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Journal of Alloys and Compounds 317–318 (2001) 479–484

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Metastable structures in α–β′ brass

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Abstract

Rapid solidification and mechanical grinding were used to induce metastable structures in a Cu–Zn alloy with a composition falling in the two phase α–β′ (face centred cubic–B2 ordered) region of this binary system. Thermal treatments were also carried out to induce further changes and transformations to more stable states starting from the conditions attained with the mentioned non-equilibrium processes routes. In the rapidly solidified material, a body centred cubic structure was observed. At this stage the presence of long-range order could be inferred. Nonetheless, upon heat treating the material at 500°C for 15 min the formation of the α–β′ mixture could be induced. A similar condition could also be achieved by grinding the starting melt-spun ribbons in a high energy ball-mill. The remarkable difference was that in this case the fcc α-phase had a non-equilibrium composition, which is compatible with that of the parent β′-phase. After heat treatment, the milled specimen has the same composition of the α-phase as the one found in the melt-spun heat treated materials. These results indicate a diffusionless transformation was induced by the milling process into the as-spun material from the parent β′-phase into the α–β′ mixture. Phase evolution and compositions were evaluated using X-ray diffraction analyses.

Keywords: Ball-milling; Brass; X-ray diffraction; Metastable structures; Cu–Zn alloys

1. Introduction

In the α-β′ brasses, the ordered β′ phase (B2 structure) has a strengthening effect on the softer and more ductile α-phase (fcc) [1]. The β′ phase, which presents an order–disorder phase transformation notoriously cited as a typical example of a second order transition [2], has been considered in many studies on the effect of the ordered atomic arrangement on different properties of the material. The activation energies for diffusion of several elements in single phase β′ brass was found to be larger in the disordered state as compared to the ordered one [3]. The influence of the ordered state on dislocation dynamics, which results in the anomalous increase of yield stress with temperature, observed in several intermetallic compounds [4], was observed for the first time in β′ brass specimens [5]. Consequently, other aspects and properties, such as recovery and recrystallisation [6], creep resistance [7] displayed a significant dependence on the long-range order conditions.

The original task of the present study was to disorder β′-brass using rapid solidification techniques. Then it turned into a broader exploration on the metastable structures which can be attained in Cu–Zn alloys by rapid solidification but also by mechanical grinding.

2. Experimental

Bulk pieces of the alloy with a nominal composition of Cu–48.7 Zn wt% (Cu–48 Zn at%) were rapidly solidified by melt-spinning in a low pressure Ar atmosphere.

Some of the as-spun ribbons were used as starting material for ball-milling experiments. The ribbons, cut into small pieces, were ball-milled in a planetary mill, using agate vials and yttria stabilised zirconia balls. To avoid oxidation, the vials were filled and sealed under an inert argon atmosphere.

Thermal treatments were conducted on the ribbons and milled powders in a furnace under flowing Ar after the chamber was evacuated to a pressure better than 10^{-5} mbar.

X-ray diffraction analyses were carried out to characterise the microstructure of the different specimens considered for this study. A wide angle diffractometer with a monochromated Cu Kα radiation was used. The melt-spun

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0925-8388/01/$ – see front matter
PII: S0925-8388(00)01374-8

ribbon specimens were prepared by sticking them to a microscope glass slide. Ball-milled powders were loaded in a conventional sample holder for powder specimens. The microstructural parameters of the analysed specimens were worked out using a full pattern fitting procedure [8]. Most important to the evaluation of the composition of the α-phase are the data on the dependence of its lattice parameter on the Zn content [9].

