Nanocrystalline ZrN particles embedded in Zr-Fe-Cu-Al-Ni amorphous matrix.

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ABSTRACT

Melt-spun $Zr_{64}Al_7Cu_{17}Ni_{10}Fe_2$ amorphous ribbons were milled under nitrogen atmosphere for different times. The resulting nitrided powders were studied by x-ray diffraction, Mössbauer spectroscopy and differential scanning calorimetry. The formation of nanosized crystalline particles, with cubic δ-ZrN structure, dispersed in the amorphous matrix was observed along with a change in the composition of the amorphous phase. Prolonged milling leads to the additional precipitation of late transition metals (Fe,Ni,Cu). The nitride particles affect the crystallization behavior and modify the thermal stability of the amorphous alloy.

INTRODUCTION

Composites based on bulk amorphous alloys are receiving considerable attention due to their improved mechanical properties, such as hardness, ductility and yield stress, with respect to single-phase amorphous alloys. These improvements are obtained by hindering propagation of shear bands and favouring the formation of multiple shear bands. Recently, the Zr-Al-Cu-Ni system has been intensively investigated as amorphous matrix in order to form composites containing a variety of particles such as W[1], TiN, AlN[2], CaO, ZrC[3], SiC[4], MgO and CeO[5].

Amorphous Zr based multicomponent alloys, like $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$, show a wide supercooled liquid region and crystallize with the simultaneous formation of tetragonal $CuZr_2$ and hexagonal Zr_6NiAl_2 [6]. However, their crystallization behavior strongly depends on chemical composition. In particular, amorphous $(Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10})_{1-x}Fe_x$ alloys are known to crystallize, primarily, to a metastable Ti_2Ni-type structure [7]. This fact has been used to obtain hybrid nanostructures after partial crystallization of the starting amorphous alloy. Alternatively, H incorporation to these amorphous alloys induces the preferential formation of crystalline Zr-hydrides, reducing the number of Zr atoms in the amorphous matrix, which is at the same time enriched in Al, Cu and Ni. This deteriorates the thermal stability and results in the formation of crystalline phases with a smaller Zr content [8].

On the other hand, ball milling of Zr alloys or compounds in N_2 atmosphere has proved to be an effective way to produce increasing fractions of δ-ZrN particles dispersed in the remaining matrix [9,10]. This processing method would offer the possibilty of studying the effect of the ceramic volume fraction on the mechanical properties and the crystallization behavior of the resulting composite.

In this work, we present results on the formation of nanocrystalline δ-ZrN particles dispersed in a Zr-Al-Cu-Ni-Fe amorphous matrix upon milling in a N_2 atmosphere. Preliminary studies on the thermal stability and structural characterization of such crystalline/amorphous composites are presented, as well.

EXPERIMENTAL DETAILS

Amorphous $Zr_{64}Al_7Cu_{17}Ni_{10}Fe_2$ ribbons 3 mm wide and 25 μm thick were prepared by single roller melt spinning. Ribbon batches, 500 mg each, were milled under N_2 atmosphere, in an oscillatory mill using one steel ball (7g) and a cylindrical steel vial O-ring sealed and connected to a N_2 reservoir (total volume $160cm^3$). The N_2 pressure was measured during milling by a strain transducer and, from its decrease, the instant number of absorbed N atoms was determined. The as-milled samples were analyzed by differential scanning calorimetry (DSC) in a Shimadzu TA50 calorimeter. The scans were carried out at a constant heating rate of 20 K/min under an argon flux. All the samples, as-quenched, milled and/or annealed, were characterized by x-ray diffraction (XRD) and Mössbauer spectroscopy (MS). XRD patterns were obtained with a Philips PW1710 diffractometer using CuK_α radiation and fitted by the Rietveld method with Thompson-Cox-Hastings pseudo-Voigt profiles. The microstrains and the mean longitude of coherently diffracting crystal domains (grain size) were calculated according to the integral breadth method. MS measurements were made at room temperature with a conventional spectrometer, employing a $^{57}CoRh$ source, in transmission geometry. All isomer shifts are given relative to α-Fe.

