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Formation of quasicrystals in ball-milled amorphous Zr-Ti-Nb-Cu-Ni-Al alloys with different Nb content

S. SCUDINO*, U. KÜHN, L. SCHULTZ
IFW Dresden, Institut für Metallische Werkstoffe, Postfach 270016,
D-01171 Dresden, Germany
E-mail: s.scudino@ifw-dresden.de

H. BREITZKE, K. LÜDERS
Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

J. ECKERT
FB 11 Material- und Geowissenschaften, FG Physikalische Metallkunde,
Technische Universität Darmstadt, Petersenstraße 23, D-64287 Darmstadt, Germany

In order to investigate the effect of the preparation technique on quasicrystal formation, amorphous $(Zr_{0.585}Ti_{0.082}Cu_{0.142}Ni_{0.114}Al_{0.077})_{100-x}Nb_x$ alloys with $x = 2.5$ and 5 at.% were produced by melt spinning and by ball milling of crystalline intermetallic compounds. The calorimetric and microstructure investigations revealed striking similarities between the differently synthesized samples. All the samples are characterized by a two-step crystallization process in which the first crystallization product does not depend on the way of preparation. In fact, the same metastable nanoscale quasicrystalline phase has been obtained by partial devitrification of ball-milled powders as well as of melt-spun ribbons. This demonstrates that ball milling is an alternative processing route to rapid solidification techniques for the preparation of quasicrystal-forming Zr-based alloys. *© 2004 Kluwer Academic Publishers*

1. Introduction

In the last years, owing to their high thermal stability and wide supercooled liquid region prior to crystallization [1, 2] as well as good mechanical properties [3–5], much attention has been paid to Zr-based glassy alloys produced by solidification techniques. The already outstanding mechanical properties of the single-phase amorphous alloys can be further improved by the presence of second phase particles embedded in the glassy matrix [6–8]. Of particular interest was the discovery of a metastable quasicrystalline phase (QC) in the first stage of crystallization of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ and $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ amorphous alloys [9, 10]. Since then, mostly due to the improved mechanical properties induced by the precipitation of nanoscale quasicrystalline particles [11, 12], the interest in QC-forming alloys has grown, leading to the discovery of an increasing number of Zr-based glassy alloys that undergo quasicrystal formation upon devitrification [13–18].

Alternatively to quenching from the melt, amorphous alloys can be produced by solid-state techniques, such as mechanical alloying of elemental powder mixtures or ball milling of crystalline prealloys [19–22]. Since solid-state amorphization involves a different mechanism, these techniques allow to by-pass most of the limitations of quenching thus enabling the synthesis of alloys having compositions not accessible by rapid solidification techniques [23]. Furthermore, metallic glasses in bulk form can be achieved by consolidation of the glassy powders in the supercooled liquid regime [23]. For this reason, the production of QC-forming alloys by ball milling would be an attractive alternative to conventional quenching techniques.

Accordingly, in this paper we investigate the possibility to produce QC-forming $(Zr_{0.585}Ti_{0.082}Cu_{0.142}Ni_{0.114}Al_{0.077})_{100-x}Nb_x$ alloys with $x = 2.5$ and 5 at.% by ball milling of intermetallic compounds and we compare the devitrification behavior with the equivalent alloys produced by melt spinning. The calorimetric and microstructure data will show that both the solid-state and the rapid quenching technique lead to material characterized by the formation of the same icosahedral phase as first crystallization product upon subsequent heating. This demonstrates that the formation of the quasicrystalline phase does not depend on the way of preparation.

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*Author to whom all correspondence should be addressed.