3. Results

From the as-spun ribbons the diffraction pattern in Fig. 1 was obtained. The reflections can be indexed according to the body centred cubic structure. No significant texture effects were noticed, which might come from a preferential solidification direction. From calorimetric data, already published in a former study on the same materials [10], it turned out the ribbons at this stage are ordered, as the order–disorder transition peak was recorded when continuously heating these ribbons up to temperatures in excess of 470°C. Therefore, the crystal structure of the as-spun ribbons is actually the ordered B2 one, typical of the β′ brass phase. It is not surprising no superlattice reflections were detected, as their intensity is intrinsically very weak, owing to the small difference in the atomic scattering factors of Cu and Zn. The impossibility to trap disorder can be explained in terms of the high interdiffusivities of the constituent elements [11]. However, the β′-phase is not the equilibrium one, as the rapid solidification and subsequent cooling have been able to suppress a phase separation reaction. A short term thermal treatment, i.e. 15 min at 500°C under Ar, was sufficient to induce the decomposition of the initial phase to a two phase mixture involving also the fcc α-phase. The relevant diffraction pattern is shown in Fig. 2, and in Table 1 the microstructural parameter for the Cu–Zn ribbons in the as-spun conditions and after heat treatment are listed. From the average crystallite size of the β′-phase, D_{100}, evaluated along the [100] direction, it is clear that the treatment induced a slight recrystallisation of this phase. Domain size for the α-phase remains to a lower value. From the

