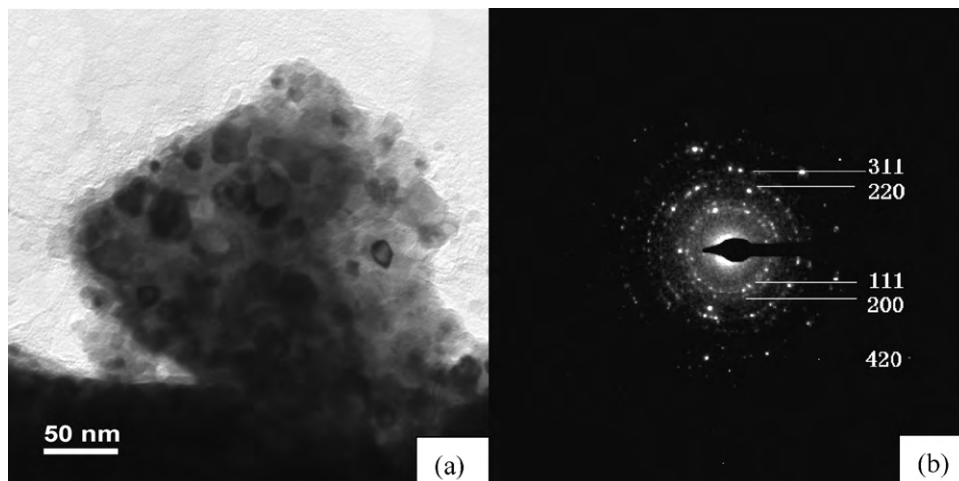


Fig. 3. (a) Bright field image and (b) corresponding SAED pattern from a $Zr_{58}Al_{16}Ni_{11}Cu_{15}$ powder after 12 h of milling.

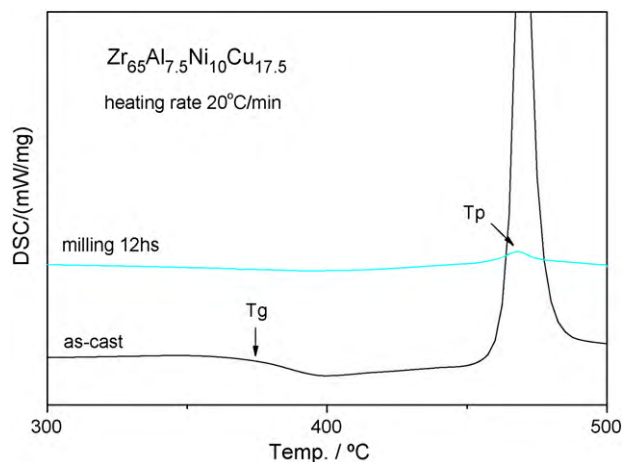


Fig. 4. DSC traces of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy in the as-cast condition and after 12 h of milling.

FCC phases precipitated – after fairly long milling times – from a precursor big cubic phase via polymorphous reactions [14,15]. Comparatively, in our case, the crystallization of the FCC phase was induced easily (within less than 1 h) and from the amorphous state in the case of the $Zr_{58}Al_{16}Ni_{11}Cu_{15}$ alloy (Fig. 1(b)). To get further insights in terms of present phases, the structure of the milled BMG powders were analyzed by TEM. Fig. 3 shows the bright field image and its selected area electron diffraction (SAED) pattern obtained from a $Zr_{58}Al_{16}Ni_{11}Cu_{15}$ powder after 12 h of milling. Nanocrystalline particles with the size of several 10 nm have precipitated in the amorphous matrix. Consistently with the XRD results, the SAED pattern can be indexed as a Zr_3Al -type phase having larger interplanar distances. The SAED also shows a faint halo diffraction indicating the presence of small amount of remaining amorphous. The presence of small amount of remaining amorphous phase was confirmed, for both alloys, by a detailed DSC analysis. This is illustrated, for example for the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy, by the DSC traces given in Fig. 4. At about 470 °C, the initial BMG displays a strong crystallization peak after the T_g temperature. Comparatively, after significant mechanically driven crystallization, the 12 h milled powder still presents a small peak at 470 °C corresponding to the thermal crystallization of a small amount of remaining amorphous.

