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THE INFLUENCE OF MILLING AND INTERVAL TIME ON THE AMORPHIZATIONPROCESS OF Cu-Ti ALLOYS

Abstract: The aim of this paper is describing a preparation, investigation and comparison of the structure size and shape of the $Cu_{50}Ti_{50}$ amorphous and nanocrystalline powders depending of the milling and interval time in cycle. The $Cu_{50}Ti_{50}$ alloy was obtained by mechanical alloying (MA) in a high energy ball mill SPEX 8000. The structure of $Cu_{50}Ti_{50}$ powders was examined by X-ray diffraction (XRD). Chemical composition, particle size and shape of the prepared powders was investigated by scanning electron microscopy (SEM). Amorphous $Cu_{50}Ti_{50}$ alloy can be prepared by a high energy ball milling. Milling and interval time determined an amorphization process of starting elements. The SEM analysis showed that the increase of milling time caused the increasing of powder particle size. The shape changing of the particles was also observed.

1. Introduction

Bulk metallic alloys exhibit many superior properties in comparison with crystalline alloys. Lately, it has been notified that rods and ribbons obtained from Cu – based alloy exhibit high tensile strength, fatigue strength, fracture strength, ductile and relatively low cost of products and good glass-forming ability [1 – 6].

The conventional methods of fabrication of amorphous materials include casting methods e.g.: melt spinning or pressure die casting method. Mechanical alloying (MA) seems to be an alternative method for preparation of metallic amorphous alloys from high purity powders in high-energy mills. During the MA process particles are subjected to multiple cold welding, cracking and rewelding. Preparation of amorphous alloy by using this method is dependent on many factors. The most important factors are: determination of the appropriate weight ratio of grinding media to the mass of powders, selection of the proper milling time and length of interruptions, provide a protective atmosphere and cleanliness of grinding media and the reactor. The selection of these factors for different materials is carried out on an experimental basis, and it is time consuming [7].

Depending on the plastic properties of starting powder the MA process can take place in different ways. Titanium is brittle metal and copper is ductile. In this case the stages of the MA process illustrates Fig. 1.

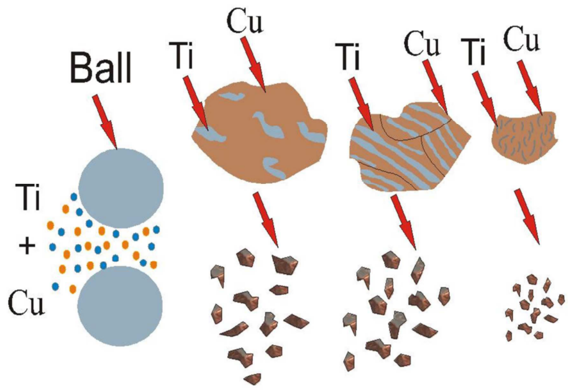

Fig. 1. MA steps for brittle and ductile elements [7]

2. Material and research methodology

Nine samples (Table 1) with composition of $Cu_{50}Ti_{50}$ (at.%) were prepared using commercially pure powders of copper (99,5 % purity, < 325 mesh) and titanium (99,5 % purity, < 325 mesh). Final weight of each sample was 8 grams with 4,5629 g of copper and 3,4371 g of titanium.

Tab. 1. Identification of prepared samples

Interruption time [min] / Milling time [min]	Time of mechanical alloying		
	6 h	8 h	10 h
0/60	sample 1	sample 2	sample 3
10/60	sample 4	sample 5	sample 6
30/30	sample 7	sample 8	sample 9

The experiments were conducted with three different milling times: 6 h, 8 h, 10 h. MA process was interrupted every 60 min (interval lasted 10 min) for samples 4 – 6 and every 30 min (interval lasted 30 min) for samples 7 – 9. Specimens 1 – 3 were milled incessantly. The long break during milling did not allow to overheating crucible and powders. Low temperature favours amorphization process. Powder composition was weighed on an analytical high precision balance AS/X. Cr steel balls of 13 mm diameter were used. The ball to powders weight ratio was 5:1. The powder mixture together with Cr steel balls were placed in austenitic crucible under argon atmosphere within a glove bag.