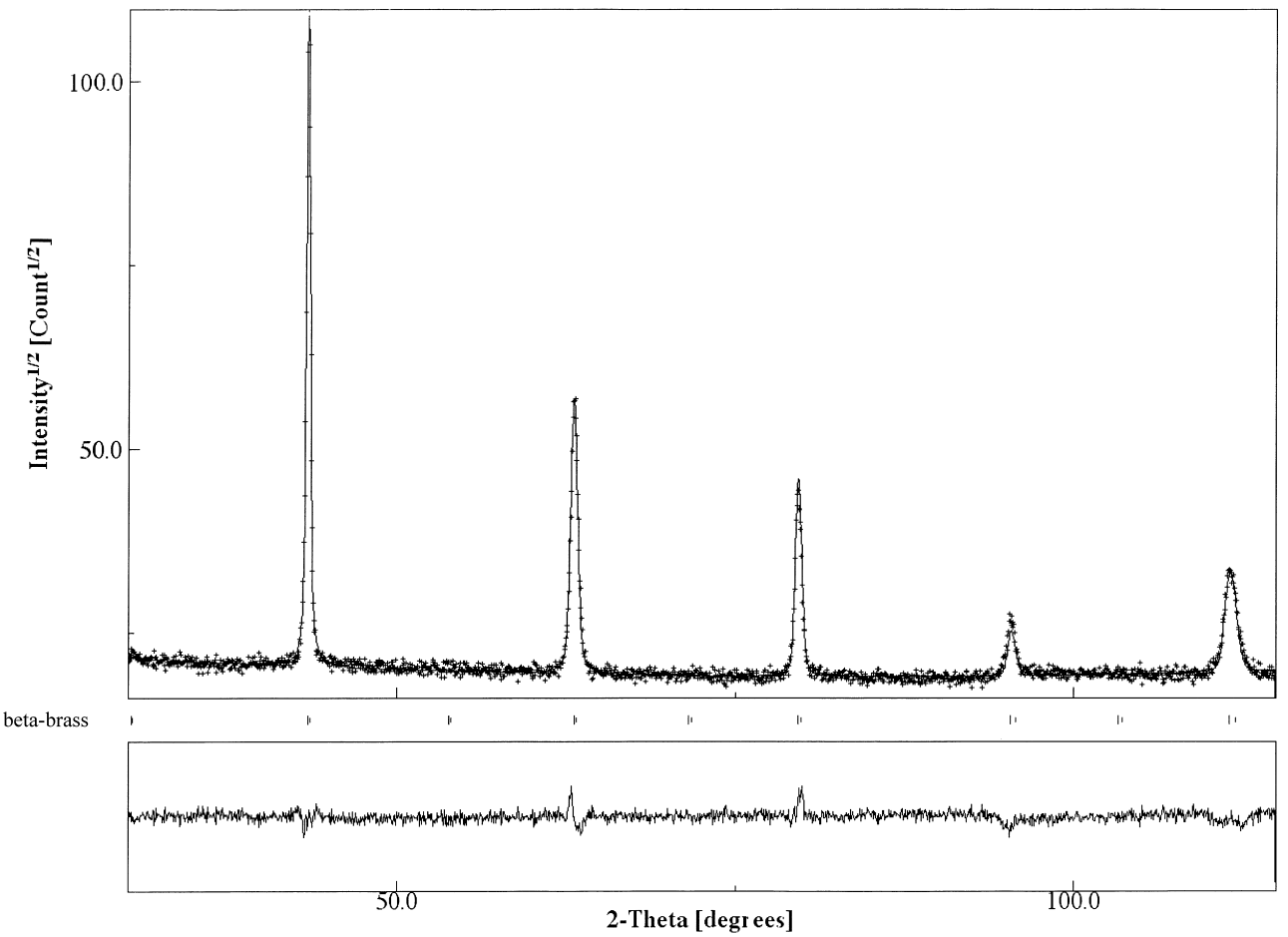

Fig. 1. XRD pattern of the rapidly solidified ribbons in the as-spun condition. No superlattice reflections were detected owing to the small difference in electron scattering factors for copper and zinc.