RESULTS

Figure 1 shows the N absorption kinetics curve for a long duration run. It displays a characteristic sigmoidal shape with an absorption rate considerable lower than that observed for pure Zr and for a variety of Zr-Fe compounds [9,10]. After 28 h of milling a value higher than 0.5 N atoms per metallic atom is attained without reaching saturation. It is worth to note that the kinetic curves for shorter runs overlap well with this long duration run. The N concentrations reached to in each run are shown in table I.

The diffractograms of all these samples ($t_m = 0, 4, 5, 6, 7, 10$ and 28 h) are shown in figure 2a. Only a diffuse maximum is visible for the as quenched sample indicating its amorphous nature. After milling a few hours, some broad reflections superimpose to the amorphous maximum but they could not be readily identified. For $t_m = 7$ h, despite their width, these reflections can be associated with the cubic structure of δ-ZrN (cF8, NaCl-type). This is confirmed for $t_m = 10$ h and further for $t_m = 28$ h when the amorphous signal have disappeared and the crystalline reflections are well defined. In these cases an additional broad line is evident at an angular position around 44°.
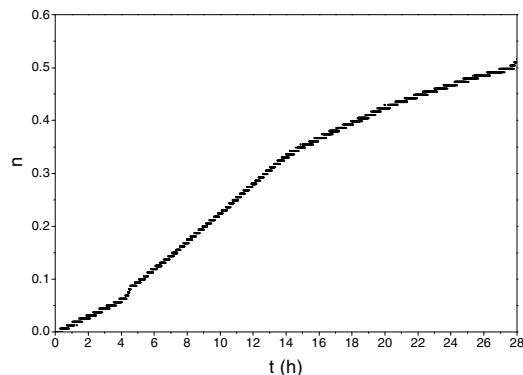

Figure 1. Absorption kinetics during milling; n is the number of absorbed N atoms per metallic atom.

Table I. The number of absorbed N atoms per metallic atom (n) for different milling times and the estimated relative area of nitride phase in the XRD patterns (X).

t_m (h)	n	X
4	0.06	30_5
5	0.09	43_5
6	0.12	44_5
7	0.14	59_5
10	0.22	73_5
28	0.52	77_5