The mechanical alloying was performed in a high energy ball mill SPEX 8000 CertiPrep Mixer/Mill "shaker" type. The mill generated vibrations of the balls and the material inside the container [8-11].

X-ray diffractometer X'Pert Pro Panalytical with Cu Kα radiation (λ=0.15418 nm) was used to structure verification of powders in as-prepared state. The data of diffraction lines were recorded by "step-scanning" method in 2θ range from 20° to 80° and 0,05° step.

Particles size and shape of studied powders were characterized by using the Scanning Electron Microscopy (SEM) SUPRA 35 ZEISS with magnification up to 500x.

Chemical characterization of prepared samples were analysed by Energy Dispersive X-ray Spectroscopy (EDS). EDS provides surface chemical analysis of the field of view, linear or spot. Values of the characteristic radiation energy permit to qualitative analysis in the test sample, and the intensity (peaks height) allows for quantitative analysis.

3. Results and discussion

X-ray diffraction analysis has revealed that the samples after 8 h milling with 30 min interruptions was amorphous. The diffraction pattern shows a single broad diffraction halo with the 2θ range of 37º - 47º from the amorphous phase only (Fig. 2). The diffraction patterns show the broadening of diffraction lines for each milled samples. The lowest intensities were recorded for samples, which were milled 6h and 8h with 30 min intervals. Amorphization process favour short milling times and long intervals used during the cycle. Therefore the amorphization must be proceed carefully at the early stages of mechanical alloying.

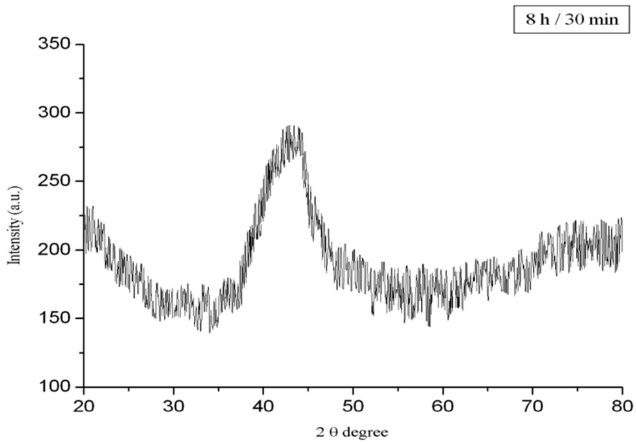

Fig. 2. X-ray diffraction pattern of $Cu_{50}Ti_{50}$ powders after 8 h of mechanical alloying with 30 min interruptions

The initial size of the powders was about 44 µm. The increasing of particle size was observed after each mechanical alloying process. Average particle size of the powders is presented in Table 2. Several relationship was observed on the basis of powders measurements. The increasing of milling time caused that the particle size also increased. The largest particles were obtained after 10 h mechanical alloying with intervals of 30 min. The particle size was five times larger than the initial powder (increase from 44 µm to 200 µm). In samples 1 – 7 was observed variety of particles (small and large), whereas powders in samples 8 and 9 were homogeneous (of similar size).

The powders after milling without interruption and with 10 min intervals characterize very heterogeneous shape. In two cases (samples 3 and 5), the particles look like small sponges. Particles after milling with intervals of 30 min resemble the shape of very similar to spherical.