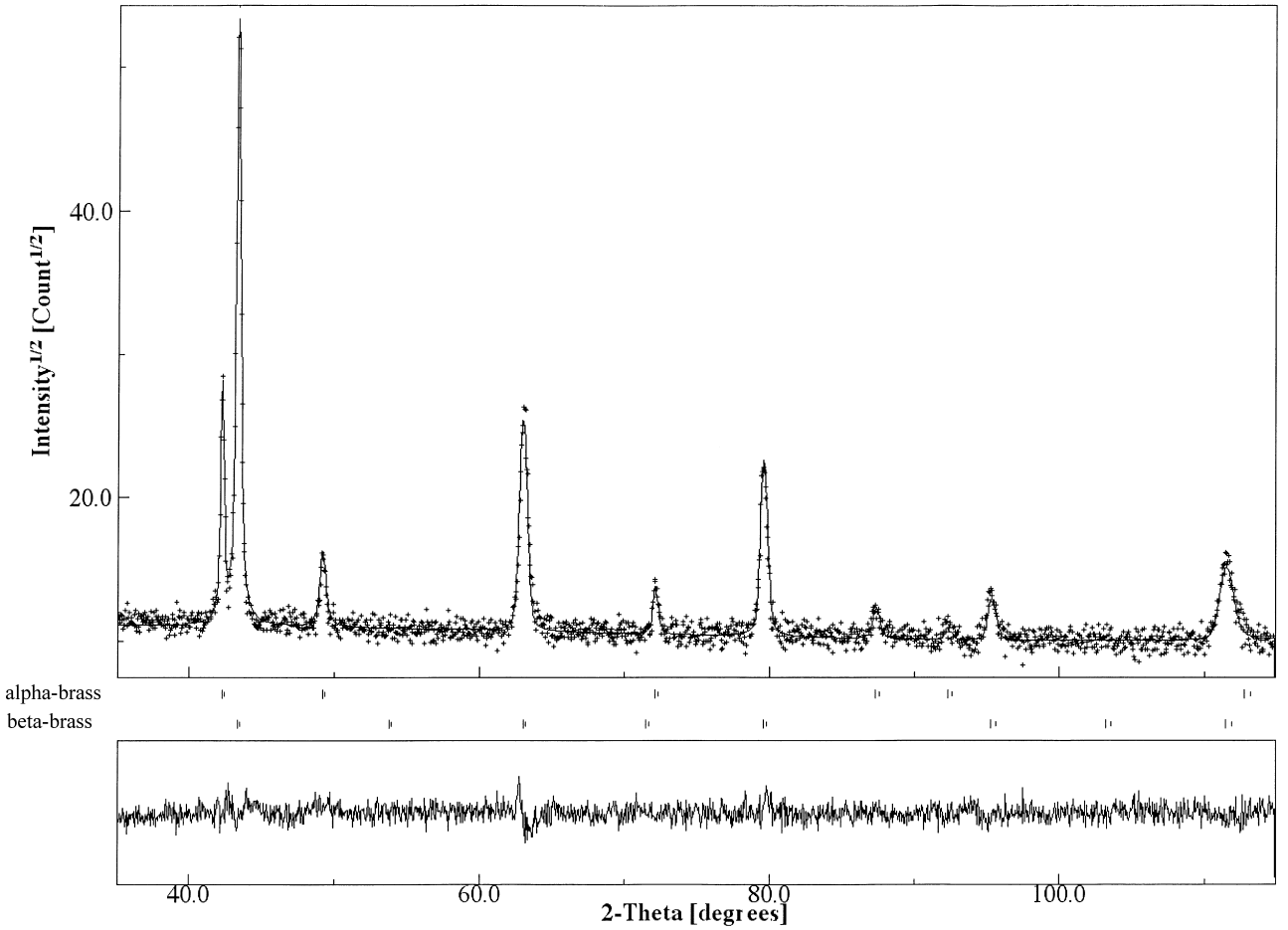

Fig. 2. XRD pattern of the rapidly solidified ribbons after 15 min at 500°C.

lattice parameter, the composition of the fcc phase was estimated, using literature data [9], and resulted equal to Cu–36.9 Zn (wt%).

The same composition was also found for the α-phase obtained when annealing the as-spun ribbons at 400°C under identical conditions as those adopted at 500°C.

Thermal treatments were not the only route to get a phase decomposition starting from the as-spun ribbons, originally featuring the ordered β′-phase only. In fact, similar results could be obtained using mechanical grinding in a high energy ball-mill, an extreme form of mechanical deformation. The as-spun ribbons were sub-

Table 1
Microstructural parameters evaluated from XRD data for samples 1–5

Sample[a]	Phase	Average domain size (Å)	Lattice parameter (Å)	rms strain
1	β′	380	2.9471	4.2×10^{-3}
2	β′	460	2.9483	4.9×10^{-3}
2	α	140	3.7003	9.0×10^{-6}
3	β′	460	2.9455	3.6×10^{-3}
3	α	320	3.6998	8.7×10^{-4}
4	β′	70	2.9483	1.2×10^{-2}
4	α	30	3.7192	8.9×10^{-3}
5	β′	700	2.9510	1.3×10^{-3}
5	α	220	3.7003	2.1×10^{-8}

[a] 1, as-spun Cu–Zn ribbons; 2, Cu–Zn ribbons annealed at 500°C for 15 min; 3, Cu–Zn ribbons annealed at 400°C for 15 min; 4, Cu–Zn ribbons ball-milled for 48 h; 5, Cu–Zn ribbons ball-milled for 48 h and then annealed at 400°C for 15 min.

jected to ball-milling in a planetary mill. After 48 h milling, the diffraction pattern displayed the presence of the fcc α-phase (Fig. 3) together with the original β′-phase. The transformation phenomena occurring during milling induced quite a different microstructure, as compared to the annealed specimens. The scattering domains of the milled material have much smaller dimensions than in the annealed samples. This is true for both β′ and α-phases. Particularly important to better understand the actual character of the mechanically induced transformation is the composition of the α-phase, once again estimated by comparing our diffraction results with literature data. A value of Cu–45.0 Zn (wt%) was found, falling in the α–β′ two phase field of the binary Cu–Zn phase diagram [12].

To check for the stability of the structures obtained by ball-milling, an annealing at 400°C for 15 min was carried out on the samples ball-milled for the longest time (48 h). The diffraction pattern in Fig. 4 is illustrating what is the phase composition in the rapidly solidified ribbons after both milling and annealing. The two phases, already present after milling (Fig. 3), are still there, although major changes have occurred. The coarsening of the average domain size can be noticed looking at the average domain size values in Table 1.

However, the most interesting aspect of the diffraction analyses concerns the change in the composition of the α-phase, which becomes equal to Cu–36.9 Zn (wt%), i.e. the same value found for the ribbons annealed after the rapid solidification process.