Figure 2b shows the corresponding Mössbauer spectra. For the as-prepared ribbons, the spectrum consists of a broad asymmetric doublet, originating in a distribution of electric field gradients characteristic of amorphous alloys. The distribution width and the fitted values of the mean quadrupole splitting $<QS> = 0.61_1$ mm/s and isomer shift $<IS> = 0.25_1$ mm/s are consistent with those observed in $Zr_{1-x}Fe_x$ amorphous alloys with similar total amount of late transition metal i.e. for $x \approx 0.29$ [11]. As milling proceeds, this paramagnetic signal evolves progressively: it broadens firstly and narrows after 7 h when an αFe-like sextet insinuates. For $t_m = 10$ h the spectrum asymmetry is reversed, which is an indication of δ-ZrN(Fe) presence [9], and the α-Fe sextet is better defined. Finally, for $t_m = 28$ h, a complex magnetic spectra is seen. It
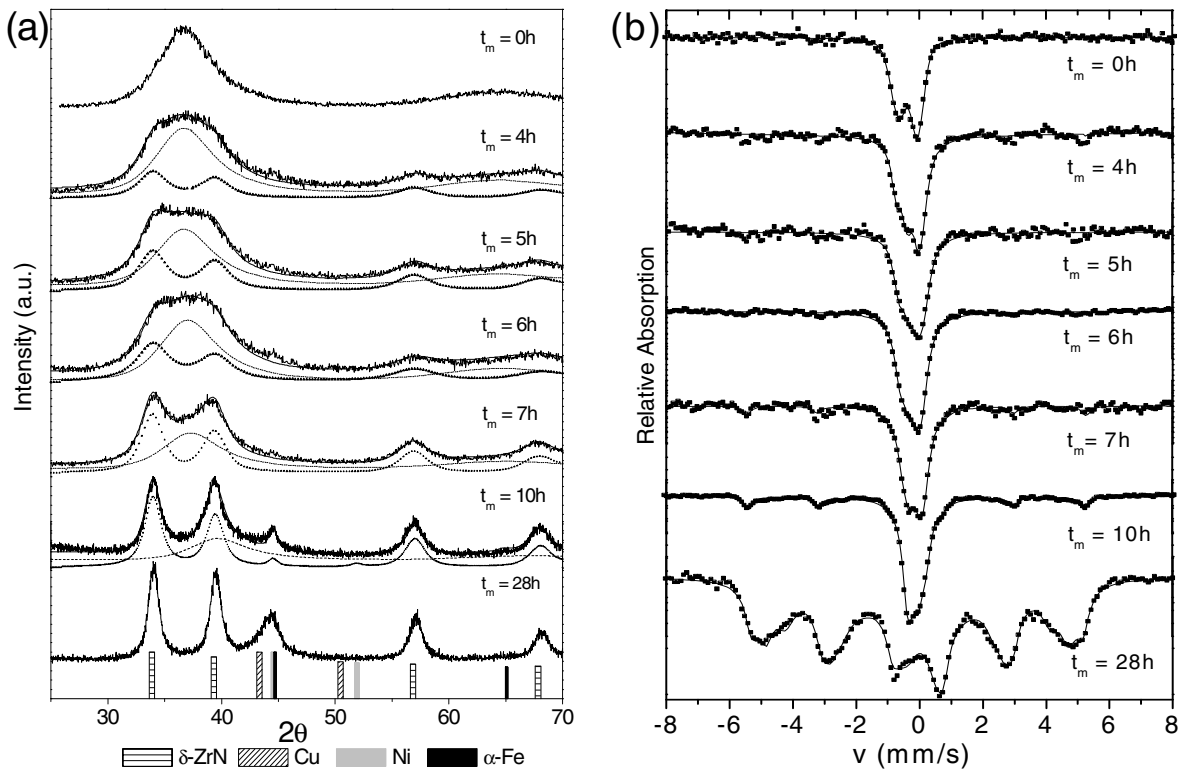

Figure 2. XRD patterns (a) and Mössbauer spectra (b) of the as quenched ribbons and after milling during 4, 5, 6, 7, 10 and 28 h.

is worth noticing that Mössbauer spectroscopy just senses the environments of Fe atoms, which are a minority component in the present alloy, presumably playing a role similar to that of the other late transition metals (Cu, Ni).

The DSC traces for the amorphous alloy and for some of the nitride-containing samples are compared in figure 3. The as cast sample shows a glass transition followed by a wide supercooled liquid region. Also, it can be seen that in the nitrided samples the primary crystallization event is shifted towards higher temperatures and is apparently suppressed (no exothermic peaks in the observed temperature range) for the sample with $t_m = 7$ h (n = 0.22). After further milling ($t_m = 10$ h) a strong endothermic effect is seen starting at about 570 K.

The XRD patterns and Mössbauer spectra taken after the DSC scans are shown in figure 4. The reflections of a crystalline phase with fcc-Zr_2Ni structure (cF96, $Ti_{.2}Ni$-type) are clearly identified together with those, already present, coming from δ-ZrN. It is worth noticing that the Zr_2Ni structure (η phase) may accommodate up to 0.125 N atoms per formula unit. For short milling times this phase is the more abundant and for large milling times ($t_m \geq 7$ h) the situation is reversed. The Mössbauer spectra of these samples show a quadrupole interaction plus a magnetic αFe-like sextet for 10 h of milling.