Tab. 2. Average particle size [µm] of the powders after MA

Interruption time [min]/ Milling time [min]	Time of mechanical alloying		
	6 h	8 h	10 h
0/60	70x89	123x138	128x163
10/60	113x133	152x176	170x189
30/30	140x135	160x165	150x190

Tab. 3. Results of chemical analysis from the surface of powder

Sample	Element	At. [%]
0	Cu	50
	Ti	50
1	Cu	51,04
	Ti	48,96
2	Cu	52,39
	Ti	47,61
3	Cu	53,76
	Ti	46,24
4	Cu	51,07
	Ti	48,93
5	Cu	51,91
	Ti	48,09
6	Cu	50,45
	Ti	49,55
7	Cu	48,82
	Ti	51,18
8	Cu	49,33
	Ti	50,67
9	Cu	51,15
	Ti	48,85

Figure 3 shows microanalysis of $Cu_{50}Ti_{50}$ powders after 8 h milling with 10 min interruptions with marked area from whole area of the sample. EDS results confirmed an existence of copper and titanium elements in studied sample. The chemical composition analysis was only a qualitative test and confirmed existing of main elements in studied alloy. The amount of atomic share of Cu and Ti depends on the time of milling. Table 3 presented detailed results of the chemical analysis for every sample. Each particle consisted only basic components (Ti and Cu). The initial atomic percentages of Cu equals 50 % and Ti 50 %. The investigation result have shown that the obtained powder particles after alloying process have very similar atomic composition in comparison with starting composition.

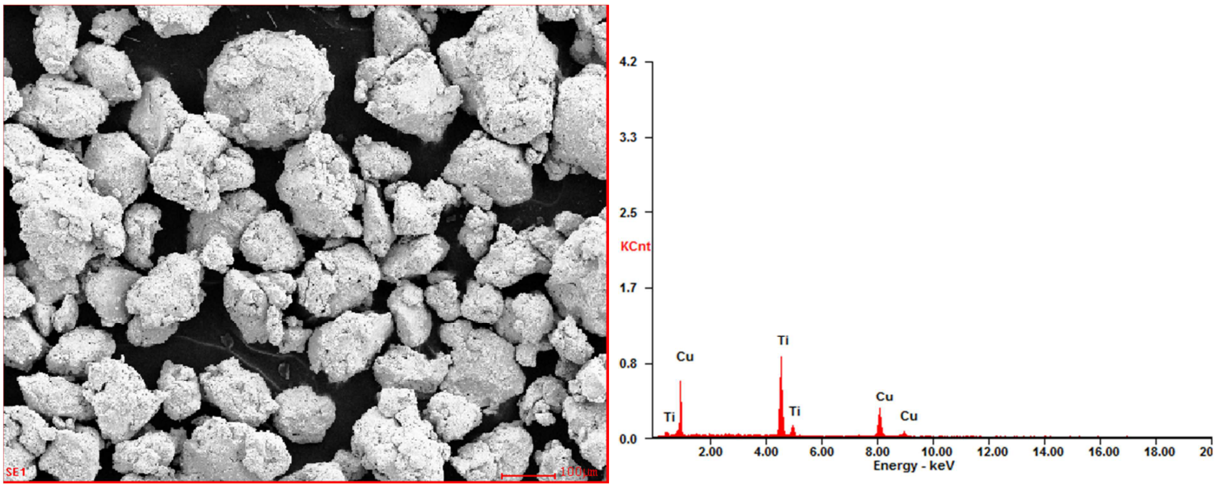

Fig. 3.The micrograph of $Cu_{50}Ti_{50}$ powders after 8 h mechanical alloying with 10 min interruption with marked area for which energy dispersive X-ray analysis (EDS) was performed from all area of sample

4. Conclusion

The obtained results after fabrication and testing of $Cu_{50}Ti_{50}$ powders allowed to state the following conclusions:

• It is possible to produce amorphous alloy by mechanical alloying method in a very short time (about 8 h),

• Both the milling time and the time of intervals have an influence on the forming of powders structure, its dimension and shape,

• The X-ray diffraction results showed that the most adequate conditions for amorphization is 8h milling with 30 min interruptions,

• In each case, regardless of the interruption length used during milling, particles size increased. The largest particles were observed after the longest milling time (10 h) and by using the longest intervals (30 min),

• Energy dispersive X-ray analysis demonstrated an occurrence of copper and titanium elements in studied powders. Each particle is characterized by a different content of copper and titanium, but very close to the initial powders.

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