The α-phase concentrations for all samples quoted in the text are summarised in Table 2.

4. Discussion

In the as-spun ribbons the ordered β′ phase was found. As pointed out earlier, in the relevant diffraction pattern (Fig. 1) the fundamental peaks only, pertaining to a body centred cubic structure, are visible. Owing to the little difference in the electron scattering factors of copper and zinc, the superlattice reflections result intrinsically very weak. However, the melt spun ribbons are not in an equilibrium condition as yet. In the first place, this can be indirectly inferred from the comparatively small value of the average domain size, 38 nm (Table 1), affected by the

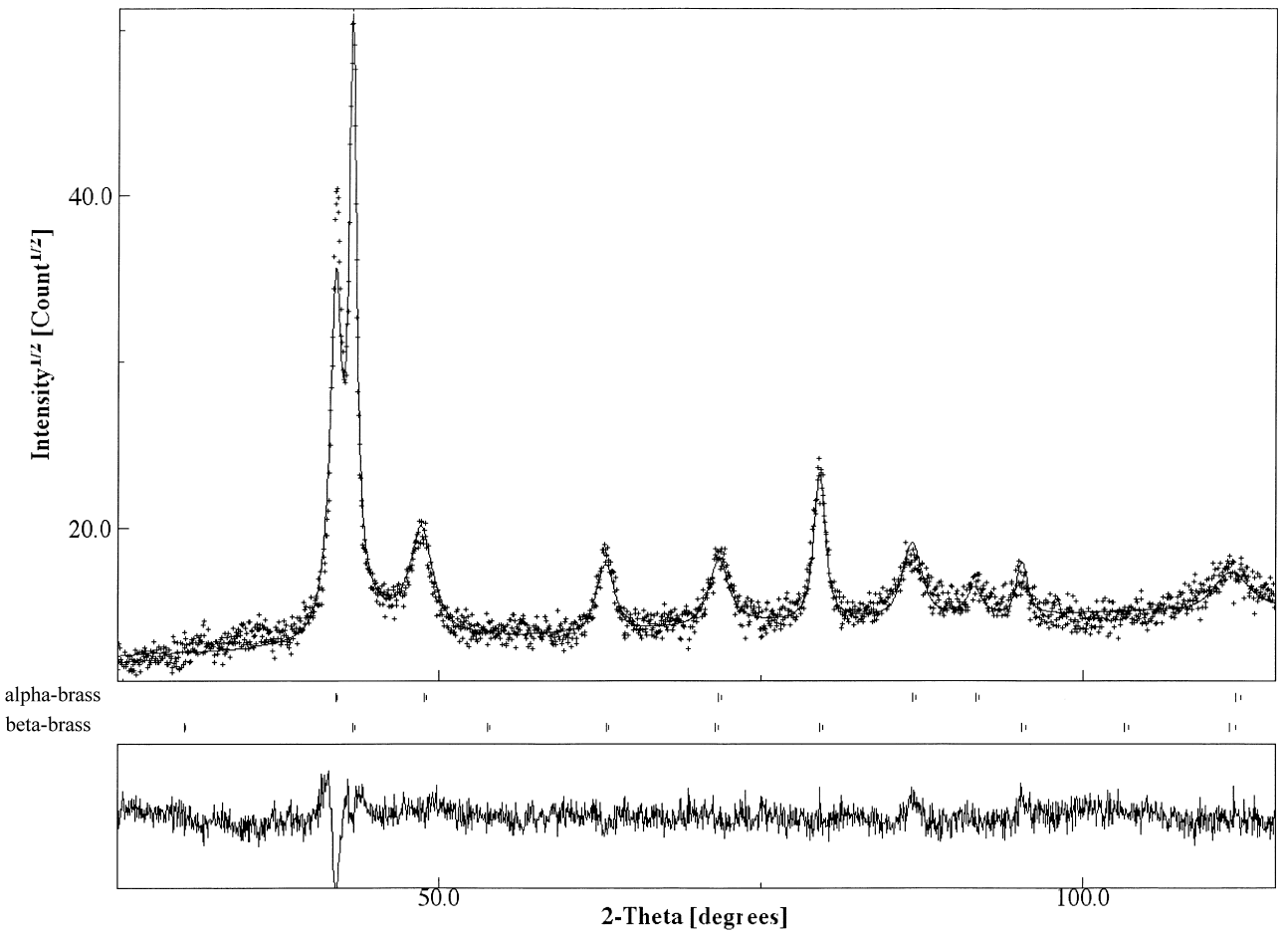

Fig. 3. XRD pattern of the rapidly solidified ribbons after 48 h ball-milling.