DISCUSSION

The milling of the amorphous ribbons under N_2 atmosphere provokes its nitridation. This mechanically assisted incorporation of atomic N has been previously observed for several metals [12,13,14] and metallic compounds [9,10]. It has been described in terms of dissociative adsorption of N_2 at grain boundaries and free surfaces, both permanently renewed by the mechanical action, and bulk diffusion, which is also assisted by the creation of defects [15]. The slower kinetics observed in the present case may be related to the absence of grain boundaries in the starting amorphous material and to its dense random packed structure. Although our interest
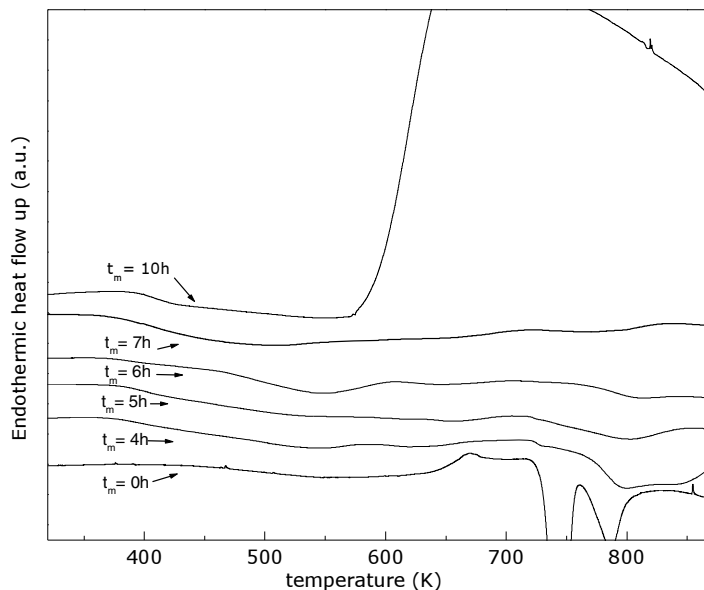

Figure 3. DSC scans of the as quenched ribbons and after milling 4, 5, 6, 7 and 10h.
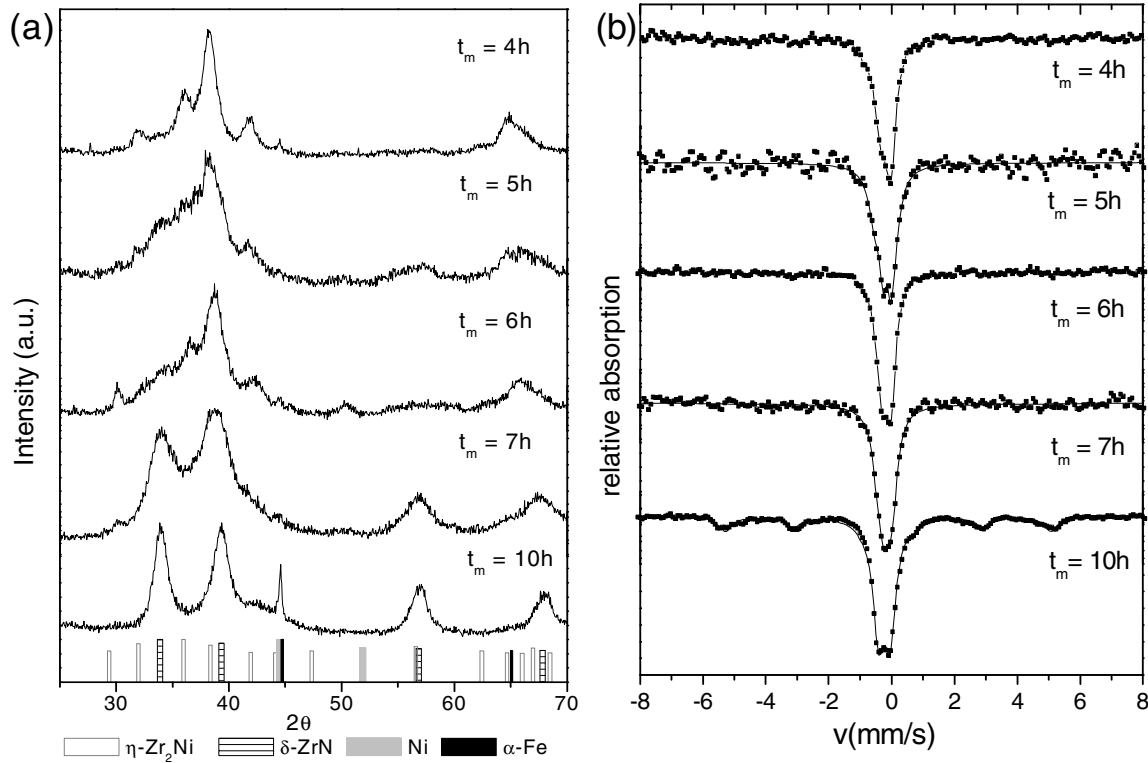
Figure 4. XRD patterns (a) and Mössbauer spectra (b) of some samples after a DSC scan up to 873K.