There are still arguments about the real causes for these MM influences. The temperature rise during milling is one possible cause that could lead to such crystallization. In a previous work on Zr–Ni alloys [22], the temperature rise of the vial measured with a thermocouple was found to be only 30–50 °C. In contrast, a modeling approach for milling Zr–Ni alloys has suggested that the local temperature may reach 247 °C [23]. In the case of our $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ metallic glass, it is clearly established that the structure can remain in the amorphous state more than 1 h when annealed below its glass transition temperature [18]. As T_g (about 370 °C) in this alloy is much higher than the calculated 247 °C [23], it is unlikely that the major driving force for crystallization lies in

the temperature change. This assumption is also consistent with the fact that the crystalline phase introduced by MM is different from the one reported in thermal crystallization. Saida et al. [24] and Scudino et al. [25] found that the ball milling process changed the local structure of the milled metallic glass due to mechanical effects, which further resulted in a change of phase transformation route during the annealing. It is clear that, compared to the presence of a homogeneous MM induced FCC phase [14,15], the powder milled for 12 h is here an amorphous–nanocrystalline composite. These different behaviors tend to confirm that the exact milling parameters are important to control the transformation sequences and kinetics [22,23].

4. Summary

The structure changes of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{58}Al_{16}Ni_{11}Cu_{15}$ bulk metallic glasses during mechanical milling were studied. The end products of the milled powders are composites consisting of the FCC nanocrystals within some metallic glass matrix. This nano FCC-type phase, which is different from the phases formed under thermal crystallization, was produced rapidly under milling using different sequences than the previously reported mechanically induced FCC phases. These findings remind the scientist to take into account the specific effects induced by MM when using this technique to prepare amorphous or amorphous/nanocrystalline samples.

References

- [1] A. Inoue, *Acta Mater.* 48 (2000) 279–306.
- [2] W.H. Wang, C. Dong, C.H. Shek, *Mater. Sci. Eng. R* 44 (2004) 45–89.
- [3] D.C. Hofmann, J. Suh, A. Wiest, G. Duan, M. Lind, M.D. Demetriou, W.L. Johnson, *Nature* 451 (2008) 1085–1089.
- [4] C. Fan, A. Inoue, *Appl. Phys. Lett.* 77 (2000) 46–48.
- [5] C. Fan, R.T. Ott, T.C. Hufnagel, *Appl. Phys. Lett.* 81 (2002) 1020–1022.
- [6] M. Calin, J. Eckert, L. Schultz, *Scripta Mater.* 48 (2003) 653–658.
- [7] C. Fan, C. Li, A. Inoue, *J. Non-Cryst. Solids* 270 (2000) 28–33.
- [8] J. Eckert, A. Kubler, L. Schultz, *J. Appl. Phys.* 85 (1999) 7112–7119.
- [9] J. Eckert, M. Seidel, L. Xing, I. Börner, B. Weiß, *Nanostruct. Mater.* 12 (1999) 439–442.
- [10] C.R. Zhou, J. Xu, *J. Non-Cryst. Solids* 297 (2002) 131–142.
- [11] S. Deledda, J. Eckert, L. Schultz, *Scripta Mater.* 46 (2002) 31–35.
- [12] M.S. El-Eskandarany, K. Aoki, K. Sumiyama, K. Suzuki, *Acta Mater.* 50 (2002) 1113–1123.
- [13] M.S. El-Eskandarany, A. Inoue, *Phys. Rev. B* 75 (2007) 224109–224119.
- [14] M.S. El-Eskandarany, J. Saida, A. Inoue, *Acta Mater.* 51 (2003) 4519–4532.
- [15] M.S. El-Eskandarany, J. Saida, A. Inoue, *Acta Mater.* 51 (2003) 1481–1492.
- [16] A. Inoue, T. Zhang, N. Nishiyama, K. Ohba, T. Masumoto, *Mater. Trans. JIM* 34 (1993) 1234–1237.
- [17] W. Chen, Y. Wang, J. Qiang, C. Dong, *Acta Mater.* 51 (2003) 1899–1907.
- [18] J. Eckert, N. Mattern, M. Zinkevitch, M. Seidel, *Mater. Trans. JIM* 39 (1998) 623–632.
- [19] A. Gebert, J. Eckert, L. Schultz, *Acta Mater.* 46 (1998) 5475–5482.
- [20] M. Seidel, J. Eckert, I. Bäcker, M. Reibold, L. Schultz, *Acta Mater.* 48 (2000) 3657–3670.
- [21] J. Bhatt, B. Murty, *J. Alloys Compd.* 459 (2008) 135–141.
- [22] E. Gaffet, *Mater. Sci. Eng.* 132 (1991) 181–193.
- [23] M. Abdellaoui, E. Gaffet, *Acta Metall.* 43 (1995) 1087–1098.
- [24] J. Saida, M.S. El-Eskandarany, A. Inoue, *Scripta Mater.* 48 (2003) 1397–1401.
- [25] S. Scudino, C. Mickel, L. Schultz, J. Eckert, X.Y. Yang, D.J. Sordelet, *Appl. Phys. Lett.* 85 (2004) 4349–4351.