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TABLE I Iron and oxygen contents of melt-spun ribbons with $x = 2.5$ and 5, and of ball-milled powders with $x = 2.5$ and 5

	Impurity content (at.%)	
	Fe	O
Ribbon with $x = 2.5$	<0.03	0.12
Ribbon with $x = 5$	<0.03	0.21
Powder with $x = 2.5$	0.22	0.29
Powder with $x = 5$	0.05	0.12

2. Experimental

Ingots with nominal composition $(Zr_{0.585}Ti_{0.082}Cu_{0.142}Ni_{0.114}Al_{0.077})_{100-x}Nb_x$ with $x = 2.5$ and 5 at.% (purity >99.9 wt%) were prepared by arc melting in a titanium-gettered argon atmosphere. The ingots were remelted several times in order to achieve homogeneity in composition. The same arc-melted ingot was used as starting material for ball milling as well as for the melt spinning experiments. Ribbons with a cross section of about 0.05×3 mm^2 were prepared in a single-roller Bühler melt spinner at a wheel velocity of 14.3 m/s. Milling experiments were performed using a Retsch PM400 planetary ball mill and hardened steel balls and vials. All sample handling was carried out in a glove box under purified argon atmosphere (less than 1 ppm O_2 and H_2O). The powders were milled for 300 h at a ball-to-powder mass ratio of 13:1 and at a milling speed of 150 rpm. The amount of typical impurities, i.e., iron and oxygen, is listed in Table I. The microstructure was characterized by X-ray diffraction (XRD) using a Philips PW 1050 diffractometer (Co-K_α radiation) and the thermal stability of the samples was investigated by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC7 calorimeter at 40 K/min heating rate under purified argon flow.

3. Results and discussion

Fig. 1 shows the DSC traces of both the melt-spun ribbons and the ball-milled powders. In the temperature range investigated, all the curves are characterized by two exothermic peaks, revealing a multi-step crystallization path that does not depend on the way of preparation. The effect of Nb on the calorimetric data belonging to the differently produced samples is summarized in Table II. The temperature of the glass transition (T_g) and the onset of the first (T_{x1}) and second (T_{x2}) exothermic DSC peaks of the ball-milled powders shift to higher temperature with increasing Nb content. However, T_g and T_{x1} do not vary in the same way. In fact, T_g increases more than T_{x1} giving rise to the decrease of the supercooled liquid region ($\Delta T_x = T_{x1} - T_g$) with increasing Nb content. Similarly to the milled powders, the values of T_g, T_{x1} and T_{x2} for the melt-spun ribbons are characterized by an increasing trend. It is worth noticing that while the ribbon with $x = 5$ displays thermal stability data that are higher than for the powder with the same composition, for the ribbon with $x = 2.5$ the values of T_g and T_{x2} can be considered equal to those of the corresponding ball-milled powder, and T_{x1} is 6 K lower. However, in spite of these differences, the values of ΔT_x for the melt-spun ribbons display a decreasing trend strikingly similar to that of the ball-milled powders.

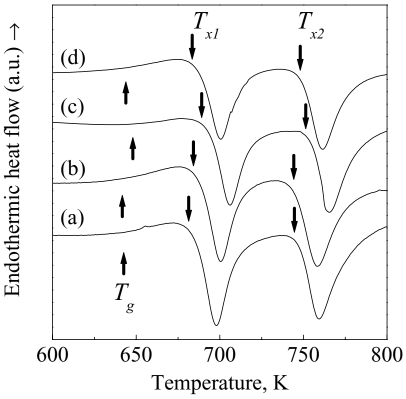

Figure 1 DSC traces (heating rate 40 K/min) for (a) ribbon with $x = 2.5$, (b) powder with $x = 2.5$, (c) ribbon with $x = 5$ and (d) powder with $x = 5$.