is focused in the first stages of this process (low values of n), it is worth to note that after prolonged milling a high N concentration can be reached (close to 1 N per Zr atom).

The incorporated N atoms show a tendency to combine with Zr to form δ-ZrN, which probably includes some of the remaining metals (Al, Cu, Ni and Fe) during the first stages of its formation. Although the diffractograms are not conclusive, they show evidence of a gradual increase of the δ-ZrN lines superimposed to the diffuse maximum from the amorphous phase. A fit to these data allows the determination of the relative area under the reflections coming from each phase. From this data, a crude estimation of the nitride phase fraction present after each milling run was made and quoted in Table I. From a Rietveld refinement of the remaining pattern, the δ-ZrN lattice parameter a was determinate to be 0.4572_1 nm in agreement with reported values. The grain size was estimated to be less than 3nm for samples milled 4, 5 and 6 h and to increase up to 9 nm for $t_m = 28$ h.

As milling proceeds, the progressive formation of δ-ZrN is accompanied by the segregation of Ni and Fe. This is well documented by Mössbauer spectroscopy and X ray diffraction in the sample with $t_m = 10$ h. On the other hand, the observed shift to higher scattering angles of amorphous maximum is compatible with a Cu enrichment of the amorphous matrix [16].

It is not clear if Fe and the other metals precipitate from the amorphous matrix or from the δ-phase. The Mössbauer spectrum from the sample with $t_m = 10$ h indicates that most of the Fe atoms are in the δ-phase, while the diffractogram shows an important reflection at an angular position corresponding to the main reflections of Fe or Ni and no traces of Al. Based on this results and on previous reports on the formation upon milling of Zr(Al)N and Zr(Fe)N with the

δ-structure [10,17], we suggest that Al and Fe are retained in the δ-structure. After prolonged milling ($t_m = 28$ h), this reflection has increased considerably while a complex magnetic MS spectrum develops, indicating the almost complete precipitation of Fe atoms.

Most of these features are confirmed by the observations made on the annealed samples. For example, in this case the precipitation of Ni is better observed in the diffractograms. The XRD patterns also show that the δ-phase precipitates remain mostly unchanged after the heat treatment and the remaining amorphous matrix crystallizes mainly to the η-structure in a process that extends to temperatures, which are higher than in the as-cast material.

CONCLUSIONS

In summary, by ball milling $Zr_{64}Al_7Cu_{17}Ni_{10}Fe_2$ amorphous ribbons in N_2 atmosphere it is possible to form nanocrystalline nitride precipitates in a variable proportion inside the amorphous matrix. Such precipitates have the cubic δ-ZrN structure and a grain size about 3nm for $t_m \leq 6$ h. Upon further milling, when the precipitation of the Ni transition metals is evident, some grain growth is observed in the nitride phase. Heat treatments up to 873K induce the crystallization of the remaining amorphous matrix mostly into a η-Zr_2Ni-type phase.

The influence of this nanosized nitride precipitates on the mechanical properties of the studied system are presently under investigation.

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