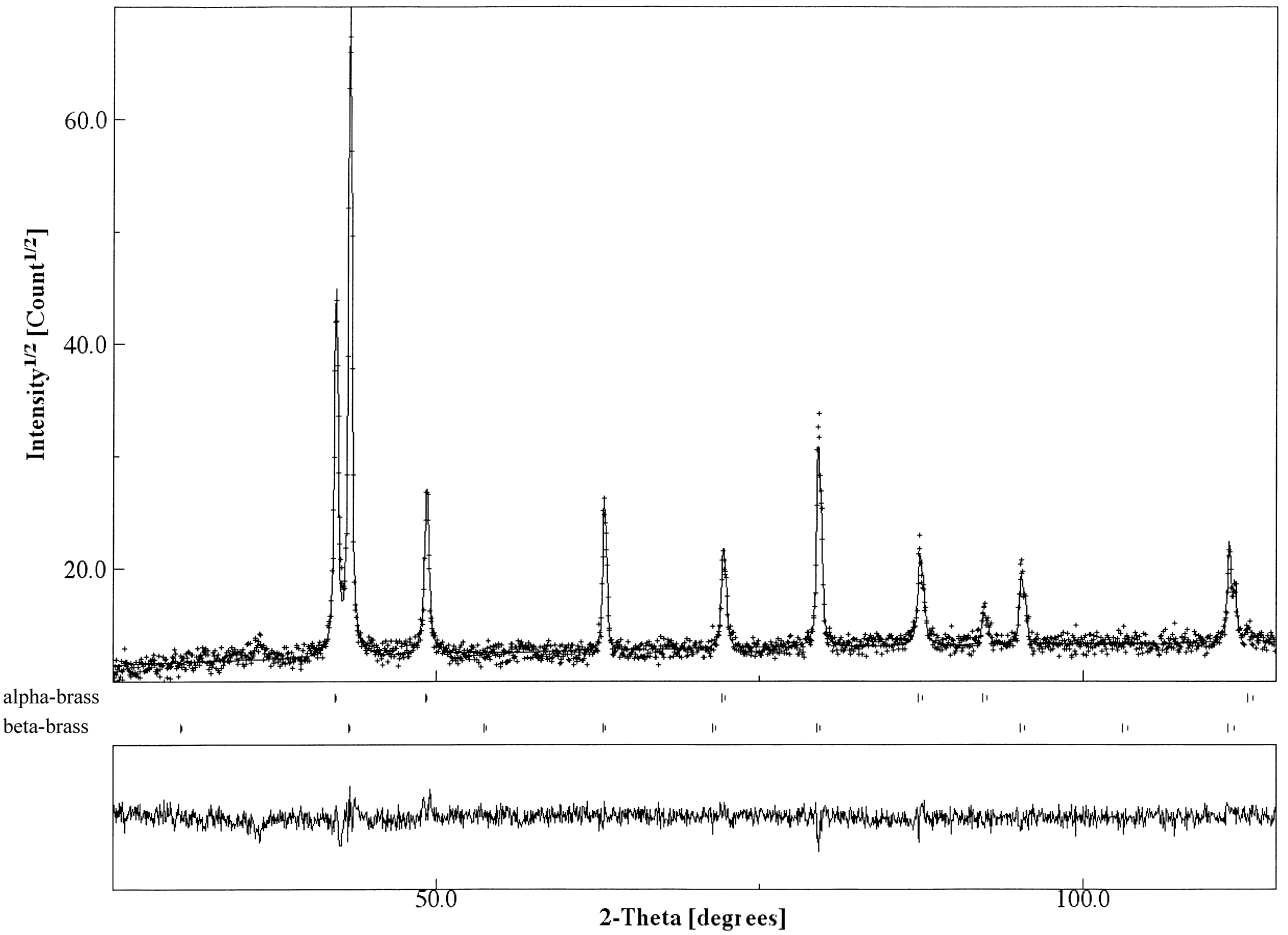

Fig. 4. XRD pattern of the rapidly solidified ribbons after 48 h ball-milling (see XRD pattern in Fig. 3) and then annealed for 15 min at 500°C.

elevated solidification and cooling rates involved with rapid quenching. More significantly, phase compositions of the ribbons after thermal treatments revealed the presence of a second phase, other than the B2 one. The face centred cubic alpha phase was detected in the ribbons after short term heat treatment at 500°C (Fig. 2), as an indication of a composition shift to the two phase field, α–β′, of the Cu–Zn system. Zinc losses probably occurred during the rapid solidification process, involving melting of the starting brass pieces at low pressure. Under this condition, zinc evaporation can very easily occur, as observed in dezincification experiment carried out on brass alloys [13]. The same value of the alpha phase composition, i.e. Cu–Zn 33.9 (wt%) was measured from the XRD results obtained with the ribbons which were annealed after milling for 48 h. Milling itself induced, in the as-spun ribbons, a transformation from an original single, although unstable, phase, to the mixture of the B2 and fcc phases. However, a very important aspect has to be underlined, i.e. the estimated composition of the fcc phase (Table 2), which is incompatible with the equilibrium Cu–Zn phase diagram. Indeed, the value Cu–45.0 Zn (wt%) would rather correspond to a single phase B2 alloy. A diffusionless massive, mechanically induced transformation has to be invoked. Such a transformation is actually foreseen for this alloy system [14]. The crystallographic changes can be described in terms of a Bain strain model, involving an expansion along a cube axis and a contraction along the other two axes of the starting β′ cell. In the present case, 26% expansion and 11% contraction were recorded, values in the same range as those reported for the stress induced bcc–fcc transformation in brass alloys [15].