TABLE II Temperature of the glass transition (T_g), onset of the first (T_{x1}) and the second (T_{x2}) crystallization peak, extension of the supercooled liquid region ($\Delta T_x = T_{x1} - T_g$) and crystallization enthalpies (ΔH_{x1}, ΔH_{x2}) for the melt-spun ribbons with $x = 2.5$ and 5, and the ball-milled powders with $x = 2.5$ and 5

	T_g (K)	T_{x1} (K)	T_{x2} (K)	ΔT_x (K)	ΔH_{x1} (J/g)	ΔH_{x2} (J/g)
Ribbon with $x = 2.5$	637	682	746	45	24.0	26.3
Powder with $x = 2.5$	635	688	745	53	18.7	21.3
Ribbon with $x = 5$	654	694	756	40	16.6	20.5
Powder with $x = 5$	641	690	752	49	16.2	19.4

The enthalpies (ΔH_x) related to the crystallization events of both powders and ribbons decrease with increasing Nb content. Differently from the samples with $x = 5$, that are characterized by similar values of the crystallization enthalpies, for the ball-milled powder with $x = 2.5$ the values are slightly reduced compared to the corresponding melt-spun ribbon. Most likely, this decrease in enthalpy is due to a lower quasicrystalline or crystalline volume fraction formed.

It has been reported [24] that the devitrification of the amorphous $Zr_{57}Ti_8Nb_{2.5}Cu_{13.9}Ni_{11.1}Al_{7.5}$ alloy prepared by ball milling is characterized by a higher value of T_{x1} with respect to the melt-spun ribbon having the same composition. A similar behavior was found by producing a ribbon with impurity content (i.e., Fe and O) comparable with the ball-milled powder, allowing to ascribe the difference in the devitrification behavior to contamination effects. This hypothesis can explain the calorimetric data presented above. In fact, while the ribbon with $x = 2.5$ has lower impurity content compared to the powder with the same composition and, therefore, a lower T_{x1}, the ribbon with $x = 5$ has slightly higher oxygen content (Table I), giving rise to a higher value of T_{x1}. Nevertheless, the overall crystallization behavior of the differently prepared specimens is strikingly similar.

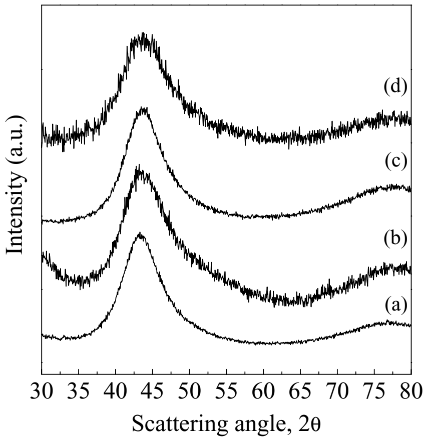

Figure 2 XRD patterns (Co-K_α radiation) for the as-prepared: (a) ribbon with $x = 2.5$, (b) powder with $x = 2.5$, (c) ribbon with $x = 5$ and (d) powder with $x = 5$.

The XRD patterns of the as-prepared samples are presented in Fig. 2. The as-spun ribbons as well as the as-milled powders show the typical wide halo of amorphous materials and no traces of crystalline phases.

In order to study the structural evolution during heating, samples of as-spun ribbons and ball-milled powders were annealed in the DSC with continuous heating at 40 K/min up to the completion of the first exothermic peak and then cooled to room temperature at 100 K/min. The phase formed after annealing was identified by XRD and the patterns are shown in Fig. 3. The phase precipitated in both the ribbon and in the powder with $x = 2.5$ was previously identified by XRD and TEM as an icosahedral phase of 5–10 nm size with a quasilattice constant of 0.478 and 0.474 nm, respectively [24, 25]. The XRD patterns of both powder and ribbon with $x = 5$ heated up to the completion of the first exothermic DSC event are characterized by some diffraction peaks that after comparison with the patterns of the samples with $x = 2.5$ heated up to the same temperature can be assigned to an icosahedral phase having a quasilattice constant of about 0.474 nm. The broader XRD peaks of the QC produced by annealing the ball-milled powders compared to the diffraction peaks of the melt-spun ribbons might be caused by residual strain in the powder, which is not completely recovered during the heat treatment.

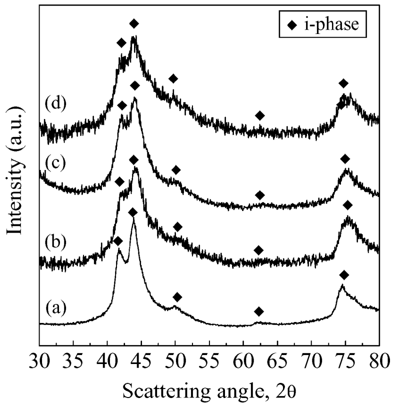

Figure 3 XRD patterns (Co-K_α radiation) after heating up to the completion of the first exothermic DSC peak for (a) ribbon with $x = 2.5$, (b) powder with $x = 2.5$, (c) ribbon with $x = 5$ and (d) powder with $x = 5$.

The remarkable similarities between the calorimetric and microstructure data of ball-milled powders and melt-spun ribbons demonstrate that ball milling leads to the formation of the same amorphous QC-forming alloy and, therefore, to the same SRO as the quenched samples. This is in contrast to recent investigations regarding the devitrification of Zr-based amorphous alloys prepared by different techniques. For instance, it has been reported for the $Zr_{70}Pd_{30}$ alloy [26, 27] that, contrary to the melt-spun ribbon, the ball-milled powder shows no QC formation upon partial devitrification. In order to explain this feature, it has been proposed that the mechanism of amorphization by ball milling, not requiring quenching of the melt, prevents the formation of the quenched-in nuclei of icosahedral short-range order (SRO), responsible for the formation of quasicrystals in the rapidly solidified glass. As a consequence, the lack of the quenched-in nuclei in the glassy powders would lead to a different SRO and, therefore, to a different crystallization behavior than that obtained by quenching the melt [27]. Furthermore, Saida *et al.* [28] reported for a Zr-based multicomponent alloy on the change in the primary devitrified phase from icosahedral QC to fcc Zr_2Ni phase by ball milling. The authors proposed that the distortion due to the mechanical treatment induces changes of the local icosahedral structure in the glassy state and, therefore, leads to a different crystallization behavior. However, in the latter paper the effect of the impurities, introduced during milling, was not discussed. The impurity content, especially oxygen and iron, is of great importance in Zr-based glassy alloys. For example, oxygen provokes the change in the crystallization mode of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ glassy ribbons [29] from a single to a double-step process, inducing the precipitation of a QC phase as first crystallization product, whereas iron addition to the same alloy changes the crystallization sequence inducing the formation of a metastable *big cube* phase [30]. Therefore, since there are some indications that impurities, such as iron and oxygen, might be the dominant factor for affecting the QC-formation in ball-milled powders rather than the absence of quenched-in nuclei of icosahedral SRO [24], the effect of contaminants should be considered with more attention. Furthermore, previous investigations have shown that amorphous Ni-Zr alloys prepared by mechanical alloying and melt spinning are characterized by a similar SRO [22, 31]. Moreover, Mattern *et al.* [32] did not find for different ZrTiCuNiAl glassy alloys any special atomic arrangement for the particular alloy forming quasicrystals upon heating. Finally, since it is well-known for several Al-based alloys [33–35] that it is possible to form QC directly during ball milling of elemental powders as well as crystalline prealloys, the presence of quenched-in nuclei is not a mandatory prerequisite for QC formation.

4. Conclusions

The effect of the preparation technique on quasicrystal formation in amorphous $(Zr_{0.585}Ti_{0.082}Cu_{0.142}Ni_{0.114}Al_{0.077})_{100-x}Nb_x$ alloys with $x = 2.5$ and 5 at.% produced by melt spinning and by ball milling of crystalline intermetallic compounds has been investigated. The comparison between the ball-milled powders and the same alloy produced by melt spinning reveals that both types of samples are characterized by the formation of a QC phase as first devitrification product. This demonstrates that solid state processing is an alternative route for rapid solidification techniques for the preparation of QC-forming alloys. Furthermore, it suggests that the short-range order of the amorphous phase in both the melt-spun ribbon and the ball-milled powder is the same.

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