Table 2
Composition for the alpha phase samples 2–5[a]

Sample[a]	Composition (Zn wt%)
2	36.9
3	36.7
4	45.0
5	36.9

[a] 2, Cu–Zn ribbons annealed at 500°C for 15 min; 3, Cu–Zn ribbons annealed at 400°C for 15 min; 4, Cu–Zn ribbons ball-milled for 48 h; 5, Cu–Zn ribbons ball-milled for 48 h and then annealed at 400°C for 15 min.

The very limited domain size featuring both mechanical-

ly ground phases, together with a possible too a limited milling time, may both explain an incomplete transformation. When the average domain size goes down to too a low value the deformation efficiency of the milling media decreases as well, thus leaving the single domains in the original condition, as far as the crystal phase is concerned.

5. Conclusions

Different metastable structures of the Cu–Zn system have been obtained by non-equilibrium techniques, like rapid solidification through melt-spinning, and high energy ball-milling.

The β' phase obtained by melt-spinning, although ordered and well crystallised, has not an equilibrium composition, because of a dezincification occurred when the raw material was melted at low pressure in the melt-spinner furnace. The equilibrium phase composition could be attained by suitable heat treatments carried out on the as-spun ribbons. Alternatively, mechanical grinding of the ribbons lead to the formation of an additional non-equilibrium structure, isomorphic to the fcc alpha phase, having a composition falling in the single β' phase field. In this case too, thermal treatments succeeded in achieving a more stable condition, i.e. a mixture of the β' and α phases, with their own right compositions.

Acknowledgements

Partial financial support to the present work has been obtained from the Italian Ministero della Ricerca Scientifica e Tecnologica in the frame work of a National Research Project entitled ‘Leghe e composti intermetallici. Stabilità termodinamica, proprietà fisiche e reattività’.

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